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Preface

The International Joint 20th AIRAPT and 43th EHPRG Conference provides an excellent platform to review and to discuss the state-of-the-art and recent advances in High Pressure Research. The conference is highly multidisciplinary covering high pressure phenomena in Chemistry, Physics, Material Science and Technology, Geophysics, Bioscience and Biotechnology and Food Science.

The last conferences have been held on Hawaii (1999), in Bejing (2001) and Bordeaux (2003). In 2005, the International Conference on High Pressure Science and Technology will take place in Karlsruhe. Its Technical University has a long tradition in High Pressure Research and Development starting the Sixties of the last century, when E.U. Franck began with his outstanding work in the field of supercritical fluids, particularly fascinated by water. Motivated by geochemical aspects his work resulted in important contributions to chemical and energy engineering issues.

For the scientific programme, 14 regular as well as 5 special sessions on most actual topics are planned. Three plenary lectures and 18 keynotes will introduce and highlight particular areas of High Pressure Research. In addition, a special lecture in the honour of E.U. Franck will be held. Both, AIRAPT and EHPRG will have general assemblies and will award meritorious scientists. During this conference, the actual state-of-the-art in High Pressure Science and Research is reported and interdisciplinary cross-linking to new experimental and theoretical approaches as well as to new applications is possible. Young researchers have the opportunity to present their work on a high international standard. A social programme and a technical tour will complete the conference.

We did our best to prepare the conference to be an exiting event, setting up a demanding scientific programme provided in a comfortable environment, in which new friendships and joint activities can be formed and new ideas are created to further develop the field of our common interests, High Pressure Research and Technology.

Eckhard Dinjus

Conference Chairman

June, 2005

General Information

First, there was nothing ...

Karlsruhe was founded in 1715 as "dream city" of Margrave Karl-Wilhelm - in those days the official residence in Baden.

From the very start, Karlsruhe was lined up as a city without walls, open for friends and guests. The Rhine plains between the Black Forest and the Vosges mountains of France offered the very best conditions and features for a successful new city.

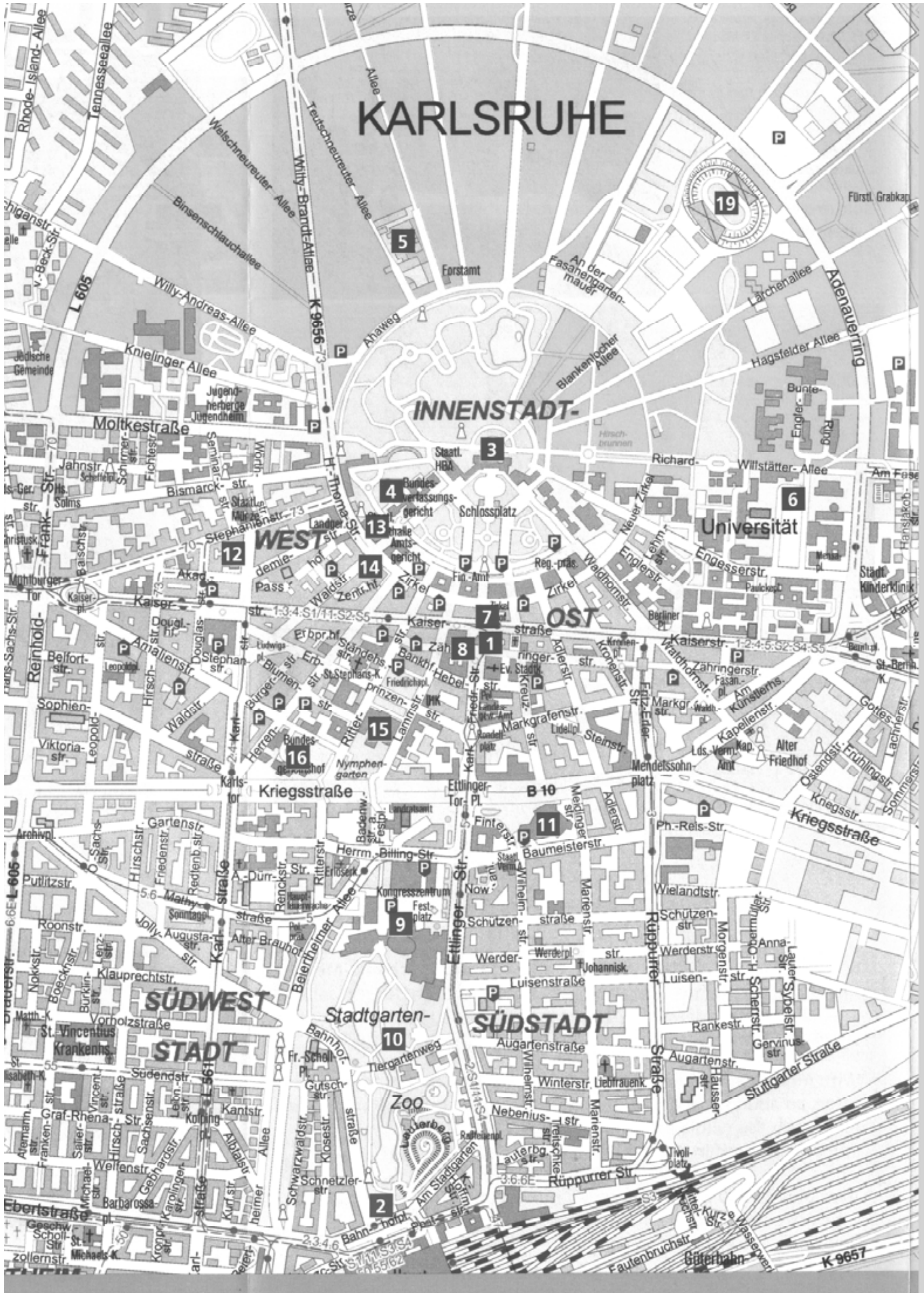
The fascinating structure - radial in shape like a fan - aroused worldwide interest. The master builder and architect, Weinbrenner, created the numerous classical buildings which today attract a great number of visitors from all over the world.

In 1823 the city landmark, the Pyramid, was built. Two years later, in 1825, the senior technical college, or Technische Hochschule, commenced its teaching programme.

In 1950, the Federal Supreme Court (Bundesgerichtshof) moved to Karlsruhe, followed by the Federal Constitutional Court one year later. Karlsruhe became home to the West German administration of justice.

And today ...

Karlsruhe has 272,268 residents (status 2003). The city has an area of 173.49 km^2 and stretches 16.8 km from north to south, and 19.3 km from east to west. Karlsruhe has a circumference of 82.4 km, of which 11.5 km are alongside the Rhine.



Overview

1 KMK City Information Office

2 KMK Tourist Information Office

3 Palace and gardens, State Museum

4 Federal Constitutional Court and botanical gardens

5 State Majolica Manufacturing Works

6 University

7 Museum am Markt, the marketside museum

8 Market square and pyramid, town hall, ev. municipal church

9 Festival Square, Congress Centre, Concert Hall

10 Zoological gardens

11 Baden State Theatre

12 Prinz-Max-Palais and City Museum, the Literature Museum of the Upper Rhine

13 State Art Gallery and Orangerie

14 Baden Art Society

15 State Museum for Natural Sciences and vivarium

16 Federal Supreme Court

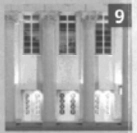
17 ZKM, Municipal Gallery, Museum for New Art

18 KMK Europahalle and Günter Klotz park

19 Wildpark football stadium

20 Turmberg and funicular railway

21 Karlsruhe Trade Fair Centre and multipurpose arena



Tours & Social Programme

Evening Programme

Welcome Reception
June 26, 2005

The organisers are pleased to welcome the congress participants and their accompanying person(s) to Karlsruhe as well as to the Joint AIRAPT and EHPRG Congress. The informal reception will take place on June 26, 2005 at 7 pm. You will have the possibility to meet friends and colleagues and exchange experiences with them.

Conference Dinner in a breath-taking atmosphere
The Castle of Schwetzingen
June 29, 2005

Schwetzingen is used to treat guests like kings. When in the 18th century the Elector of Schwetzingen, Carl Theodor, had chosen the Castle of Schwetzingen and its gardens to be his summer residence, he wanted to create a place of enthusiastic well-being. In our opinion this Castle is the right setting for our Conference dinner on June 29, 2005.

The buses will pick up those participants registered for the conference dinner at the main entrance of the Stadthalle of the Congress Centre Karlsruhe at 6.15 pm. It will take about 45 minutes from Karlsruhe to Schwetzingen.

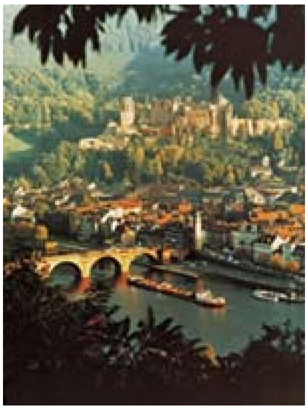
Upon arrival at the Castle at about 7 pm you will be welcomed by old familiar tunes presented by the baroque group "Aqua Viva". The ladies will be enthusiastic about the dresses, maybe the gentlemen as well. After the short official reception in the foyer of the Castle the delicious buffet will be opened at about 8 pm lasting until 10.30 pm. At about 11 pm the buses will leave to bring you back to the Stadthalle at the congress centre in Karlsruhe.

Tours

Tour 1: "Loose Your Heart To Heidelberg"
Monday, June 27, 2005

With its delightful location at the edge of the Odenwald and its harmonious appearance of the old part of the town, the castle ruins and river Neckar, Heidelberg is rightly regarded as one of the most beautiful cities of Germany. After a guided sightseeing tour and a visit to the castle you will have the opportunity to discover Heidelberg on your own. Enjoy the international flair and the charm of this romantic city.

Meeting Point: Congress Center Karlsruhe (Stadthalle), departure 9.30 am



Quelle KMK-Archiv

Tour 2: "Life In The Black Forest"
Tuedsday, June 28, 2005

The Black Forest is one the most fascinating regions of Germany. Typical features are the Black Forest Farms. You will find 6 of them built in the 16th and 17th century in the open-air museum "Vogtsbauernhof" at Gutach. Afterwards a visit to "Dorotheenhütte" at Wolfach is scheduled. This is the only glass hut in the region which is still celebrating the fascinating art of hand-made glass production. You recover from these impressions during a typical luncheon served at Zell before your journey will be continued to the legendary "Mummelsee".

Meeting Point: Congress Center Karlsruhe (Stadthalle), departure 9.30 am

Quelle KMK-Archiv

Tour 3: "What's Going On In Karlsruhe"
Wednesday, June 29, 2005

Congress participants and their accompanying persons are invited to see the particular sites of Karlsruhe. Registering for this tour is absolutely necessary for giving us the possibility to arrange for corresponding transfers.

Meeting Point: Congress Center Karlsruhe (Stadthalle), departure 1.15 pm

Quelle KMK-Archiv

Tour 4: "Visit Our French Neighbours"
Thursday, June 30, 2005

Vis-à-Vis of Karlsruhe you will find France. Use this opportunity to visit the cultural capital of the Alsace: Strasbourg.

The Minster of Strasbourg towers over the romantic Old City with its numerous picturesque stores, bistros and cafés. In a guided tour Strasbourg will show at its best. This tour is followed by a relaxing boat trip to "La Petite France", the famous water district of Strasbourg.

Meeting Point: Congress Center Karlsruhe (Stadthalle), departure 9.30 am

Quelle CUS – G. Engel

Technical Tour
Friday, July 1, 2005

On Friday, July 1, a technical tour visiting the **Forschungszentrum Karlsruhe** is offered. Forschungszentrum Karlsruhe is one of the biggest scientific and engineering research institutions in Europe and funded jointly by the Federal Republic of Germany and the State of Baden-Württemberg. Its research and development programme is embedded in the superordinate programme structure of the Hermann von Helmholtz Association of National Research Centres and concentrates on the five research areas of Structure of Matter, Earth and Environment, Health, Energy, and Key Technologies. From these topics four highlights have been selected for the visit, which will be presented during the 2 hours tour:

- **Institute for Synchrotron Radiation** - Light for lithography and analytics from far infrared to hard X-ray from the 2.5 GeV electron synchrotron radiation source ANKA
- **Institute for Technical Chemistry** - Converting biomass to hydrogen by supercritical water gasification - the 100 kg/h plant VERENA
- **Institute for Solid State Physics** - Preparation and high-resolution spectroscopy of systems with strongly correlated electrons
- **Institute for Technical Physics** - Development and structure of superconductors

Busses will depart at the Karlsruhe Congress Centre on Friday, July 1, at 2.15 pm leaving for the Forschungszentrum which is located around 10 km north of Karlsruhe. The participants will be back at the Congress Centre and the Main Station of Karlsruhe at 5 pm latest.

International Advisory Committee

- **Wolfgang Arlt,**
  Friedrich-Alexander-Universität Nürnberg-Erlangen, Germany

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  Research Center Karlsruhe, Germany

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- **Nicolaus Dahmen**
  Research Center Karlsruhe, Germany

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  Max-Planck-Institut für Festkörperforschung Stuttgart, Germany
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  Université Paris Nord, France
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  University of Umea, Department of Physics, Sweden
- **John Tse**
  University of Saskatchewan, Canada

EHPRG Committee Members

Since the EHPRG Meeting in Lausanne, 2004:

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  Universidad de Cantabria, Spain, Chairman
- **Roland Winter,**
  University of Dortmund, Germany, Secretary
- **Konstantin V. Kamenev,**
  The University of Edinburgh, UK, Treasurer
- **Giuseppe G. N. Angilella,**
  Università di Catania, Italy

* **Susan C. Bayliss,**
De Montfort University, UK: passed away, 2004

* **Eckhard Dinjus,**
Forschungszentrum Karlsruhe, Germany

* **F. Dumas,**
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* **Rudi Vogel,**
Technische Universität München, Germany

* **Gerhard Wortmann,**
University of Paderborn, Germany

* Ex-officio members:

* **William J. Nellis,**
Harvard University, USA, President of the AIRAPT

* **Hans Rudolf Ott,**
ETHZ Hönggerberg, Switzerland, Chairman of the Condensed Matter Division of the European Physical Society

Programme at a Glance

Scope

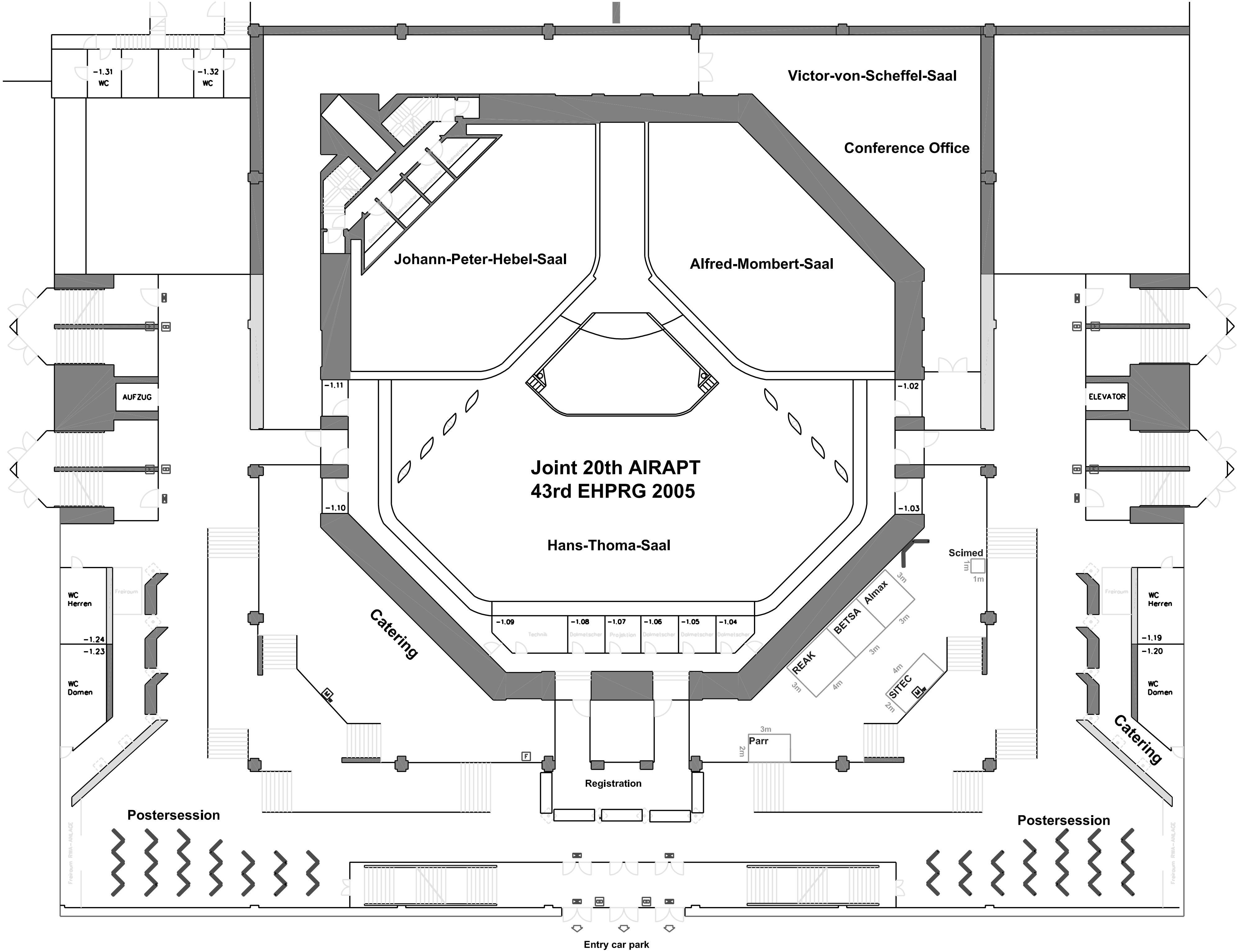
In 2005, the International Conference on High Pressure Science and Technology as the Joint 20th AIRAPT and 43th EHPRG Meeting will be held in Karlsruhe. Karlsruhe has a long tradition in High Pressure Research and Development back to the Sixties of the last century, when E.U. Franck started his outstanding work in the field of supercritical fluids, particularly fascinated by water. Motivated by geochemical aspects his work also resulted in important contributions to chemical and energy engineering issues. Today, several institutes of different research facilities around Karlsruhe are working in the field of Supercritical Fluids contributing to a broad range of fundamentals and applications. Technical Tours to visit a selection of these institutions are offered on Friday, July 1,2005.

During the conference the actual state-of-the art in High Pressure Science and Research will be reported providing an excellent platform to present your work to an international audience. The conference is highly multidisciplinary covering high pressure phenomena in Chemistry, Physics, Materials Science and Technology, Geophysics, Bioscience, Biotechnology and Food Science.Topical as well as Special Sessions are planned. In addition a lecture in honour of Prof. E.U. Franck will be given.

The scientific programme is embedded in a framework of social events, the highlight being the conference dinner in the unique baroque palace in Schwetzingen near Heidelberg.

Scientific Programme

To cover the entire diversity in methodology, experimental techniques, application, and theory of high pressure science and technology, the scientific programme will be organized in plenary lectures (PL), a set of parallel oral sessions (OS) and poster sessions (PS). Attention is paid to selected topics in Special Sessions.


Victor-von-Scheffel-Saal
Conference Office
Johann-Peter-Hebel-Saal
Alfred-Mombert-Saal
Joint 20th AIRAPT
43rd EHPRG 2005
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Freiraum RWA-ANLAGE
Entry car park

Topics of Orals and Posters

TOPICS

T1	Theory, molecular dynamics and equation-of-state
T2	Synchrotron based studies
T3	Electrical and magnetic properties
T4	Optical and acoustic properties
T5	Spectroscopy under high pressure
T6	Synthesis and properties of novel materials
T7	Pressure dynamics and shock waves
T8	Geological, marine and planetary science
T9	Bioscience and food technology
T10	Phase transitions and transformations of fluids and solids
T11	Photoluminescence under pressure
T12	Structural studies
T13	Chemical reactions in supercritical fluids
T14	Advances in Equipment and Methods

SPECIAL SESSIONS

1) Superhard Materials, SHM
2) Water, Ice and Clathrates, WIC
3) Correlated Electron Systems, CES
4) Nanostructured Materials, Nanomat
5) Workshop: International Practical Pressure Scale (IPPS)

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
08:00		**Registration**	**Plenary** Prof. Isaac F. Silvera	**IPPS** **T13** **T9**	**EHPRG Award**	**Plenary** Prof. Rudi van Eldik
08:30		**Opening**				
09:00		**Plenary** Prof. Russel J. Hemley	**T1** **T6** **Nanomat**		**EHPRG General Assembly**	**T7** **T3** **T2**
09:30				**Coffee Break**		
10:00		**Coffee Break**	**Coffee Break**	**AIRAPT General Assembly** **Lecture in Honour of Prof. E. U. Franck (Prof. F. Hensel)**	**Coffee Break**	**Coffee Break**
10:30		**AIRAPT Award**	**T4** **T12** **Nanomat**		**T7** **T13** **T9**	**T11** **T3** **T2**
11:00						
11:30				**Lunch**		
12:00		**Lunch**	**Lunch**		**Lunch**	**Closing Remarks**
12:30				**Social Excursion - Tour 3**		**Lunch**
13:00		**T8** **T10** **T1**	**Poster Session T1, T6, T8, T10, T12, CES, IPPS, Nanomat, SHM**		**Poster Session T3(includes T2, T4, T11), T5, T7, T9, T13, T14, WIC**	
13:30						**Technical Tour**
14:00			**CES: Correlated oxide and related systems**			
14:30					**Coffee Break**	
15:00		**Coffee Break**	**Coffee Break**		**T5** **T13** **WIC**	
15:30		**SHM** **T12** **T1**	**CES: f-electron systems (valence, magnetism)** **T10** **T6**			
16:00	**AIRAPT Comm. Meeting**					
16:30					**T14** **T13** **WIC**	
17:00		**SHM** **T12** **T5**	**CES: Quantum critical phenomena** **T10** **T6**			
17:30	**EHPRG Comm. Meeting**			**Conference Dinner at Schwetzingen Castle**		
18:00						
18:30						
19:00	**Conference Welcome Reception**					
20:00						
21:00						
22:00						

Programme Monday

Location	Alfred-Mombert-Saal	Hans-Thoma-Saal	Johann-Peter-Hebel-Saal
8:00	Registration		
9:00		Opening Remarks	
9:30		Plenary	
10:30	Coffee Break		
11:00		AIRAPT Award	
12:00	Lunch		
13:00	**Artem R. Oganov** **(T8 - KN)** *ETH Zürich, Switzerland* High-pressure mineralogy: state of the art and future	**Vadim Brazhkin** **(T10 - KN)** *Institute for High Pressure Physics, Russia* Structural study of phase transformations in solid and liquid halogenides ($ZnCl_2$, $AlCl_3$) under high pressure	**John Tse** (**T1 – KN)** *University of Saskatchewan, Canada* Molecular Dynamics and Equation of State
13:30	**Gerd Steinle-Neumann** **(T8 - O23)** *University of Bayreuth, Germany* Absence of charge localization in compressed magnetite from first principle computations	**Céline Sortais-Soulard** **(T10 - O30)** *CEA – DPTA, France* Thermodynamic and electronic structure study of two pressure-induced stuctural phase transitions of $PdSe_2$: interconversion path and structural preferences between the CdI_2-, PdS_2- and pyrite-type structures.	**Eunja Kim** **(T1 - O161)** *University of Nevada, USA* Pressure-induced B1-to-B2 phase transition in $AgSbTe_2$: A first-principle study
13:50	**Daniel Jung** **(T8 - O62)** *ETH Zürich, Switzerland* Ab initio treatment of minerals at high pressures and temperatures	**Marina Bastea** **(T10 - O50)** *Lawrence Livermore National Laboratory, USA* Kinetics of dynamically driven polymorphic and freezing phase Transformations	**Agnès Dewaele** **(T1 - O160)** *Commissariat a l'Energie Atomique – DPTA, France* Equations of state of metals at ultrahigh pressure
14:10	**Gerd Steinle-Neumann** **(T8 - O88)** *University of Bayreuth, Germany* Al, Fe incorporation into post-perovskite from first principles	**Valery Levitas** **(T10 - O74)** *Texas Tech University, USA* Crystal-Amorphous and Crystal-Crystal Phase Transformations via Virtual Melting	**Daniel Orlikowski** **(T1 - O147)** *Lawrence Livermore National Laboratory, USA* Thermoelasticity at High Temperatures and Pressures: Molybdenum and Tantalum
14:30	**Artem R. Oganov** **(T8 – O33)** *ETH Zürich, Switzerland* New high-pressure phase of Al_2O_3 and implications for Earth's D" layer.	**Yuichi Akahama** **(T10 - O89)** *University of Hyogo, Japan* Structure transition of Sc to 295 GPa	**Aitor Bergara** **(T1 - O120)** *University of the Basque Country, Spain* Pressure Induced Fermi Surface Evolution in Ligth Alcalies
14:50	Coffee Break		
15:20	**Vladimir Turkevich** **(SHM - KN)** *National Academy of Sciences of Ukraine, Ukraine* Diamond and cBN Crystallization: Thermodynamics and Kinetics	**Arthur Ruoff** **(T12 - KN)** *Cornell University, USA* Metallization of Silane at 100 GPa	15:20 **Tian Cui** **(T1 – O115)** *Jilin University, China* Pressure effects on the absorption of phase Nb-H system

Programme Monday

			15:40	**Donat Adams** **(T1 – O49)** *ETH Zürich, Switzerland* Molecular Dynamics Simulations of cubic $CaSiO_3$ at lower mantle conditions
15:50	**Yann Le Godec** **(SHM - O68)** *Universite Pierre et Marie Curie, France* Cubic boron nitride crystallization in fluid systems - in situ studies	**Christine Kuntscher** **(T12 - O41)** *Universität Stuttgart, Germany* Infrared properties of the quasi-one-dimensional superconductor β-$Na_{0.33}V_2O_5$ under pressure	16:00	**Julia Contreras-Garcia** **(T1 – O51)** *Universidad de Oviedo, Spain* Quantum mechanical simulation of pressure induced polymorphism in AgCl
16:10	**Ted Lowther** **(SHM - O14)** *University Witwatersrand, South Africa* Potential super-hard phases and the stability of diamond-like B_nC_m structures	**Takanori Hattori** **(T12 - O64)** *Keio University, Japan* Structure of Liquid Silver Halides at high pressures	16:20	**Mehul Patel** **(T1 – O57)** *Lawrence Livermore National Laboratory, USA* Molecular dynamics simulations of pressure-induced solidification
16:30	Break		16:40	Break
17:00	**Natalia Dubrovinskaia** **(SHM – O130)** *Bayreuth University, Germany* New Bulk Superhard Semiconducting C-B Composite	**Reed Patterson** **(T12 – O59)** *Lawrence Livermore National Laboratory, USA* Structural Studies on Dy to 119 GPa and Applications to Lanthanide Systematics		**Julio Pellicer-Porres** **(T5 – O141)** *University of Valencia, Spain* Experimental and theoretical investigation of the electronic structure of $CuAlO_2$ delafossite under high pressure
17:20	**Guangtian Zou** **(SHM – O156)** *Jilin University, China* Synthesis and Novel Properties of Pure Phases of C_3N_4 at High Pressure and High Temperature	**Hyunchae Cynn** **(T12 – O118)** *University of California, USA* X-ray diffraction and Raman of GaP using a laser heated diamond anvil cell		**Anatoly Tsvyashchenko** **(T5 – O32)** *Russian Academy of Sciences, Russia* High Pressure ^{111}Cd - TDPAC Spectroscopy of $YbAl_2$ compound
17:40	**Takashi Taniguchi** **(SHM – O81)** *National Institute for Materials Sciences, Japan* High-pressure synthesis of high purity single crystal of cubic and hexagonal boron nitride and their band-edge natures	**Gennady Kanel** **(T12 – O85)** *Russian Academy of Sciences, Russia* A failure wave phenomenon in brittle materials		**Tetsuji Kume** **(T5 – O78)** *Gifu University, Japan* High-pressure Raman study on type III clathrate compounds
18:00	**Valery Levitas** **(SHM – O73)** *Texas Tech University, USA* Strain-Induced Disorder, Phase Transformations and TRIP in Hexagonal Boron Nitride under Compression and Shear in a Rotational Diamond Anvil Cell: In-Situ X-ray Diffraction Study and Modeling	**Gwenaelle Rousse** **(T12 – O21)** *University Paris VI, site Boucicaut, France* Structure of intermediate high pressure phase of PbX compounds		**Martine Castellà-Ventura** **(T5 – O19)** *Université Pierre et Marie Curie, France* Proton Transfer under High Pressure

Programme Tuesday

Location	Alfred-Mombert-Saal	Hans-Thoma-Saal		Johann-Peter-Hebel-Saal	
8:30		Plenary			
9:30	**Stanislaw Krukowski (T1 – O203)** *Polish Academy of Sciences, Poland* Nitrogen (N_2) equation of state in pressure up to 10 kbar - molecular dynamic simulation	**Jonathan Crowhurst (T6 – O154)** *Lawrence Livermore National Laboratory, USA* Synthesis of a noble metal nitride under extreme conditions		**Alfonso San Miguel (Nanomat – O302)** *University Lyon 1, France* Resonant Raman spectroscopy of single wall carbon nanotubes under pressure	
9:50	**Sven Rudin (T1 – O58)** *Los Alamos National Laboratory, USA* Density Functional Theory Calculations on EOS and Phase Stability of Beryllium	**Alexander Goncharov (T6 – O96)** *Lawrence Livermore National Laboratory, USA* Cubic boron nitride under extreme conditions of high pressure and temperature: a combined Raman and theoretical study		**Michael Popov (Nanomat – O206)** *Technological Institute for Superhard and Novel Carbon Materials, Russia* Superhard nanocluster-based materials synthesized from single wall nanotubes	
10:10	**Takahiro Ishikawa (T1 – O97)** *Osaka University, Japan* Exploring the structure of the P-IV phase for phosphorus by using metadynamics	**Gerard Demazeau (T6 – O45)** *CNRS and University Bordeaux 1, France* Synthesis of novel materials under high pressures		**Wei Gao (Nanomat – O66)** *Jilin University, China* Behavior of Structural Metastability in Nanocrystalline FeS	
10:30	Coffee Break				
11:00	**Michel Gauthier (T4 – KN)** *Université Pierre et Marie Curie, France* Progress in ultrasonic measurement at high pressure	11:00	**Vijayakumar Viswanathan (T12 – O116)** *BARC – HPPD, India* The chalcogenide spinel,$CuIr_2S_4$, under high pressure	11:00	**Y. Iwasa (Nanomat – KN)** *Tohoku University, Japan* Nanocarbon materials under high pressure
		11:20	**Alfonso San Miguel (T12 – O83)** *University Lyon 1, France* High pressure properties of carbon and silicon clathrates		
11:30	**Jeffrey Nguyen (T4 – O111)** *Lawrence Livermore National Laboratory, USA* Crystal Characterization Using Optical Properties			11:30	**Alexander V. Soldatov (Nanomat – O196)** *Lulea University of Technology, Sweden* Physical properties of Carbon Nanostructures derived from Fullerene C_{70} at high pressure
		11:40	**Itzhak Halevy (T12 – O70)** *NRCN, Israel* High pressure study and electronic structure of the NiAl and Ni_3Al alloys		
11:50	**C.K. Jayasankar (T4 – O305)** *Sri Venkateswara University, India* Luminescence study of Eu^{3+}:phosphate glass under pressure			11:50	**C. Q. Jin (Nanomat - O304)** *Chinese Academy of Sciences, China* The properties of nano $BaTiO_3$ ceramics fabricated by high pressure
		12:00	**Anthony Williams (T12 – O54)** *University of Edinburgh, UK* High Pressure Synthesis, Crystal Structure, Magnetic & Transport properties of Cr-doped strontium ruthenates, $SrCr_xRu_{1-x}O_3$		
12:10	**Lucie Nataf (T4 – O36)** *Université P. et M. Curie, France* Elastic properties of invar $Fe_{64}Ni_{36}$			12:10	**Bingbing Liu (Nanomat – O133)** *Jilin University, China* High pressure induced polymerization of C_{60} nanorod
		12:20	Lunch		
12:30	Lunch			12:30	Lunch

Programme Tuesday

13:30	Poster Session		Poster Session		Poster Session
14:30	**Ingo Loa** **(CES – O192)** *Max-Planck-Institut FKF, Germany* Pressure-Driven Orbital Reorientation and Band Gap Closure in Transition-Metal Perovskites				
15:00	**M. Paz-Pasternak** **(CES – O201)** *Tel Aviv University, Israel* Pressure Stimulated Charge-Crossover in Transition-Metal Oxides and Hydroxides				
15:30	Coffee Break				
16:00	**H. Kobayashi** **(CES – O199)** *University of Hyogo, Japan* Structural and vibrational properties on $CuFeS_2$ under pressure	16:00	**Alexander Lyapin** **(T10 – O140)** *Russian Academy of Sciences, Russia* Transitional high-pressure diagrams of amorphous fullerene-based molecular and quasi-chain forms of carbon	16:00	**Eugene Gregoryanz** **(T6 – KN)** *Carnegie Institution of Washington, USA* Synthesis and Characterization of Transition Metal Nitrides
		16:20	**Anurag Srivastava** **(T10 – O157)** *Guru Ghasidas University, India* Pressure Induced Phase Transitions in PbSnTe Alloy		
16:30	**A. Barla** **(CES – O198)** *IPCMS-GEMME, France* Pressure-induced magnetic phase transitions in selected lanthanide and actinide compounds			16:30	**Wataru Utsumi** **(T6 – O53)** *Atomic Energy Research Institute, Japan* Single crystal growth of gallium nitride by slow cooling of its congruent melt under high pressure
		16:40	**Serge Desgreniers** **(T10 – O168)** *University of Ottawa, Canada* On the Nature of Solid Oxygen Beyond the epsilon-zeta Phase Transition		
				16:50	**Hubert Huppertz** **(T6 – O43)** *Ludwig-Maximilians-Universität München, Germany* Associating Borate and Silicate Chemistry by Extreme Conditions: High–Pressure Synthesis and Crystal Structure of the Novel Borates $RE_3B_5O_{12}$ (RE = Er - Lu)
17:00	**Vladimir Sechovsky** **(CES – O158)** *Charles University, Czech Republic* Pressure influence on magnetism in uranium intermetallics	17:00	**Marek Tkacz** **(T10 – O170)** *Institute of Physical Chemistry, PAS, Poland* Pressure-induced hexagonal to cubic transition in the Yttrium and Rare-Earth trihydrides		
				17:10	**Graziella Goglio** **(T6 – O48)** *CNRS and University Bordeaux 1, France* About the synthesis and magnetic behavior of new layered oxides structurally related to natural micas
		17:20	Break		
17:30	Break			17:30	Break

17:40	**D. Jaccard** **(CES – O202)** *University of Geneva, Switzerland* High pressure transport and AC calorimetric studies of some correlated electron systems	17:40	**Choong-Shik Yoo** **(T10 – O16)** *Lawrence Livermore National Laboratory, USA* Pressure-induced electronic Mott transition in MnO	**Michael Popov** **(T6 – O181)** *Technological Institute for Superhard and Novel Carbon Materials, Russia* Photo-induced polymerization of nitrogen at multi-Mbar pressure
		18:00	**Chrystèle Sanloup** **(T10 – O163)** *University Paris-6, France* Polymolecular high-pressure phase of nitrogen	**Eugene Dizhur** **(T6 – O12)** *Institute for High Pressure Physics of RAS, Russia* High Pressure Study of Many-Particle Interactions at Metal-Insulator Transition in Low Dimensionality Electron Systems
18:10	**E. Bauer** **(CES – O197)** *Vienna University of Technology, Austria* Tuning of superconductivity and magnetic order of heavy fermion CePt$_3$Si by substitution and pressure			
		18:20	**O. Grasset** **(T10 – O42)** *UMR 6112, France* The high-pressure phase diagram of the NH_3-H_2O system	**Gabor Laurenczy** **(T6 – O146)** *EPFL – ISIC, Switzerland* Synthesis and characterisation of the ruthenium(II) hydride/ dinitrogen complex under gas pressures in aqueous solution
18:40	**Gendo Oomi** **(CES – O200)** *Kyushu University, Japan* Pressure-induced quantum instability in highly correlated f-electron systems			**Changqing Jin** **(T6 – O123)** *Chinese Academy of Sciences, Inst. of Physics, China* Novel perovskite Compounds at Elevated High Pressure

Programme Wednesday

Location	Alfred-Mombert-Saal	Hans-Thoma-Saal		Johann-Peter-Hebel-Saal
8:30	IPPS	8:30	**Gerard Demazeau** **(T13 – KN)** *CNRS and University BORDEAUX 1, France* Solvothermal reactions:new trends in Materials Sciences	**W. Kremer** **(T9 – KN)** *Universität Regensburg, Germany* Characterization of pressure-stabilized functional important protein states by high resolution NMR spectroscopy
		9:00	**Tetsuo Aida** **(T13 – O138)** *Kinki University, Japan* The Development of a Novel Methodology for Observing Discontinuous Behavior of Density of Compressed Gases by Light Scattering	**Marwen Moussa** **(T9 – O184)** *University of Burgundy, France* Synergistic or antagonistic effects of combined high pressure subzero temperature microbial-inactivation: Involvement of thermodynamic properties of water
		9:20	**Valerie Tanneur** **(T13 – O10)** *CEA - DTCD/SPDE/LFSM, France* Fluidised bed in supercritical phase	**Philipp Heindl** **(T9 – O175)** *Federal Research Centre for Nutrition and Food, Germany* High pressure effects on the infectious prion protein
		9:40	**Jan Jansen** **(T13 – O185)** *Helmut-Schmidt-University/University of the Federal Armed Forces Hamburg, Germany* Controlling the selectivity of separation processes by pressure	**Roland Winter** **(T9 – O105)** *University of Dortmund, Germany* Composition Fluctuations and Microdomains in Three-component Model Biomembrane Systems - The Effects of Temperature, Pressure and Lipid Composition
10:00	Coffee Break			
10:30		AIRAPT General Assembly		
12:00	Lunch			
13:00	Social Excursions			
17:00				
18:30	Conference Dinner at Schwetzingen Castle			

Programme Thursday

Location	Alfred-Mombert-Saal	Hans-Thoma-Saal	Johann-Peter-Hebel-Saal
8:30		EHPRG Award	
9:30		EHPRG General Assembly	
10:30	Coffee Break		
11:00	**Vladimir Fortov** **(T7 – KN)** *Russian Academy of Sciences, Russia* Pressure Ionization of Multiple Shock Compressed Plasmas at Megabar Pressures	**Tadafumi Adschiri** **(T13 – KN)** *Tohoku University, Japan* Supercritical hadrothermal synthesis of organo-inorganic hybrid nano particles	**Rudi Vogel** **(T9 – KN)** *Technische Universität München, Germany* High Pressure Effects in Cell Biology
11:30	**Jon Eggert** **(T7 – O152)** *Lawrence Livermore National Laboratory, USA* Anisotropic Shock Propagation in Single Crystals	**Juan Carlos Rendon-Angeles** **(T13 – O144)** *Research Institute for Advanced Studies of the NPI, Mexico* Pseudomorphic Conversion of Mineral $SrSO_4$ to $SrCrO_4$ under Hydrothermal Conditions	**Milan Houska** **(T9 – O90)** *Food Research Institute Prague, Czech Republic* Functional food components prepared with assistance of high pressure treatment
11:50	**Oliver Tschauner** **(T7 – O128)** *University of Nevada Las Vegas, USA* Transient states of reconstructive phase transitions captured in shock retrieval experiments	**Yurii Ivakin** **(T13 – O18)** *Moscow State University, Russia* Synthesis of luminophores – powders in supercritical water fluid	**Benjamin Frey** **(T9 – O87)** *Technische Universität München, Germany* High hydrostatic pressure treated tumour cells. – Cell death pathways and immunogenicity of treated cells
12:10	**Jeffrey Nguyen** **(T7 – O112)** *Lawrence Livermore National Laboratory, USA* Tailored Dynamic Thermodynamic Paths: Implications for Phase Transitions and Planetary Isentropes	**Georgii Panasyuk** **(T13 – O193)** *Russian Academy of Sciences, Russia* Hydrothemal Synthesis and Investigation of Aluminum Terephthalate	**Mareile Müller-Merbach** **(T9 – O1)** *University of Hohenheim, Germany* Kinetics of the high pressure inactivation of Bacteriophages
12:30	Lunch		
13:30	Poster Session		
15:00	Coffee Break		

Programme Thursday

15:30	**A. Segura** **(T5 – KN)** *Instituto de Ciencia de los Materiales de la Universidad de Valencia, Spain* Correlation between spectroscopic and transport experiments under pressure in semiconductors: Some examples with III-IV and II-VI semiconductors	**Douglas Elliott** **(T13 – KN)** *Pacific Northwest National Laboratory, USA* The Use of Catalysts in Near-Critical Water Processing	15:30	**Thierry Straessle** **(WIC – O34)** *Universite Pierre et Marie Curie, France* Structure of Liquid Water up to 6.5 GPa and 672 K
			15:50	**Leonid Dubrovinsky** **(WIC – O94)** *Bayreuth University, Germany* High-Pressure High-Temperature Amorphous Ice
16:00	**Taku Okada** **(T5 – O98)** *Osaka University, Japan* Lattice dynamical implication of ilmenite MgXO$_3$ (X=Si, Ge, Ti) using Raman spectroscopy at high-pressures and high-temperatures	**Frédéric Vogel** **(T13 – O44)** *Paul Scherrer Institut, Switzerland* Efficient production of synthetic natural gas from biomass by hydrothermal gasification		
			16:10	**Eugene Gregoryanz** **(WIC – O218)** *Carnegie Institution of Washington, USA* Melting behavior of H2O at high pressures and temperatures
16:20	**Walter A. Großhans** **(T5 – O129)** *University Of Applied Sciences, Germany* Lattice vibrations and electronic transitions in the Rare-Earth metals: Praseodymium under pressure	**Andrea Kruse** **(T13 – O22)** *Forschungszentrum Karlsruhe, Germany* Biomass gasification in supercritical water: Key compounds as a tool to understand the influence of biomass components.		
			16:30	**Alexander Goncharov** **(WIC – O95)** *Lawrence Livermore National Laboratory, USA* Dynamic ionization and superionic state of water under extreme conditions
16:40	Break			
			16:50	Break
17:00	**Reinhard Boehler** **(T14 - O171)** *Max-Planck-Institut für Chemie, Germany* New Anvil and Gasket Designs	**Nikolaos Boukis** **(T13 – O26)** *Forschungszentrum Karlsruhe, Germany* Hydrogen and Methane Production from Biomass in Supercritical Water		**Jon Eggert** **(WIC – O176)** *Lawrence Livermore National Laboratory, USA* Observation of metallic helium: Equation of state and transport measurements under astrophysical conditions.
17:20	**Michael Popov** **(T14 - O31)** *Technological Institute for Superhard and Novel Carbon Materials, Russia* Pressure measurements from Raman spectra of stressed diamond anvils	**Sandrine Moussiere** **(T13 – O165)** *CEA Valrhô, France* Stirred double shell reactor for waste treatment by supercritical water oxidation		**Valentina Giordano** **(WIC – O60)** *Universite Pierre et Marie Curie, France* High-pressure High-temperature liquid carbon dioxide
17:40	**Igor Goncharenko** **(T14 - O177)** *Laboratoire Leon Brillouin CEA-CNRS, France* Neutron diffraction in 40 GPa - pressure range: a tool to study magnetic and crystal structures	**Dirk Klingler** **(T13 – 204)** *TU Darmstadt, Germany* Energy Recovery from Wet Biomass Feedstock in Supercritical Water		**Dennis D. Klug** **(WIC – O301)** *National Research Council of Canada* Infrared and X-ray Diffraction Study of Symmetric Hydrogen Bond Formation in the Methane Clathrate
18:00	**Takehiko Yagi** **(T14 - O187)** *University of Tokyo, Japan* A New Opposed-Anvil type High-Pressure and High-Temperature Apparatus Using Sintered Diamond	**Yukihiko Matsumura** **(T13 – O108)** *Hiroshima University, Japan* Heat transfer to the turbulent flow of supercritical water where glucose oxidation is taking place		**Yukihiro Yoshimura** **(WIC – O300)** *National Defense Academy, Japan* New transformation of ice in aqueous RbCl solution to a high-pressure phase at low temperature
18:20	**Akobuije Chijioke** **(T14 – O303)** *Harvard University, USA* The Ruby Pressure Standard to 150 GPa			

Programme Friday

Location	**Alfred-Mombert-Saal**	**Hans-Thoma-Saal**	**Johann-Peter-Hebel-Saal**
8:30		Plenary	
9:30	**Zbigniew Dreger (T7 – O114)** *Washington State University, USA* Electronic Structure Changes in Anthracene Crystals under Static and Shock Compression: Role of Nonhydrostaticity	**Damon Jackson (T3 – O24)** *Lawrence Livermore National Laboratory, USA* Magnetic Susceptibility Experiments on the Heavy Lanthanides Using Designer Diamond Anvils	**Sakura Pascarelli (T2 – O159)** *European Synchrotron Radiation Facility, France* Differential EXAFS: a tool to measure the effect of hydrostatic pressure on magnetostriction
9:50	**Mikhail Mochalov (T7 – O6)** *Russian Federal Nuclear Center, Russia* Experimental Measurement of Compressibility, Temperature and Light Absorption in a dense shock-compressed gaseous Deuterium	**Denis Kozlenko (T3 – O40)** *Joint Institute for Nuclear Research, Russia* Pressure-Induced Magnetic Phase Transitions in $Pr_{1-x}Sr_xMnO_3$ Manganites (x = 0.48 – 0.85)	**Kristina Lipinska-Kalita (T2 – O63)** *University of Nevada Las Vegas, USA* High-Pressure Synchrotron Radiation X-Ray Diffraction Studies of Pentaerythritol Tetranitrate $C(CH_2ONO_2)_4$
10:10	**Mikhail Zhernokletov (T7 – O7)** *Russian Federal Nuclear Center, Russia* Characterization of liquid Argon under Shock Compression in 125-515 GPa Pressure Range	**Gabriel Alejandro Dionicio (T3 – O178)** *Max-Planck-Inst. for Chemical Physics of Solids, Germany* Electrical resistivity of $YbRh_2Si_2$ under extreme conditions	**Kazuhiko Tsuji (T2 – O80)** *Keio University, Japan* Pressure dependence of the structure of liquid II-VI compounds up to 20 GPa
10:30	Coffee Break		
11:00	**Fernando Rodriguez (T11 – KN)** *University of Cantabria, Spain* Electric properties of Jahn-Teller and photoluminescence Systems under Pressure	**V. Struzhkin (T3 – KN)** *Carnegie Institution of Washington, USA* Superconductivity and magnetism in compressed materials: Novel phenomena	**Kenichi Takemura (T2 – KN)** *National Institute for Materials Science (NIMS), Japan* New structural aspects of Elements appearing under hydrostatic pressure
11:30	**I. Hernandez (T11 – O143)** *University of Cantabria, Spain* Pressure-induced photoluminescence in MnF_2 at Room Temperature.	**Anatoly Tsvyashchenko (T3 – O56)** *Russian Academy of Sciences, Russia* Superconductivity and magnetism of new rare earth ternary borides synthesized under high pressure	**Takamitsu Yamanaka (T2 – O28)** *Osaka University, Japan* Electron density distribution under high pressure analyzed by MEM using single-crystal diffraction intensities -ABO_3 ilmenites (A = Mg, Fe; B = Si, Ge, Ti)
11:50	**Toshihiko Kobayashi (T11 – O91)** *Kobe University, Japan* Band alignment in GaAs/GaInP heterostructures studied by low temperature photoluminescence under high pressure	**Kirsten Rupprecht (T3 – O173)** *Universität Paderborn, Germany* Ferromagnetic order up to 300 K in CsCl-type EuX (X = S, Se, Te)	**Suhithi (Sue) Peiris (T2 – P86)** *NAVSEA, India* X-ray Diffraction Studies of Single Crystals at High Pressure using Synchrotron Radiation
12:10	**Zbigniew Wisniewski (T11 – O55)** *Institute of Electron Technology, Poland* Tailoring of photoluminescence of Czochralski silicon by high temperature -pressure treatment	**Vladimir Shchennikov (T3 – O72)** *Institute of Metal Physics of RAS, Urals Division, Russia* Experimental high-pressure study of thermomagnetic and thermoelectric effects	**Gerhard Wortmann (T2 – O179)** *Universität Paderborn, Germany* High-Pressure Phonon Spectroscopy of Oriented hcp Iron by NIS: Anisotropy of Sound Velocities
12:30		Closing Remarks	
13:00	Lunch		
14:00	Technical Tour		

Plenary Lectures

The Bizarre Properties of Solid Hydrogen at High Pressure

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Hydrogen and its isotopes exhibit unusual, difficult to predict properties at high pressure in the condensed state. These unusual properties are a result of the large translational and rotational zero-point energy as well as the Pauli principle which results in profoundly different states of the solid depending on the ortho or para species, all a result of the nuclear spin states of the molecules. We discuss how the properties of hydrogen evolve with increasing density or pressure, new high pressure phases, and challenges. We conclude with a discussion of the challenges to produce metallic hydrogen, including new fascinating predictions that hydrogen may be a liquid at megabar pressures and zero Kelvin temperature.

Compressing Materials from Simple to Complex: New Findings and Phenomena

Russell J. Hemley, Geophysical Laboratory, Carnegie Institution, Washington, D. C. 20015 U.S.A., hemley@gl.ciw.edu

The accelerating developments in high-pressure experimentation in the last decade have culminated in a new era of research on materials under extreme conditions. Modern static high-pressure techniques provide the ability to tune interatomic and intermolecular interactions over a broad range of conditions, from very low pressures to >300 GPa and variable temperatures from cryogenic to thousands of degrees. Coupled with the increasing array of measurements that can be performed, these investigations have led to numerous new findings and phenomena of importance in fundamental physics and chemistry, materials science and technology, earth and planetary science, as well as biology. Examples include novel transitions in hydrogen and related materials; molecular chemistry and hydrothermal systems; pressure-induced metallization and superconductivity, and unexpected discoveries in living systems. Continued advances are expected using a new generation of devices made possible by the development of methods for producing large single crystal diamond by chemical vapour deposition.

ELUCIDATION OF INORGANIC AND BIOINORGANIC REACTION MECHANISMS FROM VOLUME PROFILE ANALYSIS

Rudi van Eldik

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Insight into the mechanisms of chemical reactions in solution, in many cases depends to a large extent on rate and activation parameters that can be determined for individual reactions steps. Over the past two to three decades, kineticists have studied the effect of pressure on many different types of inorganic and bioinorganic reactions in solution, and have constructed volume profiles that can reveal important mechanistic information [1]. These studies include the application of a wide range of different high pressure thermodynamic and kinetic techniques. The mechanistic elucidation of solvent and ligand exchange processes on metal ions could be largely resolved from systematic pressure dependence studies [2]. We have applied volume profile analysis to a wide range of chemical processes that include thermal, photo-induced and radiation-induced reactions, dealing with ligand substitution, electron transfer, activation of small molecules and oxidative addition/reductive elimination processes [1,3,4]. An overview of the fascinating mechanistic insights gained from volume profile analysis will be presented. A selection of typical examples from our most recent published [5] and unpublished studies will be used to demonstrate the type of mechanistic information that can be obtained from such analysis.

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[1] *High Pressure Chemistry: Synthetic, Mechanistic and Supercritical Applications*, R. van Eldik, F.-G. Klärner (Eds.), Wiley-VCH, Weinheim **2002**.

[2] F.A. Dunand, L. Helm, A.E. Merbach, *Adv. Inorg. Chem.* **2003**, *54*, 1.

[3] P.C. Ford, L.E. Laverman, in Ref 1, Chapter 6.

[4] R. van Eldik, D. Meyerstein, *Acc. Chem. Res.* **2000**, *33*, 207.

[5] R. van Eldik and collaborators: *J. Am. Chem. Soc.* **2001**, *123*, 285 and 9780; **2004**, *126*, 4181; **2005**, *127*, 5360; *Inorg. Chem.* **2002**, *41*, 4, 1579, 2565, 2808, 3802 and 5417; **2003**, *42*, 1688, 3718, 4179 and 6528; **2004**, *43*, 1429, 5351, 6093 and 7832.

Oral Presentation

Topic T3 Electrical and magnetic properties

Topic T4 Optical and acoustic properties

Topic T7 Pressure dynamics and shock waves

Topic T8 Geological, marine and planetary science

Topic T9 Bioscience and food technology

Topic T10 Phase transitions and transformations of fluids and solids

Topic T13 Chemical reactions in supercritical fluids

SCF:

SCW - Fundamentals:

SCW - Synthesis:

Topic 14 Advanced Equipment and Methods

CES **Correlated Electron Systems**

Nanomat **Nanostructured Materials**

Structural stability, elastic properties and dynamics of some elemental solids at high pressures

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University of Saskatchewan, Saskatoon, Canada S7N 5E2
2 Steacie Institute for Molecular Sciences
National Research Council of Canada, Ottawa, Canada K1A 0R5

Recent developments and the availability of accurate electronic codes have greatly enriched the understanding of the properties and phase transformation mechanisms of solids at high pressure. In this presentation, results of recent investigations on the dynamic and elastic properties of several high pressure solids will be reported. A generalization of the stress-strain method to the calculation of the elastic constants of any crystal symmetry will be illustrated. We will present experimental vibrational density of states of krypton determined from 83Kr nuclear inelastic scattering experiments. In comparison with theoretical calculations, we note that even in this simple system, subtle discrepancies between theory and experiment remains. Dynamical calculations were also employed to study the stability and superconductivty of the Si-V and Si-VI phases. It is found that the Si-VI, though energetically more stable than the Si-V and Si-V phases, it is found to be dynamically unstable and therefore maybe entropically stabilized at high temperature. Quantum mechanical dynamical and transport calculations were used to characterize the electron topological transitions and superconductivity in high pressure Nb. We found that a similar transition may explain the anomaly observed in the equation of state for Os.

Molecular Dynamics Simulations of cubic CaSiO3 at lower mantle conditions

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First-principles projector-augmented wave (PAW) molecular dynamics was used to investigate structure and properties of what is thought to be the third most abundant phase in the Earth's lower mantle, $CaSiO_3$ perovskite. The commonly assumed cubic structure was found to be stable at high temperatures and unstable at low temperatures at all pressures. On the basis of these results, we predict that the low temperature structure of $CaSiO_3$ perovskite is tetragonal space group I4/mcm. This phase would transform into an orthorhombic Imma structure under non-hydrostatic conditions. It is also obtained by fast quenching of cubic $CaSiO_3$ perovskite. This Imma structure explains hitherto puzzling experimental X-ray powder diffraction patterns.

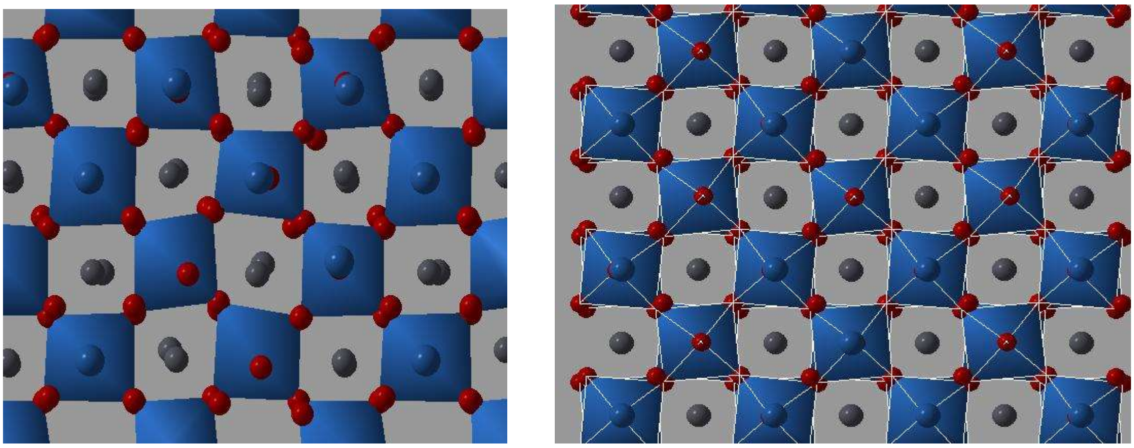

Fig1.(a) Snapshot of MD Simulations at 100GPa and 2500K. One can see clearly the strong deviations from the ideal cubic position because of the strong thermal movement. However, in average the structure remains cubic.

Fig1(b) Quenched structure. At 100 GPa $CaSiO_3$ was cooled down from 2500 K to 0K.

$CaSiO_3$ perovskite is thought to comprise between 6 and 12 wt% of the lower half of the Earth's transition zone and lower mantle. Its structure throughout this regime is generally assumed to be cubic [1, 2] because temperature generally increases symmetry. At lower temperature deviations towards a tetragonal structure were found [1, 3].

Using VASP code in the PAW frame the CaSiO3 cubic structures were first optimized at 0 K for pressures of 0, 50, 100, 150 GPa [6]. For MD simulations we used an N-V-T-ensemble with Nosé thermostat [5]. Temperatures of 500, 1500, 2500 and 3500 K were simulated. The lattice parameters were not relaxed but on the difference of stress in the three spacial directions we could observe a phase transition from the cubic phase at high temperatures to a tetragonal phase at low temperatures. As we observe a significant difference in stress components, we predict that transition takes place between 1500K and 500K.

Experiments [4, 1] indicate a tetragonal structure with $c/a = 0.993$, in apparent contrast to static energy minimization which gives structures with from $c/a = 1.012$ to 1.016. To resolve this question, we also performed quenches, which at the end gave new structures. Brute force changes of lattice parameters $c/a < 1$ and $c/a > 1$ were also performed. Fast quenching always gave Imma symmetry at the end. Slow quenching gave different results: Imma for $c/a>1$ and I4/mcm for $c/a<1$. This Imma symmetry structure is the only one explaining experiment as it gives the correct ratio of (440) and (004) intensities.

We suggest that the Imma symmetry phase is energetically more favorable at non-hydrostatic pressures, as it occurs both in experiment and simulations. In experiment non hydrostaticity comes from crystallization of pressure medium at low temperatures. In computations non-hydrostaticity comes from the cubic shape of the box the atoms are enclosed in whereas from their energetics the atoms would prefer a slightly distorted box.

As the Gibbs free energy has a hydrostatic and a non hydrostatic term, we suggest, that in the Imma phase the contribution from the non hydrostatic term is smaller than in the I4/mcm phase, which under hydrostatic condition is energetically preferable in agreement with [6,7].

The non hydrostatic term is given by

$$\frac{1}{2}\sum_{ij,kl}\sigma_{ij}\frac{\partial^2 G}{\partial\sigma_{ij}\partial\sigma_{kl}}\sigma_{kl}$$

where σ_{ij} is the stress tensor and $\frac{\partial^2 G}{\partial\sigma_{ij}\partial\sigma_{kl}}$ is equal to the elastic compliances. By lowering the symmetry from I4/mcm to Imma under non hydrostatic stress $CaSiO_3$ perovskite lowers the symmetry of the elastic constants and thus can minimize the non hydrostatic contribution to the Gibbs free energy. Further calculations will include computation of the elastic constants and minimization of Gibbs free energy under non-hydrostatic pressure.

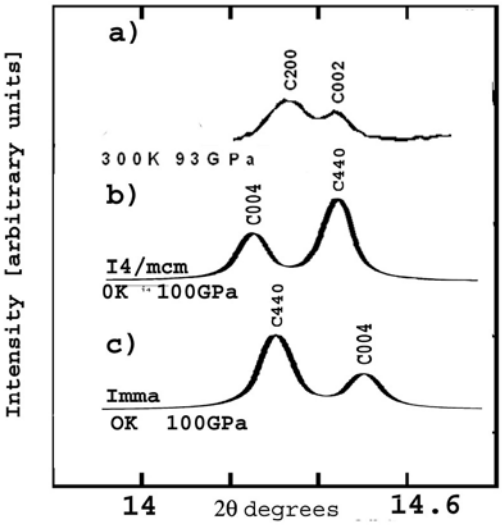

Fig2. Comparison of diffraction patterns at high pressure. (a) Experiment from [1]. Peaks are indexed by phase (C: $CaSiO_3$) and the corresponding hkl indices. (b) Theory: Computed powder diffraction pattern of optimized I4/mcm structure. (c) Theory: Computed powder diffraction pattern of optimized Imma structure coming from a quench.

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[3] Shim, S.-H.,Duffy, T.S. (2000). The stability and P-V-T equation of state of $CaSiO_3$ in the Earth's lower mantle. J. of Geophys. Res.

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Quantum mechanical simulation of pressure induced polymorphism in AgCl

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High pressure experiments in silver halides have recently identified non-cubic structures in their pressure induced polymorphic sequence connecting the B1 and B2 phases [1]. Most surprisingly, those same structures have been also found as intermediates [2] along proposed B1-B2 mechanisms in alkali halides. These facts have drawn us to undertake a detailed study of the thermodynamic and mechanistic aspects of the polymorphic sequence of AgCl, which includes monoclinic (KOH-type) and orthorhombic (TlI-type) phases. The electronic structure has been determined in the framework of the DFT as implemented in VASP [3]. Thermodynamic results are promising due to their good agreement with a number of observable properties. On the one hand, these results allow us to extend the limited experimental knowledge of the AgCl response to hydrostatic pressure. A non-expected energetic quasi-degeneration has been found for the TlI-type and anti-TlI-type structures. On the other hand, this agreement allows us to go one step further, and try to determine the involved transition paths. Different approximations (complete and partial interpolations, as well as full optimizations) have been dealt with in order to study the cell changes under the maximal common subgroup ($P2_1/m$). Historical reasons have also animated us to explore the virtual B1 to B2 $R3m$ energy surface (Buerger mechanism). Shocking results have been obtained: the appearance of several relative minima in the Gibbs energy profile of AgCl in contrast with a path without intermediates found in alkali halides. This feature is probably related, as well as the existence of non-cubic structures in the polymorphic sequence, to the partially covalent nature of the chemical bonds.

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Molecular dynamics simulations of pressure-induced solidification

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Molten metals subjected to rapid pressurization may undergo a phase transition to a solid phase if the final conditions are chosen appropriately. Specifically, the details of the final structure and the time scales for arriving at that structure should depend on the final magnitude and rate of pressurization. We study these dependencies using large scale atomistic modeling of copper (fcc prototype) and tantalum (bcc prototype). Results of many simulations on copper, modeled using a embedded-atom potential, allow us to construct a time-presssure-transition plot that shows the sensitive dependence of the solidification time on the final pressure. For, Ta, a more complex MGPT potential including up to 4 body interactions is required to adequately capture the d-electron bonding, and the presense of energetically competitive phases in this case results in extended solidification times.

Work performed under the auspices of the U.S. DOE at the University of California/Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

Density Functional Theory Calculations on EOS and Phase Stability of Beryllium

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Our current equation of state (EOS) for Beryllium [1] is based on experimental data and empirical models. This construction does not fully constrain the resulting EOS, and recently uncovered experimental results in the literature [2] show slight disagreement with the established EOS of Be. To address this disagreement we have calculated the cold curve and the phonons for Be in the hexagonal close-packed (hcp) structure using density functional theory. From these we extract the thermal expansion and the Grüneisen parameter; the former agrees well with experiment, the latter leads to a slight adjustment of the EOS. The same calculations for Be in the body-centered cubic (bcc) structure leads to a predicted structural phase transition from hcp to bcc at a pressure of 450 GPa (at 0 K) that decreases to 360 GPa near the melting temperature.

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Ab-initio Calculations of Spall Strength, Elastic Constants and EOS of Mo in Negative Pressure Region

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The shock compression experiments generate not only the compressive high pressures but also high tensile stresses. In recent years, the sophisticated diagnostic techniques like VISAR and ORIVIS, which are being used to measure such tensile stresses, have opened the possibility of understanding the material behaviour in the negative pressure regimes [G.I. Kanel et al., J. Appl. Phys., 90, 136, 2001].

In the present work we have determined the ideal spall strength (σ_S) and ideal tensile strength (σ_T) of Mo from first principles total energy calculations using full-potential linearised augmented plane wave (FP-LAPW) method (WIEN97 Package). Additionally, we have determined the equation of state (EOS) and calculated the elastic constants of this metal in the negative pressure regime.

The σ_S is calculated using uni-axial strain without allowing the Poison contraction (figure 1), however for σ_T the Poison contraction was also allowed. The calculated σ_S along [1 0 0] is 21 GPa as compared to the experimental value of 16.5 GPa measured after unloading the sample from peak pressure of 75 GPa (strain rate ~3×10^7/s) [Kanel et al, J. Appl. Phys, 74, 7162, 1993]. However, for determination of ideal σ_S, experiment should be performed at still higher stresses, and consequently at still higher strain rates, to minimize the effects of material defects. Our calculated σ_T value is 23 GPa. The theoretically determined EOS in the negative pressure region is shown in figure 2. The calculated equilibrium volume is 15.96 $(\text{Å})^3$/atom, elastic constants c11, c12, c44 are 439, 175, 100 GPa, and B0, Y(1 0 0), Y(111) are 272, 339, 266 GPa, respectively. All these values agree well with available experimental data [F.H. Featherstone and J.R. Neighbours, Phys. Rev. 139, 1324, 1963].

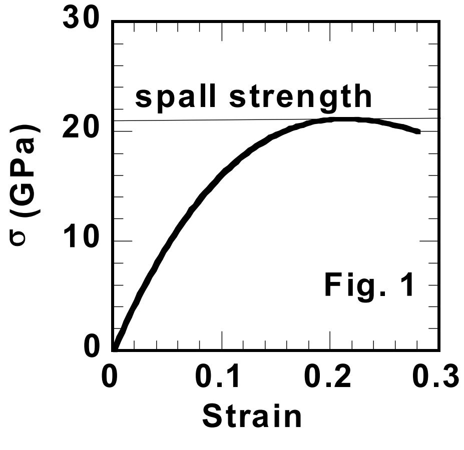

Fig. 1

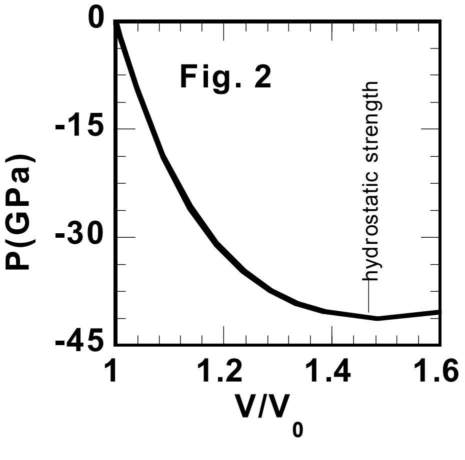

Fig. 2

Pressure effects on the absorption of α–phase Nb-H system

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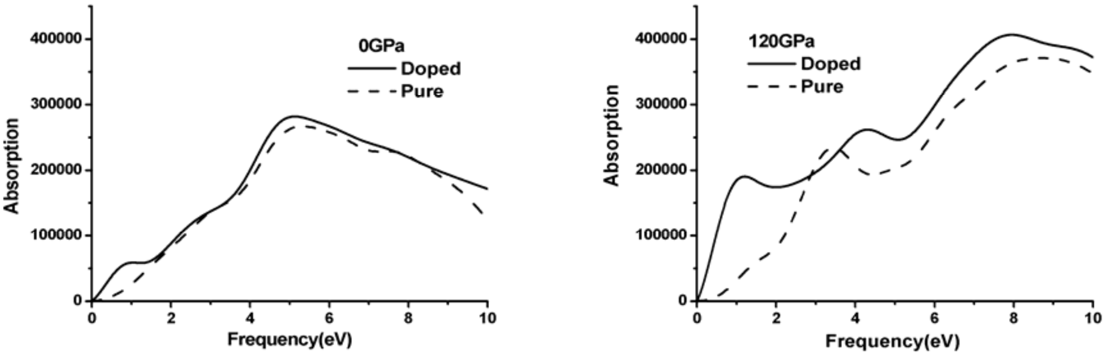
An *ab initio* calculation is performed on the α-phase Nb-H system based on density functional theory, for investigating pressure effects on the optical properties. The hydrogen concentration of the system is 1/16. The supercell of such a system consists of 16-atom bcc niobium and an interstitial hydrogen impurity placed at the center of an octahedron. Geometry-optimizations at 0K and within the pressure range from 0GPa to 200GPa are carried out. Then the electronic structures and optical properties of the system at different pressures are calculated.



(a) 0GPa (b) 120GPa

Figure 1 The absorption spectra of pure Nb and alpha-phase Nb-H systems under (a) 0GPa and (b) 120GPa

Figure 1 shows the pressure effect on the absorption spectra of pure Nb and alpha-phase Nb-H systems. The band structure calculations show that their Fermi Levels are all in 4d bands in the pressure range from 0GPa to 200GPa, resulting in similar absorption properties. A pressure induced absorption peak in the pure system is observed, e.g. in Figure 1(b) at about 3.5eV. The hydrogen impurity lowered the symmetry of Nb-H systems, leading to band splitting and distortion. New absorption peaks appear at some special frequencies such as the mini peak at ~1eV under 0GPa, which become strongest at pressure of 120GPa as shown in Figure 1(b).

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Pressure Induced Fermi Surface Evolution in Ligth Alcalies

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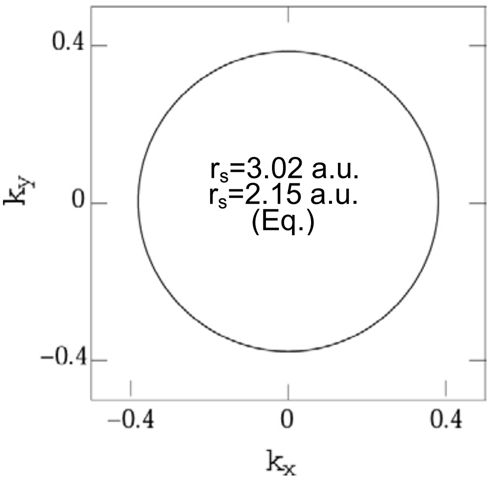
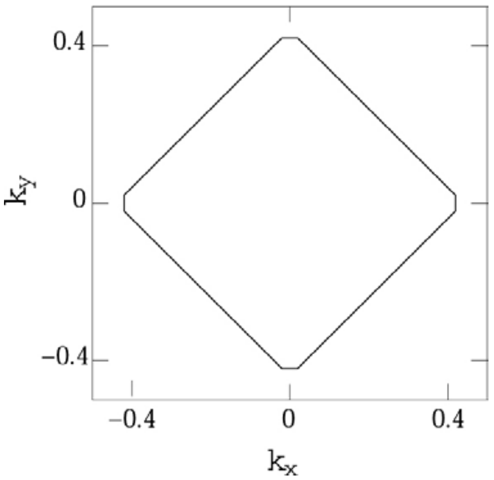
Light alkali metals have usually been considered as *simple* metals due to their monovalency and high conductivity. In these metals ionic pseudopotentials are weak and the nearly free electron model (NFE) becomes quite accurate at normal conditions. However, very recent theoretical calculations and experiments[1] have shown that at high pressures their electronic properties deviate radically from a NFE model and even become unexpected good superconductors with high T_c[2]. In this work we present *ab initio* calculations to analyze the deviation from simplicity of the Fermi surface (a sphere at equilibrium shown below) when pressure is applied. We have seen that, as a result of the increasing non-local character of the atomic pseudopotential with pressure, the nesting in the surprising half filling Hubbard type Fermi surface (a perfect cube below) might become the physical origin of the observed interesting correlation between structural, electronic and even magnetic properties.





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Thermoelasticity at High Temperatures and Pressures: Molybdenum and Tantalum

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In an effort to develop multi-phase constitutive strength models that extend with some certainty beyond the thermodynamic regimes of experiments, two quantum-based methods that calculate either anharmonic or quasi-harmonic effects to elastic moduli have been developed for temperatures up to 26,000 K and for pressures up to 10 Mbar. In either approach, both the electron-thermal and ion- thermal contributions are combined to compose the elastic moduli. The full potential linear muffin-tin orbital(FP-LMTO) method for the cold and electron-thermal contributions is closely coupled with ion-thermal contributions. For the ion contribution two separate approaches are used. In one approach, the quasi-harmonic ion contribution is obtained through a Brillouin zone sum of the strain derivatives of the phonons, and in the other the anharmonic ion contribution is obtained directly through Monte Carlo (MC) canonical distribution averages of strain derivatives on the multi-ion potential itself. Both methods for the ion-contribution use many-body, quantum-based interatomic potentials derived from model generalized pseudopotential theory (MGPT). The resulting elastic moduli compare well to available ultrasonic measurements and diamond-anvil-cell compression experiments, as well as to sound speeds along the Hugoniot. Over this range of temperature and pressure, the results are used in a polycrystalline averaging for a comparison to large-scale constitutive models like the Steinberg-Guinan strength model. Both molybdenum and tantalum elastic moduli are compared for varying anharmonic effects.

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Equations of state of metals at ultrahigh pressure

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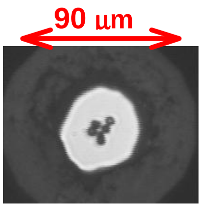
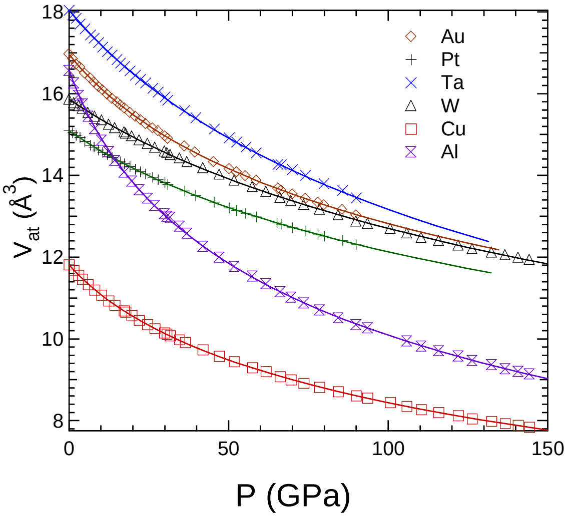
Compression versus pressure at ambient temperature has been measured for several metals (Be, Al, Fe, Co, Ni, Cu, Zn, Mo, Ag, Ta, W, Pt, Au) under quasi-hydrostatic conditions in a diamond anvil cell, up to at least 65 GPa and at a maximum pressure of 153 GPa (see figure below). Standard synchrotron x-ray diffraction accuracy in the volume determination could be achieved to the maximum pressure.

This data set can been used to re-calibrate the static pressure scale based on the ruby luminescence wavelength measurement [1]. The accuracy of various forms of luminescence wavelength vs. pressure in different pressure ranges will be discussed. In particular, this recalibration confirms recent suggestions of an underestimation of pressure by [1] at ultra-high pressure. We will show that using an updated pressure calibration, consistency between ultrasonic, dynamic and static measurements of the equations of state is improved [2].
This new consistency allows to test the predictive power of density functional theory, with different approximations, for equations of state calculations.



Sample geometry : grains of different metals, together with a ruby chip, embedded in helium.
Example of data obtained (see Ref. [2]) :



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Pressure-induced B1-to-B2 phase transition in $AgSbTe_2$: A first-principle study

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We have performed density functional (DFT) calculations to investigate the pressure-induced B1-to-B2 phase transitions in functional gradient materials such as $AgSbTe_2$ and $AgSbSe_2$. B1-$AgSbTe_2$ phase is energetically stabler by 0.18 eV/atom than B2-$AgSbTe_2$ phase at ambient condition. The calculated lattice constant and bulk modulus of B1-$AgSbTe_2$ phase are 5.93 Å and 44.5 GPa, in excellent agreement with experimental results. Equation of state of B1- and B2-$AgSbTe_2$ phases indicates that B1-$AgSbTe_2$ phase is stable up to 16 GPa and B2- $AgSbTe_2$ phase becomes stable after 26 GPa, consistent with experiments. At the intermediate pressure between 16-26 GPa, our experimental data also implicate the existence of the intermediate phases on the way to the pressure-induced phase transition from B1 to B2 phase. Theoretical study of the possible intermediate states including amorphous phase is advanced, and pressure-induced structural phase transition of $AgSbTe_2$ is also under investigation.

This work was supported in part by the Department of Energy under Cooperative Agreement DE-FC08-01NV14049.

Nitrogen (N_2) equation of state in pressure up to 10 kbar – molecular dynamic simulation

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Molecular dynamic simulation program using N_2-N_2 interaction potential, obtained be van der Avoird et al [1], has been used to determine nitrogen equation of state. Using this potential the pressure temperature dependence has been obtained by intensive molecular dynamic simulation. The temperature range spans from 1000K to 2000K while the pressure range extends from 1 bar to 10 kbar.

For low pressures the obtained pressure-temperature-density dependence follows that of ideal gas. The pressure range depends on the temperature, but generally ideal gas-like behavior is observed for pressure below 1 kbar. For these pressures the MD data are in very good agreement with the data of Jacobsen et al [2].

For higher pressure significant deviation from the ideal gas law, stems from strong molecule-molecule repulsion. This has been accounted for in the revised version of equation of state of nitrogen by Jacobsen et al [2]. The MD simulation were used to recover p-T-ρ dependence for the pressures, up to 10 kbar. For high pressure range i.e. from 1 to 10 kbar, the deviation from Jacobsen data was much larger, about 10%, which is larger that estimated standard error [2]. The possible sources of discrepancy are the approximate accounting of the vibrational motion and also the finite size of the simulation domain.

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New structural aspects of Elements appearing under hydrostatic pressure

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Importance of hydrostaticity in high-pressure research has well been recognized in recent years. Specifically for diffraction studies with synchrotron sources, hydrostatic conditions are effective for getting better angular resolution and reliable diffraction intensity without preferred orientation. Furthermore, hydrostaticity reduces pressure gradients in the sample chamber, thereby minimizing phase mixture near the transition pressure. This unique feature leads us to identify new phases, which are stable in a small pressure interval and sometimes hidden under nonhydrostatic conditions. A good example is the recent discovery of the incommensurate phase of iodine near the molecular dissociation [1], where hydrostaticity played a crucial role. In this talk, I will describe some technical features of hydrostatic experiments with the diamond-anvil cells, followed by detailed description of the incommensurate phase of iodine. Other examples will also be presented for structural studies of elemental metals under hydostatic conditions.

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Electron density distribution under high pressure analyzed by MEM using single crystal diffraction intensities

– ABO_3 ilmenites (A=Mg, Fe, B=Si,Ge,Ti) –

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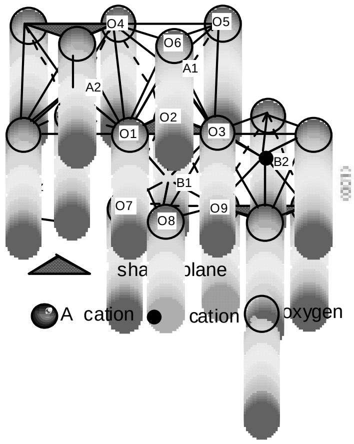
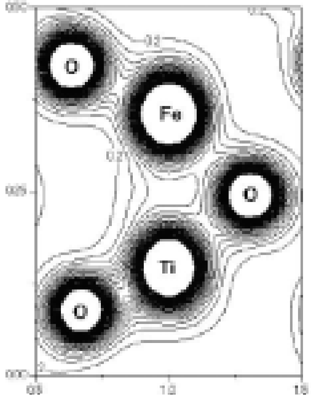
Most of ilmenites ABO_3 bearing transition elements have semiconductive and antiferromagnetic properties. In order to elucidate the electron conductivity change with pressure, electron density distribution of ABO_3 ilmenites (A=Mg, Fe, B=Si,Ge,Ti) have been executed by single-crystal diffraction intensities measurement at high pressures up to 15GPa with synchrotron radiation at KEK using new DAC with large single-crystal diamond plate windows. Compression mechanisms of $A^{2+}B^{4+}O_3$ ilmenites were also investigated by the structure analyses. All structure refinements converged to reliable factors R=0.05. The distortion of AO_6 and BO_6 octahedra under pressure was parameterized by interatomic distances, site-volume ratio and A^{2+}-B^{4+} interatomic distance across the shared edges and shared face (Fig. 1). Maximum entropy method (MEM) based on $F_{obs}(hkl)$ was applied to reveal electron density map (exp. Fig. 2) and compared with difference Fourier synthesis based on $F_{obs}(hkl)$-$F_{calc}(hkl)$. Radial distribution of electron (exp. Fig. 3) indicates more localization of electron around atomic position. Bonding electron density found in bond A-O and B-O reduces with pressure.

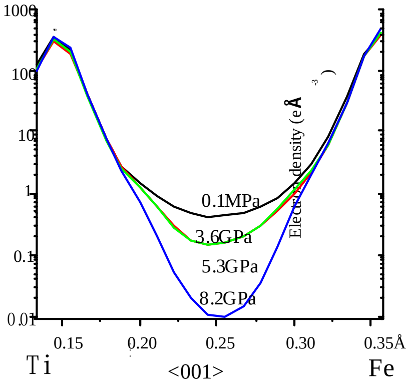
Part of ilmenite structure



Electron density map by MEM on (010) plane of FeTiO3 ilmenite



Radial distribution of electron between Fe and Ti atoms



High-Pressure Synchrotron Radiation X-Ray Diffraction Studies of Pentaerythritol Tetranitrate $C(CH_2ONO_2)_4$ [**]

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High-pressure x-ray diffraction studies of pentaerythritol tetranitrate, $C(CH_2ONO_2)_4$, (PETN), have been performed *in-situ* (diamond anvil cell) at ambient temperature using synchrotron radiation. The pressure-induced alterations in the profiles of the diffraction lines, including their positions, widths, and intensities have been followed up to 30 GPa in a compression cycle. The spectral changes at low pressures indicated continuous densification of the tetragonal structure (space group $P\bar{4}2_1c$). The diffraction patterns confirmed that the studied compound compressed rapidly from ambient pressure up to about 7 GPa with a 17% decrease in the unit cell volume. At 8 GPa and above several new diffraction lines appeared in the patterns. These lines suggested that the lattice undergoes a pressure-induced reconstructive phase transition (structural transformation) from the tetragonal to an orthorhombic structure. For a range above this pressure both phases coexisted indicating that the transformation is first order. The progressive broadening of the diffraction lines with pressures beyond 10 GPa limited detailed analysis at higher pressures. Further results and analysis will be reported.

[*] *deceased, September 12, 2004*

[**] Supported by th U.S. DoE cooperative agreement no. FC08-01NW14049

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Pressure dependence of the structure of liquid II-VI compounds up to 20 GPa

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X-ray diffraction measurements have been performed for liquid II-VI compounds, HgTe and CdTe up to 20 GPa using a synchrotron radiation. Pressure was generated by using cubic type apparatuses, MAX80 installed at PF- KEK and SPEED-1500 installed at SPring-8.

For liquid HgTe, the main peak of structure factor $S(Q)$ has two peaks at 2.2 A^{-1} and 3.0 A^{-1}. With increasing pressure, the height of the peak at 2.2 A^{-1} increases and the position shifts towards a higher Q value while the height of the peak at 3.0 A^{-1} decreases. On the other hand, the second peak at 4.9 A^{-1} shifts towards a lower Q value in spite of volume contraction. The first peak position of pair distribution function $g(r)$ does not change or rather shifts towards a larger r value and its height increases with increasing pressure. The second peak shifts towards a smaller r value.

For liquid CdTe, a remarkable structural change is observed in a narrow pressure region (1.8-3.0 GPa). The local structure in the low pressure region is similar to the zincblende structure, while that in the high pressure region is similar to the rocksalt structure. Another structural transformation occurs above 9 GPa.

These pressure dependences are different from those of liquid group 14 elements and liquid III-V compounds [1-4]. These results are discussed in relation to the bonding nature, such as covalency, ionicity and metallicity, and compared with the pressure-induced structural changes in the crystalline phases.

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Differential EXAFS: a tool to measure the effect of hydrostatic pressure on magnetostriction

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We have recently assessed the feasibility of performing X-ray differential EXAFS measurements of anisotropic (Joule) magnetostriction at high pressure on a test sample of polycrystalline FeCo. Joule magnetostriction is an anisotropic deformation which results from the application of an external magnetic field, and acts to transform a sample under the action of a 4th rank tensor with the strain related to the magnetisation direction cosines measured with respect to the principle axes of the tensor. The phenomenon arises from changes in electron density and hence interatomic bonding as the electron spins follow the domain magnetic field through spin-orbit coupling [1]. The method we used, based on the measurement of a differential EXAFS signal, has been developed in the past 2 years on the dispersive XAS beamline [2] of the ESRF, ID24, through a collaborative effort between the beamline staff and the University of Warwick (UK). This pioneering work opened the field to measurements of tiny atomic displacements [3]. For these first tests at high pressure, a chip of annealed polycrystalline FeCo film provided by the University of Sheffield (UK), was inserted into a CuBe Diamond Anvil Cell which was then placed at the center of a rotating magnetic field device. The system allows the rotation of the magnetic field on a plane perpendicular to the propagation of the X-rays. EXAFS measurements at the Fe K edge were acquired with the magnetic field parallel ($\mu\|$) and perpendicular ($\mu\perp$) to the polarization of the electric field of the X-rays emitted by one of the planar undulators of the ID24 straight section. The normalized differential EXAFS signal is defined as: $\mu\|-\mu\perp)/\mu\|+\mu\perp)$. The maximum P-P amplitude is about 5 10^{-4}. We performed measurements up to a maximum pressure of ~ 7.5 GPa. A clear reduction of the amplitude is observed as pressure is increased, the signal at 0.5 GPa and 3.7 GPa being respectively of about 3.5 10^{-4} and 1.0 10^{-4}. At 7.5 ± 0.5 GPa no signal, or a very weak one, is visible within the noise level. Absorption spectra as a function of pressure up to 7.5 GPa clearly indicate that the ambient pressure bcc structure is preserved in this pressure range, and the reduction in frequency of the oscillations indicates that the lattice contracts uniformly.

For the future, we plan to carry out, as a function of pressure, Fe K- edge XMCD simultaneously to differential EXAFS on FeCo, in order to disentangle the evolution with pressure of magnetostriction from that of the magnetic moment on Fe.

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In-situ determination of the melting diagram of Fe-alloys at high pressure

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We report *in-situ* observations of the melting behavior of iron alloyed with 10 to 20 atom% Si, S, or C, at pressures between 15 and 27 GPa. The experiments were performed in the SPEED-1500 multi-anvil press installed on the BL04B1 beamline of the Spring8 synchrotron (Japan). Melting and progressive recrystallization was evidenced by diffraction peak disappearance or apparition. We would quantified the degree of partial melting of the iron-alloys from the analysis of the diffuse x-ray scattering (due to the presence of liquid iron) nicely visible in the diffraction patterns. Coupled with micro-analysis of recovered samples, the *in-situ* observations bring direct and quantitative constraints on shape and positions of the main boundary-lines in the melting diagrams. Our results evidence a sharp melting loop for the Fe-Si phase diagram, thanks to a good compatibility of Si (and also C) in solid iron. In contrast, the melting loop in Fe-S system remains large in the pressure range investigated, even if the S-content in solid iron is found to increase with pressure. At 25 GPa, the S partition coefficient between solid and liquid iron is found to be of 7(1).

Understanding the thermal and chemical state of the Earth's inner core boundary (ICB) relies on the knowledge of the high-pressure melting diagrams of iron-alloys, which are poorly constrained. Extrapolations of our measurements to the ICB conditions remain very speculative; still, we already confirm an increased compatibility of S for solid iron with increasing pressure. Another important observation is the relatively large melting temperature depression observed in our experiments, which confirms the dominant effect of the light elements on the temperature at the Earth's ICB.

High-Pressure Phonon Spectroscopy of Oriented hcp Iron by NIS: Anisotropy of Sound Velocities

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This talk will first give a short introduction to the methodological aspects connected with nuclear inelastic scattering (NIS) of synchrotron radiation (SR) for phonon spectroscopy under high pressure, using the 14.413 keV Mössbauer resonance of ^{57}Fe, as exemplified in previous NIS studies of iron [1,2]. Then recent NIS studies of oriented hcp iron up to 130 GPa will presented, where the pressure-induced texture is used to derive the phonon density-of-states (DOS) as seen parallel and perpendicular to the hexagonal c-axis, as demonstrated in a previous study up to 40 GPa [3]. We observe a clear anisotropy in the elastic properties of hcp iron, indicating that the lattice is stiffer parallel than perpendicular to the c-axis. Of particular interest is the observed mean sound velocity v_D, from which the longitudinal and transversal sound velocities, v_p and v_s can be derived [2]. In accordance with the other elastic properties, the derived sound velocities are faster parallel than perpendicular to the c-axis. The derived values of v_p are of actual geophysical interest in conjunction with the observed anisotropy of v_p in the inner Earth´s core and will be discussed in comparison with other experimental and theoretical results.

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Superconductivity and magnetism in compressed materials: Novel phenomena

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Compression of a solid presents a natural means to tune interatomic distances and induce a variety of transitions (e. g. insulator-metal transitions, spin-crossover transitions, etc..) in a variety of materials. The most widely used technique for this purpose - diamond anvil cell (DAC) technology - has developed rapidly over the past few years. A number of techniques, which were previously limited to ambient pressure (because of the requirement of a large sample volume), may now be used at high and even ultrahigh pressures. Recent breakthrough results in transport measurements at very high pressures are discussed, as well as the progress at synchrotron facilities in phonon and electron spectroscopies. The novel techniques developed in our laboratory address fundamental properties of compressed materials, e. g. vibrational, electronic, and spin excitations. The presented techniques were made possible both by the development of multiple probes in bench-top experiments with diamond anvil cells and by the developments at the 3rd generation synchrotron x-ray sources. Brief list of topics is given below:

(1) superconductivity in multi-megabar pressure range studied by the magnetic susceptibility technique
(2) transport measurements in multi-megabar pressure range performed by four probe technique using van der Pauw method
(3) magnetic collapse and high-spin to low-spin transitions probed by the x-ray K-β emission process in transition metal compounds
(4) application of nuclear resonant x-ray technique to the measurements of magnetic transitions and the phonon density of states of iron-containing materials at megabar pressures

Few important applications of these techniques are described, with an emphasis on the superconducting properties of elements, transition metal nitrides and oxides. An overview of x-ray emission spectroscopy in iron compounds is given, as well as new results on the pressure effect on the valence band of germanium. Raman scattering from magnetic excitations under pressure is briefly reviewed.

Keywords: superconductivity; inelastic scattering;, high-spin; low-spin; x-ray emission spectroscopy; nuclear resonance; insulator-metal transition.

Magnetic Susceptibility Experiments on the Heavy Lanthanides Using Designer Diamond Anvils

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The high pressure magnetic properties of the heavy lanthanide elements Gd, Tb, Dy, Ho, Er, and Tm have been investigated by ac magnetic susceptibility using designer diamond anvils. It is found that the magnetic transition temperatures monotonically decrease with increasing pressure. In addition, the amplitudes of the magnetic transition signals decrease with increasing pressure, with the signals all eventually disappearing at pressures by 20~GPa. The transition temperatures, T_{Crit} are all found to drop at a rate proportional to their de Gennes factor, and the values of $T_{Crit}/T_{Crit}(P=0)$ vs P/P_{Crit}, where P_{Crit} is the pressure where the magnetic transition disappears, all sit on a single phase diagram.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Pressure-Induced Magnetic Phase Transitions in $Pr_{1-x}Sr_xMnO_3$ Manganites (x = 0.48 – 0.85)

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The crystal and magnetic structures of manganites $Pr_{1-x}Sr_xMnO_3$ (x = 0.48 - 0.85) have been studied by means of neutron diffraction at high pressures up to 4.8 GPa in the temperature range 16 – 300 K using sapphire anvil high pressure cells with the DN-12 spectrometer at the IBR-2 high flux pulsed reactor (Dubna, Russia).

At ambient pressure $Pr_{1-x}Sr_xMnO_3$ compounds (x = 0.48 – 0.85) have a tetragonal crystal structure (sp. gr. *I4/mcm*) and different magnetic properties for particular x values. $Pr_{0.52}Sr_{0.48}MnO_3$ exhibits a ferromagnetic state below T_C = 290 K. $Pr_{0.5}Sr_{0.5}MnO_3$ at 175 K < T < T_C = 265 K exhibits an intermediate ferromagnetic (FM) state followed by the onset of the A-type antiferromagnetic (AFM) state at $T_N \approx$ 175 K which is accompanied by a phase transformation to the orthorhombic structure (sp. gr. *Fmmm*). In $Pr_{0.44}Sr_{0.56}MnO_3$ at $T_N \approx$ 215 K the onset of the orthorhombic A-type AFM state occurs. $Pr_{0.15}Sr_{0.85}MnO_3$ transforms to the C-type AFM state at $T_N \approx$ 260 K.

Under high pressure, in $Pr_{0.52}Sr_{0.48}MnO_3$ the onset of the A-type AFM state ($T_N \approx$ 250 K) accompanied by the structural transformation from the tetragonal to the orthorhombic structure of *Fmmm* symmetry was observed. In $Pr_{0.5}Sr_{0.5}MnO_3$ at high pressures the noticeable increase of the FM – A-type AFM transition temperature from $T_N \approx$ 175 up to 230 K and formation of the phase separated state below 150 K, consisting of the mixture of orthorhombic A-type AFM phase and tetragonal phase without long range magnetic order occur. In $Pr_{0.44}Sr_{0.56}MnO_3$ at high pressures a tetragonal C-type AFM phase ($T_N \approx$ 125 K) appears and the phase separated state is formed, consisting of its mixture with the initial orthorhombic A-type AFM phase ($T_N \approx$ 220 K) [1]. In $Pr_{0.15}Sr_{0.85}MnO_3$ the initial C-type AFM state remains stable under high pressure. The stability of different magnetic states of $Pr_{1-x}Sr_xMnO_3$ under high pressure is discussed. The work has been supported by the Russian Foundation for Basic Research, grant 03-02-16879.

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Superconductivity and magnetism of new rare earth ternary borides synthesized under high pressure

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A new group of ternary borides has been synthesized at pressure of 8 GPa. The formula of ternary borides is RRh_4B_4. These materials were also found to crystallize, like $R(Rh_{0.85}Ru_{0.15})_4 B_4$, in a body-centered-tetragonal structure with space group $I4_1/acd$ like and 8 formula units per unit cell[1]. The superconducting and magnetic transition temperatures and lattice constants for new RRh_4B_4 compounds are shown in Table. The magnetism of RRh_4B_4 (where R=Dy, Ho, Er) is evident in the upper critical field H_{c2} vs. temperature data that are displayed in Figure. The data of heat capacity C/T of $DyRh_4B_4$ vs. temperature in zero applied magnetic field have revealed two lambda-type anomalies at T_{c2}=3.3 K and T_{c3}=2.5 K as well.

This work was supported by the Russian Foundation for Basic Research (project nos. 04-02-16061).

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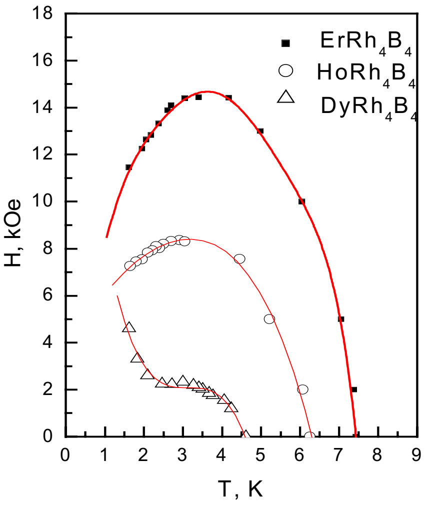
R	a (A^o)	c (A^o)	T_c (K)	T_m (K)
Dy	7,453	14,950	4,6	3,3
Ho	7,452	14,862	6,1	
Er	7,432	14,822	7,4	
Tm	7,412	14,870	7,2	
Yb	7,449	14,851	-	-
Lu	7,449	14,815	9,0	-
Y	7,434	14,934	10,7	-



Experimental high-pressure study of thermomagnetic and thermoelectric effects

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In the presentation the following items will be given:

i) the original stationary and autonomous high-pressure apparatuses and chambers made from non-magnetic materials for measurements both at hydrostatic (up to 2.3 GPa) and also at quasi-hydrostatic pressure P up to 30 GPa.

ii) the original experimental techniques of investigation of thermoelectric (Seebeck effect) and thermomagnetic effects (longitudinal and transverse Nernst-Ettingshausen effects, Maggi-Righi-Leduc) in microsamples at ultrahigh pressure.

iii) The results of high-pressure study of semiconductors of IV, VI, IV-VI and II-VI Groups.

Advantages of thermomagnetic and thermoelectric techniques over galvanomagnetic one are discussed.

The work was supported by the RFBR (Gr. 04-02-16178), INTAS (Ref. Nr. 03-55-629), US CRDF (TGP- 656).

Ferromagnetic order up to 300 K in CsCl-type EuX (X = S, Se, Te)

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The Eu(II)-chalcogenides are considered as model systems for Heisenberg magnetism because of the spin-only J = S = 7/2 4f-moment of the Eu^{2+}-ions and their simple NaCl structure. The variation of the magnetic ordering temperatures within the chemical series is described by the ferromagnetic J_1 exchange between neighbouring Eu-ions and the mostly antiferromagnetic J_2 exchange via the chalcogen ligands. High pressure studies of the EuX series with conventional ^{151}Eu Mössbauer spectroscopy as well as neutron studies [1, 2, 3] have contributed important information on the pressure dependence of the magnetic interactions of EuX in the NaCl phase.

Here we use the ^{151}Eu nuclear forward scattering (NFS) technique at pressures up to 120 GPa (1.2 Mbar) to perform systematic measurements of the magnetic and electronic properties of EuX in the NaCl phases and, for the first time, in the CsCl-type high pressure phases. We observe a dramatic increase of the ferromagnetic ordering temperatures up to 295 K for EuS at 120 GPa and up to 300 K for EuSe at 77 GPa. The corresponding hyperfine fields in the CsCl structure exhibit a variation with pressure which is markedly different from the behaviour in the NaCl structure, attributed to the different coordination and magnetic exchange paths in the CsCl-type structure. A possible valence change of the Eu-ions towards Eu^{3+} will be discussed in conjunction with the observed isomer shifts, hyperfine fields and magnetic ordering temperatures as well as information from optical and Eu-L_{III} edge spectroscopy.

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Electrical resistivity of $YbRh_2Si_2$ under extreme conditions

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Among the ternary Yb-compounds, $YbRh_2Si_2$ has the lowest magnetic ordering temperature $T_N \approx 70$ mK at ambient pressure. The proximity to a quantum critical point makes $YbRh_2Si_2$ an ideal candidate to study its unusual transport and thermodynamic properties related to quantum criticallity as a function of an external control parameter, like magnetic field [1] or pressure [2,3]. Since pressure stabilizes the $4f^{13}$ (Yb^{3+}) configuration, an enhancement of the weak antiferromagnetic order ($\mu_{\mathrm{eff}} \approx 0.01\ \mu_B$) is expected as pressure increases. Indeed, it was observed that T_N increases up to 0.9 K upon applying a pressure of 2.5 GPa [2]. Moreover, at higher pressures, Mössbauer studies revealed an unusual pressure dependence of T_N, showing a sudden increase of T_N at 10 GPa [3], which might be related to a first order magnetic phase transition from a low moment to a high moment state ($\mu_{\mathrm{eff}} \approx 1.9\ \mu_B$) [3].

Motivated by this, the electrical resistivity $\rho(T)$ of $YbRh_2Si_2$ was measured on a single crystal up to 15 GPa in the temperature range $0.1\ \mathrm{K} < T < 300\ \mathrm{K}$. Based on this experiment, $T_N(p)$ can be divided in three pressure ranges: (*i*) For $p < 4.1$ GPa, T_N increases strongly, followed by (*ii*) a quasi-pressure independent behavior in the range $4.1\ \mathrm{GPa} < p < 8\ \mathrm{GPa}$. After a sudden increase of T_N, the system eventually (*iii*) exhibits a weak pressure dependence above 10 GPa with $T_N \approx 7$ K at 15 GPa. This $T_N(p)$ is in agreement with the dependence deduced from Mössbauer measurements [3]. In regarding to the electronic scattering process at low temperatures, the results might indicate that there is a unique scattering mechanism in the entire pressure range. In addition, the pressure dependence of several high temperature maxima in $\rho(T)$ can be understood as an incoherent Kondo scattering process on the ground state and the excited crystal field levels.

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Progress in ultrasonic measurement at high pressure

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Elastic properties of invar $Fe_{64}Ni_{36}$

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Since its discovery in 1897 by C.E. Guillaume, invars has been the subject of numerous theoretical and experimental studies [1]. All these works agree to relate the invar effect, anomalous low thermal expansion over a wide temperature range, to magnetoelastic properties. However, a detailed microscopic explanation still remains puzzling for scientists.

We have made simultaneous x-ray diffraction and ultrasonic measurements [2], up to 7 GPa at ambient temperature on a polycrystalline sample of $Fe_{64}Ni_{36}$. We found a linear variation with pressure of the bulk modulus B with an abrupt discontinuity at 3.1 GPa. The slope dB/dP goes from an unusual low value (1.4) to a regular one (3.6). This result can be interpreted using the 2γ-state model [3] : up to 3.1 GPa, a gradual population of the low spin-low volume state at the expense of the high spin-high volume one compensates the thermal expansion due to the anharmonicity of the lattice vibrations.

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Crystal Structure Characterization Using Optical Properties

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Recent developments in tailored dynamic compression techniques have given us the ability to explore the dynamic phase space along prescribed thermodynamic paths. However, our ability to characterize the crystal structure under ultra-fast (sub-ns) and extreme pressure-temperature conditions is lacking. Here, we will report a novel idea of using optical properties to characterize phase transitions and crystal structures under such conditions. We have measured optical properties of various metals (Fe, Sn, Bi, and Al) at high pressures and temperatures. Preliminary analysis of these results will be reported. In particular, we will focus on changes in optical properties across phase boundaries: Fe (α–>ε), Sn and Bi (solid –> liquid). Implications of these measurements on emissivities, temperature measurements and on phase diagrams will be explored. We will also discuss the possibility of using this technique to explore the differences between the dynamic and static phase diagrams.

[1] Work performed under the auspices of the U.S. DOE at the University of California/Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

Luminescence study of Eu^{3+}:phosphate glass under pressure

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The pressure dependence of the luminescence of $^5D_0 \rightarrow {}^7F_{0,\,1,\,2}$ transitions of Eu^{3+} ions in 58.5 P_2O_5-9 Al_2O_3-14.5 BaO-17 K_2O-1 Eu_2O_3 (PKBAEu) glass has been investigated up to 38.3 GPa. As the pressure increases from ambient, the $^5D_0 \rightarrow {}^7F_{0,\,1,\,2}$ transitions are shifting towards the lower energy indicating an expansion of 4f electron wave functions with increasing covalency [1,2]. The Stark splitting of $^7F_1$ level increased with pressure as shown in Fig. 1, indicating an increase in the crystal field strength around the Eu^{3+} ions. As seen from Fig. 2, the decay curves obtained for the $^5D_0 \rightarrow {}^7F_2$ transition are found to be single exponential for all the pressures with shortening lifetime due to an increase in transition probabilities and pressure induced defects [2]. All these results are reversible when pressure is released.

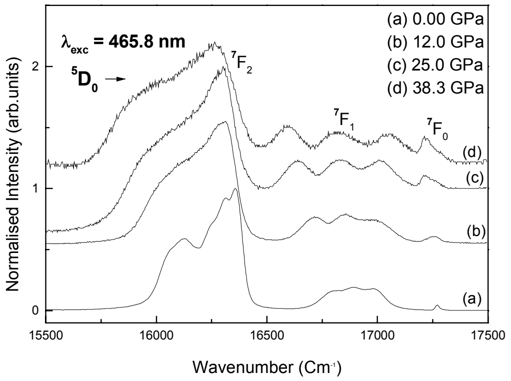

Fig. 1: Emission spectra of PKBAEu glass under pressure.

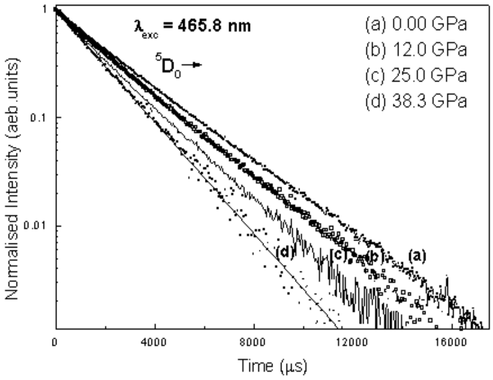

Fig. 2: Decay profiles of $^5D_0$ level in PKBAEu under pressure.

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Correlation between spectroscopic and transport experiments under pressure in semiconductors: some examples based on III-VI and II-VI semiconductors.

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This lecture will focus on the reliability of transport measurements under pressure as a source of accurate information on the electronic structure of semiconductors. The reliability of transport measurements will be discussed by correlating transport and spectroscopic experiments.

After discussing some confusions currently found in the literature about the transport properties of semiconductors, we will present some experiments on III-VI layered semiconductors in which transport measurements under pressure at different temperatures have given interesting keys about the evolution of the electronic structure of InSe and GaSe under pressure.

By using the phase transitions in InSe and CdTe as an example, we will also show how transport measurements are very sensitive to precursors effects and phase instabilities and provide useful information in some cases in which optical or structural experiments do hardly detect any change.

Finally, on the base of recent results on ZnO, we will focus in some optical measurements that are directly related to the transport properties of semiconductors: Moss-Burnstein band-gap shift, free carrier absorption and plasma-reflection. Some of these experiments yield the high frequency values of standard transport parameters and allow for useful correlations with resistivity and Hall effect measurements under pressure.

Proton Transfer under High Pressure.

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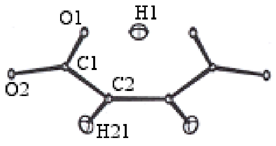
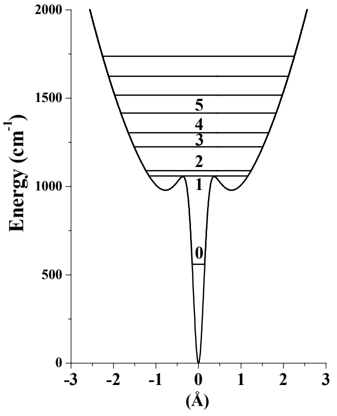
Our study is devoted to a better understanding of the complex relations between the proton transfer dynamics along a hydrogen bond in the quantum regime, and the chemical nature of donor and acceptor, the distance between the two proton sites, and the shape of the potential function. This distance depends on the pressure.

In AH•••B hydrogen bonds, the proton transfer is governed by a double minimum potential. In symmetric AH•••A systems, the two wells can be equivalent: two tautomeric forms exist and proton tunneling may occur. For shorter hydrogen bonds, the distance and the barrier height between the two minima decrease. The potential may become a single minimum potential and the symmetric structure can be considered as the "intermediate state" for proton transfer.

This dynamics can be observed by infrared and Raman spectroscopy. Very high pressures can be obtained with diamond anvil cell.

The mono-anion of maleic acid in potassium hydrogen maléate, KH(OOC–CH=CH–COO) is a typical example of a symmetric intramolecular hydrogen bond. This bond is strong (2.437 Å), with the proton located at the center. At ambient pressure, the potential function is symmetrical with a central minimum between two secondary minima at higher energy.





The main results are the following ones. Below 29 GPa, three pressure ranges (~3.9, ~6.4 and >1.8 GPa) related to irreversible spectral discontinuities can be distinguished. At ~4 GPa, the splitting of the CH stretching mode suggests a distortion of the "ring" of the molecule, leading to a disymetrization of the molecule. At ~6.4 GPa, the simultaneous appearance and disappearance of some intramolecular modes indicate a phase transition, with opening of the "ring".

High pressure ^{111}Cd – TDPAC spectroscopy of $YbAl_2$ compound

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The first measurements of perturbed γ - γ angular correlation (PAC) were done in the early 1950's, but the interest in the interaction between electric field gradients (EFG) *eq* and nuclear quadrupole moments *Q* has increased only recently.

The EFG is an impotent guiding concept for the description of the electronic structure of solids. From the time-differential perturbed angular correlation (TDPAC) measurement of the 173-247 keV γ cascade, and knowing electric quadrupole moment *Q* of the 5/2 intermediate level in ^{111}Cd, we can extract the EFG *eq* acting on the probe nucleus.

The physical properties of $YbAl_2$ exhibit typical signatures of non-integer valence, i.e. the Yb valence is directly related to the number of 4*f* holes n_h (or to the number of 5d-band electrons $n_d=n_h$) by $\upsilon=2+n_h$. Recently, the Yb valence in $YbAl_2$ has been investigated by resonant inelastic x-ray emission[1]. It was found that the Yb valence increases from 2.25 at normal pressure to 2.8 at 80 kbar. Thus, there is an opportunity to examine the EFG in relation to the valence of Yb ions in YbAl2 by the high-pressure TDPAC spectroscopy. The effect of high pressure on the EFG, present on ^{111}Cd impurity nuclei in $YbAl_2$ compound, has been measured by using a TDPAC installation[2]. The pressure range was up to 80 kbar.

As a result, linear dependence between the quadrupole frequency $\nu_Q = e^2qQ/h$ and the number of 5d-band electrons n_d (valence $\upsilon=2+n_d$) has been found. This linear dependence can be expressed by ν_Q = 7,5(10 n_d – 1) MHz.

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High-pressure Raman study on type III clathrate compounds

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Silicon clathrates are sp^3-bonded crystals composed of Si polyhedron cages, in which various guest atoms are usually trapped. Recently, type III new Si and Ge clathrates, $Ba_{24}Ge_{100}$ and $Ba_{24}Si_{100}$ were synthesized by several authors [1-4]. For conventional type I and II Si clathrates, the high-pressure phase transition has been investigated. However, there have been only a few high pressure studies on type III clathrate. The present work is the first investigation for the phase transition and the cage stability of type III Si and Ge clathrates ($Ba_{24}Si_{100}$ and $Ba_{24}Ge_{100}$) using high-pressure Raman scattering measurements up to about 30 GPa.

Raman scattering spectra of $Ba_{24}Si_{100}$ obtained at ambient pressure were different from that of Ba_8Si_{46} which shows three peaks assigned with Ba related vibrations below 100 cm^{-1}. In $Ba_{24}Si_{100}$, there were at least five peaks in the similar frequency region. In the high pressure experiments, two phase transitions were found. At around 6-8 GPa, the Raman peak at 125 cm^{-1} split into two, and became suddenly weakened, and at 23 GPa, all the Raman peaks suddenly disappeared. The latter phase transition is thought to be due to the transition into the amorphous state, because the spectrum obtained after complete decompression was similar to that of the amorphous silicon. Similar experiments were performed for $Ba_{24}Ge_{100}$, and the results are compared with those of the Si clathrates.

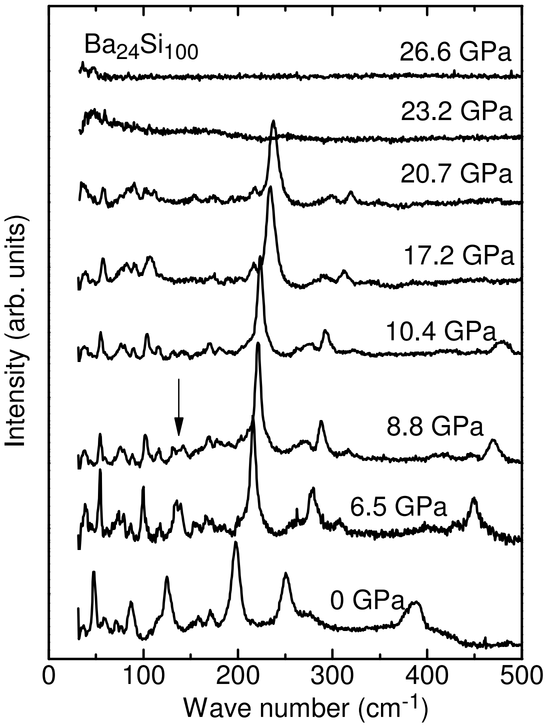

Fig. 1. Pressure dependence of Raman spectra of $Ba_{24}Si_{100}$.

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Lattice dynamical implication of ilmenite $MgXO_3$ (X=Si, Ge, Ti) using Raman spectroscopy at high-pressures and high-temperatures

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Ilmenite-type $MgX^{4+}O_3$ (X=Si, Ge, Ti) have various stable P-T regions due to their compositions: $MgSiO_3$-, $MgGeO_3$- and $MgTiO_3$-ilmenite are stable at high-pressures, moderate-pressures and ambient pressure, respectively. In this study, we conducted a high-pressure and high-temperature Raman spectroscopic study of ilmenite-type $MgSiO_3$, $MgGeO_3$ and $MgTiO_3$. From the viewpoint of elasticity and bonding energy, we investigate their behaviours at high-pressures and high-temperatures and compare structure change with different compositions.

Raman spectroscopy was a triple microspectrometer equipped with an optical microscope and an Ar ion laser. High-temperature experiments were performed using a Pt-electric resistant heater. For the high-pressure experiments, a diamond-anvil cell (DAC) was used using H_2O as the pressure media. Raman spectra of those samples were collected up to 770 K at ambient pressure and 30 GPa at room temperature, respectively.

From the obtained Raman bands, we calculated the force constant, k, of the stretching modes ($A_g(1)$ and $E_g(1)$) and obtained the temperature and pressure dependence of k. The temperature dependence of k was the order of Ge-O, Si-O and Ti-O stretching bands. The tendency induces the relative expansion rate for each XO_6 (X=Si, Ge, Ti) octahedron. This is consistent with the fact that $MgTiO_3$ ilmenite is the only stable phase at the present HT experimental conditions. On the other hand, the orders of the pressure dependence of k of $A_g(1)$ and $E_g(1)$ are different. For Si-O and Ge-O bonds, the pressure dependence of k of $A_g(1)$ is larger than that of $E_g(1)$. Namely, shorter X-O bonds ($A_g(1)$) are more shortened under pressure than longer X-O bonds ($E_g(1)$), indicating that the distortion of XO_6 octahedra is enhanced at higher pressures. For Ti-O bond, the pressure dependence was contrary. These phenomena obtained are consistent with the results of the single-crystal structure analyses by Yamanaka et al. (2005, *Am. Mineral.*, in press).

Lattice vibrations and electronic transitions in the Rare-Earth metals: Praseodymium under pressure

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Praseodymium was investigated by Raman spectroscopy under pressure. A negative pressure shift of the E_{2g} mode is observed in the dhcp phase, which indicates that the initial structural sequence hcp→Sm-type→dhcp→fcc as a whole in the regular lanthanides is associated with a softening of this mode. The pressure response of the phonon modes, observed in the monoclinic and α-uranium phases, where 4f-bonding becomes important, is characteristic for anisotropic bonding properties.

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Experimental and theoretical investigation of the electronic structure of $CuAlO_2$ delafossite under high pressure

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In spite of the large interest aroused by the p-type transparent conductor CuAlO2 since its discovery [1], the nature and value of its band-gap remains controversial [2]. In this communication we report on the evolution of the electronic structure of $CuAlO_2$ delafossite under pressure and determine the value and character of its band-gap on the basis of optical measurements and ab-initio electronic structure calculations. The absorption spectrum in the NIR-VIS-NUV range has been measured on single crystals up to 20 GPa for light polarization perpendicular and parallel to the symmetry axis. In the near-infrared and visible range the absorption spectrum consists of several absorption bands that are proposed to be related to internal transitions in Cu^{+2} ions near to Cu vacancies. Absorption in the ultraviolet corresponds to the fundamental transition that exhibits a quadratic dependence on the photon energy, corresponding to an indirect gap of 2.95 eV at ambient pressure, that increases under pressure at a rate of 15 meV/GPa. At higher energy we detect the onset of an intense allowed transition that moves with a pressure coefficient 1.8 meV/GPa and was previously identified as the fundamental transition from absorption measurements on thin films.

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Synthesis and Characterization of Transition Metal Nitrides

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The interest in the synthesis of the new materials has been always driven by the applications relevant to the technology and fundamental science. Transition metal carbides and nitrides form refractory high-strength high-hardness materials [1]. Recent discovery of platinum nitride (PtN) [1] showed the possibility of synthesis of the novel materials at high pressures (e.g. 50 GPa) and temperatures and their recovery to the ambient conditions in the diamond anvil cell. Here, we present two novel transition metals nitrides IrN and OsN_2 synthesized at extreme conditions having exceptionally high bulk moduli. Using synchrotron x-ray radiation, Raman spectroscopy and electron microprobe analysis we characterize the new materials and compare them with other known transition metals nitrides.

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High Pressure Study of Many-Particle Interactions at Metal-Insulator Transition in Low Dimensionality Electron Systems

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We used the high pressure technique as an instrument in experimental studies of many-particle interactions in concern with the MIT in 2D electron system formed in Al/*n*-GaAs:δ(Si) structure as well as in NbS_3 that is an example of quasi-1D physical system with a collective electronic charge transport by a charge density wave.

The effects of many-particle interactions become more clear when lowering the dimensionality of the system due to weaker screening and due to stronger carrier density dependence of potential-to-kinetic energy ratio that manifests itself not only in the energy spectra but also in kinetic properties of electron systems, in particular, in the drastic change of conductance regime called metal-insulator transition (MIT).

Using the pressure in studies of the GaAs type semiconductors provides a unique possibility to study the influence of the carrier density keeping the same static distribution of the impurities and structural defects over the sample. We report the results on the tunneling and the lateral conductance of 2DEG measured simultaneously at hydrostatic pressures in 2.5 GPa range at helium temperatures. The sharp resistivity rise along the delta-doped layer shows that the MIT in 2DEG at about 2 Gpa is accompanied by significant evolution of many-particle interaction induced features (electron - LO-phonon and Zero Bias Anomaly due to the inter-electron interaction) in the tunneling spectra.

NbS_3 is a member of MX_3 family (M=Ta,Nb, X=S,Se) with a chain-like structure. The coupling along the chains is much stronger than in the perpendicular direction, and the interaction between the electrons condensed in the CDW gives the main contribution to the elastic properties of the electron crystal and determines many physical parameters of q-1D conductors. We observed a 5 orders drop of resistance of NbS3 wiskers in 4-5 GPa pressure range that we attribute to the change of the dimensionality of electron subsystem under pressure.

The work was supported by RFBR and Phys. Sci. Dept. of RAS grants.

Associating Borate and Silicate Chemistry by Extreme Conditions: High–Pressure Synthesis and Crystal Structure of the Novel Borates $RE_3B_5O_{12}$ (RE = Er – Lu)

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The diagonal relationship B↔Si enables the partial substitution of silicon for boron, leading to the substance class of borosilicates, which are widespread accessory minerals. Unfortunately, a complete substitution of silicon against boron in the tetrahedral position, keeping up the silicate structure, is hardly so simple.

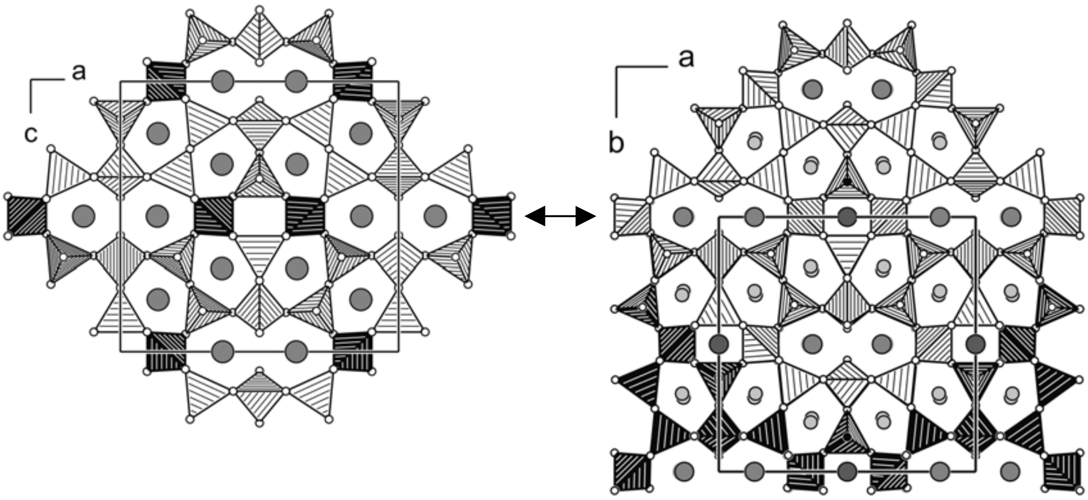

Fig. 1. Comparison of the crystal structures of $RE_3B_5O_{12}$ (RE = Er – Lu) (left; light polyhedra Q^3, dark polyhedra Q^4) and semenovite (right). The light polyhedra in the structure of semenovite visualize the identity of the tetrahedral layers in $RE_3B_5O_{12}$ (RE = Er – Lu) and semenovite.

By the use of high–pressure [1] (10 GPa, 1100 °C, Multianvil–technique) we were able to synthesize oxoborates with the new composition $RE_3B_5O_{12}$ (RE = Er – Lu) (S. G. *Pmna*), which are homeotype to the beryllo–silicate mineral semenovite ($(Fe^{2+}$, Mn, Zn, Ti)$RE_2Na_{0-2}(Ca, Na)_8(Si, Be)_{20}(O, OH, F)_{48}$) (Fig. 1). These results have important implications for the geochemistry of the Earth´s mantle. This work is supported by the Deutsche Forschungsgemeinschaft and the European Science Foundation (COST D30/003/03).

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Synthesis of novel materials under high pressures.

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Through an analysis of the research works involving the high pressure synthesis of novel materials during these last 20 years, high pressures can be involving either as thermodynamical parameters or reactive component. These both aspects of high pressure synthesis can be developed roughly at two different scales: (i) the macroscopic one when a material (including composition and structure) is involved or (ii) the nanoscopic scale when pressure can modify some atomic parameters (size, electronic structure…).

The first approach involving a pressure domain more accessible (from 10 MPa to 20 GPa) using different equipments (reaction vessel, piston-cylinder, belt, multianvils…) and different reaction medium (gas, liquid, solid), was the most developed.

The second approach requiring high pressure values can be mainly developed through Diamond Anvil Cell.

In the near future two research areas seems to be promising: (i) the high pressures involving in addition a fluid phase (Solvothermal Reactions) due to the improvement of the reactivity and (ii) the materials chemistry in Diamond Anvil Cell.

About the synthesis and magnetic behavior of new layered oxides structurally related to natural micas

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Layered silicates are common components of many soils, so they arouse much interest in geology and mineralogy areas. In addition, phyllosilicates such as smectites constitute a naturally occurring class of inorganic catalyst and are studied for their interesting properties including cation exchange, intercalation and swelling [1]. These earth's crust compounds can be used as structural models to develop new functional materials. For example we have evidenced that it is possible to synthesize some new layered oxides structurally related to natural phyllosilicates such as biotite or phlogopite mica : the phyllosiloxides [2,3]. This new class of layered oxides was expanded to three new compositions : $KMg_2Fe^{3+}Si_4O_{12}$, $KFe^{2+}{}_2AlSi_4O_{12}$, and $KFe^{2+}Fe^{3+}{}_3Si_3O_{12}$. The sol-gel route was adopted to prepare a precursor and the polycrystalline samples were obtained by solvothermal treatments at 750°C/650MPa. The three powder X-ray diffraction patterns were successfully indexed by 1M polytype of mica. Platelet morphologies of these samples were observed through the images of scanning electron microscopy. Mossbauer spectroscopy and squid measurements have been performed to determine the magnetic behavior of these compounds which will be discussed as a function of the repartition of transition ions in the materials.

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SINGLE CRYSTAL GROWTH OF GALLIUM NITRIDE BY SLOW-COOLING OF ITS CONGRUENT MELT UNDER HIGH PRESSURE

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We were successful in synthesizing single crystals of GaN (Gallium Nitride) by means of slow cooling of its congruent melt under high pressure. GaN is a key material in optoelectronic devices for blue light-emitting diodes and lasers. Large GaN single crystals from its melt cannot be synthesized by standard methods at ambient pressure such as Czochralski or Bridgman growth because it decomposes before melting. We confirmed by *in situ* X-ray diffraction study that applying high pressures above 6.0 GPa completely prevented the decomposition and allowed the congruent melt of GaN at 2220°C, Using a cubic-anvil-type large volume high-pressure apparatus and GaN powder as a starting material, single crystal growth was performed by decreasing temperature from 2400°C at 6.5 GPa. The X-ray rocking curve of the recovered sample showed very narrow line width smaller than 30 arcsec, suggesting its low dislocation density.

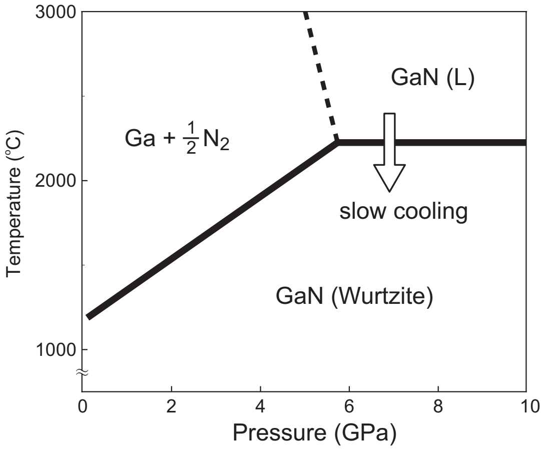

Figure 1 Phase diagram of GaN at high P-T determined by *in situ* x-ray diffraction

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Cubic boron nitride under extreme conditions of high pressure and temperature: a combined Raman and theoretical study

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Cubic boron nitride (cBN) has several remarkable properties including extreme hardness, chemical inertness, high thermal conductivity, and a wide band gap, that makes it attractive for many practical applications including abrasives, protective coating and microelectronic devices. Since most of these properties include the use of the material at extreme conditions, the study of its physical properties under these conditions is essential.

It has been suggested [1], that cBN can be used as a pressure sensor because of the stability of its crystal structure under very high pressure. Use of cBN as a Raman pressure gauge at simultaneous conditions of high pressure and temperature has been proposed recently [2-4], but the corresponding experimental studies are limited to 1550 K at approximately 9 GPa [2] and 727 K at 20 GPa [3]. No theoretical calculations of the vibrational properties *c*BN at simultaneous high pressure and temperature are reported.

In this work, Raman spectroscopy in the diamond anvil cell and density functional calculations have been used to determine the pressure dependence of the transverse zone-center optical phonon mode to 40 GPa and 2000 K. High temperatures were achieved using laser heating combined in some cases with internal (resistive) heating. Powdered alumina and argon served as pressure media. The results establish a high-pressure scale at high temperatures based on the measured and calculated frequency of the transverse optical mode. Our experiments show that cBN can be conveniently used as in situ pressure sensor to at least 2400 K and 40 GPa.

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20th AIRAPT and 43th EHPRG Meeting

Novel Perovskite Compounds at Elevated High Pressure

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High pressure synthesis is a very powerful tool to stabilize new compounds with perovskite-like structure. This has been exclusively demonstrated in the research of high Tc cuprate superconductors (HTS) which can be viewed as the derivatives of copper-oxide based perovskites containing the [CuO2] plane. This presentation will introduce our recent work on the phase formation and physical properties of the perovskite-like structures by using high pressure synthesis and diamond anvil cell technique in the A-Cu-O system (A represents the alkaline earth element), which in most case are superconductors being modulated by chlorine and oxygen occupancy at the charge reservoir block. Besides included is the work of the polymorphous transition to perovskite like structure of other related copper oxides. Also covered is the high pressure synthesis and property studies of other related transition metal oxides.

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Synthesis and characterisation of the ruthenium(II) hydride/dinitrogen complex under gas pressures in aqueous solution

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Interest in the chemistry of ruthenium(II) water soluble complexes has increased over the past few years due to potential applications in catalysis(1) and medicine(2). Several ruthenium(II) aqua complexes with small gas molecules have been reported in aqueous solution: In water $[Ru(H_2O)_6]^{2+}$ reacts with pressurised H_2 giving the dihydrogen pentaaqua Ru(II) complex(3). Two water-soluble dinitrogen complexes of the ruthenium(II) aqua ion have been characterised under N_2 pressure using multinuclear NMR spectroscopy(4). In presence of CO pressure(5), Ru(II) ion can be transformed into the monocarbonyl, *cis*-dicarbonyl and *fac*-triscarbonyl complexes. Under ethylene pressure of $[Ru(H_2O)_6]^{2+}$, beside the formation of the *mono* and *bis* ethylene complexes, the dimerisation reaction takes place(6): several isomers of butene have been isolated.

We report here the synthesis and characterisation of new water soluble hydride Ru(II) species, including a complex having both dinitrogen and hydride ligands present in the first coordination sphere.

Acknowledgement:

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Synthesis of a noble metal nitride under extreme conditions.

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Iridium nitride has been synthesized in a laser-heated diamond anvil cell at a pressure above 47 GPa and at temperature of around 2000 K. The compound is stable under ambient conditions.

Transition metal nitrides are of great technological importance traditionally because of their strength and durability, but also because of other interesting physical properties (e.g. optical, electronic, and magnetic [1]). Recently, several experimental and theoretical investigations have been made into the synthesis and properties of nitrides produced under extreme conditions of pressure and temperature. Novel phases of known nitrides have been successfully synthesized [2,3] as well as at least one entirely new compound [4]. The latter work reports the synthesis of the binary noble metal nitride PtN. This material was found to be stable under ambient conditions and to possess a bulk modulus of 372 GPa, remarkable for being nearly 100 GPa higher than the pure metal. Here we report that a recoverable nitride of iridium is produced at pressures of not less than 47 GPa and at a temperature of around 2000 K. The corresponding Raman spectrum (collected from 85 GPa to ambient pressure) exhibits many intense features. We have determined the stoichiometry of the material using x-ray photo-electron spectroscopy and compare the results thus obtained with those of SEM micro-probe investigations. We also report the crystal symmetry of the material on the basis of XRD measurements. We are currently investigating the material hardness using the technique of nano-indentation.

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Photo-induced polymerization of nitrogen at multi-Mbar pressure.

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Effect of photo-induced polymerization of nitrogen in multi-Mbar pressure range is reported. Molecular nitrogen was transformed to different atomic phases using this effect.

Previous studies [1, 2] reported a pressure-induced transformation of molecular nitrogen N_2 to a non-molecular (polymeric, or atomic) state at pressure 130-170 GPa. Interpretation of high-pressure atomic phases is difficult, because the sample composes presumably from phase mixture [2]. Heating of the sample [3] leads to possible chemical reactions of nitrogen with diamond anvil. As result, structure study reveals principal contradictions between Raman and X-ray data.

In the present study molecular nitrogen was loaded in diamond cell up to 170 GPa without an initialization of transformation to atomic phase. At pressure 170 GPa the sample was completely opaque and black. There are only bands of molecular phase in the Raman spectra and no signs of atomic phase. The illumination of the samples at 130 and 170 GPa gives strong effect of the photo-induced polymerization: the intensities of the molecular modes drop and the characteristic bands of polymeric nitrogen appear in the Raman spectra. The photo-transformation at pressure 130 GPa leads to formation of cubic gauche phase [1], whereas the photo-transformation at 170 GPa leads to formation of another new phase. In the second case the photo-induced transformation is accompanied by pressure decreasing to 165 GPa, indicating a volume decreasing of the sample. Pressure increasing to 250 GPa gives no new features in the Raman spectra.

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PRESSURE IONIZATION OF MULTIPLE SHOCK COMPRESSED PLASMAS AT MEGABARS

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Physical properties of hot dense plasmas at megabar pressures are of important for astrophysics, planetary physics, geology, ICF target design and for understanding of physical processes of intense laser and particle beam-target interactions. Moreover, the intense laser and particle beams are the unique tools for generation of shock waves with ultramegabar pressure amplitudes, which open the new possibilities for experimental investigation of physical properties of matter at high pressure. The physical properties of hot dense matter at high pressures and energy densities are analyzed in a broad region of parameters. The theoretical and experimental methods of non-ideal plasma investigations are discussed. Main attention is paid to the dynamical methods. Intense shock, rarefaction, and radiative waves in solid and porous samples, electrical explosion and bulk electron and ion heating were used for generation of high density matter at extremely high pressure. The highly time-resolved diagnostics permit us to measure thermodynamical, radiative and mechanical properties of high pressure condensed matter in the phase diagram broad region – from the compressed condensed solid state up to the low density gas range, including high pressure evaporation curves with near-critical states of metals, strongly coupled plasma and metal-insulator transition regions.

The theoretical interpretation of the opacity measurements demonstrates a strong deformation of discrete spectrum in non-ideal plasmas. The pressure ionization phenomena in hydrogen, helium, noble gases, iodine, silica, sulfur, H_2O, fullerenes and some metals are analyzed on the base of multiple shock wave electrical and explosion experiments. The data obtained were described by the non-ideal plasma model taking into account increase of charge carrier number as a result of “pressure” ionization. In contrast to these experiments the multiple shock compression of solid Li, Ca and Na shows dielectrization of these elements at megabars. The estimations of the dielectrization pressure range for some elements at ultramegabars are presented.

The experimental data obtained allow us to construct four-phase wide-range equations of states and transport properties models, which describe the physical properties of matter within a broad phase diagram region with taking into account high pressure melting, evaporation, ionization, and metal-insulator transition. The computer simulations of high-pressure fast phenomena in condensed matter were carried out using these semi-empirical models

EXPERIMENTAL MEASUREMENT OF COMPRESSIBILITY, TEMPERATURE AND LIGHT ABSORPTION IN A DENSE SHOCK-COMPRESSED GASEOUS DEUTERIUM

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Today in view of the fact of developing work on laser nuclear fusion, study of structure and evolution of astrophysical objects interest in investigation of thermodynamic and electro physical qualities of hydrogen, elementary and most distributed element in the nature, has been rekindled in megabar pressure range.

In the present work we chose deuterium in gaseous state with high initial density close to density of liquid deuterium as an object for investigation. Parameters of initial condition for deuterium were determined with high degree of reliability, because in case of gas they are entirely depend on initial pressure and temperature. Using semispherical generator of shock waves in two experiments under pressures ≈83 GPa and 93 GPa in shock compressed gaseous deuterium we measured density ρ=0,64 g/cm^3 and 0,70 g/cm^3, temperature T=23000 K and 24100 K and light absorption up to 70 cm^{-1}. The obtained results were compared with available experimental and theoretical data.

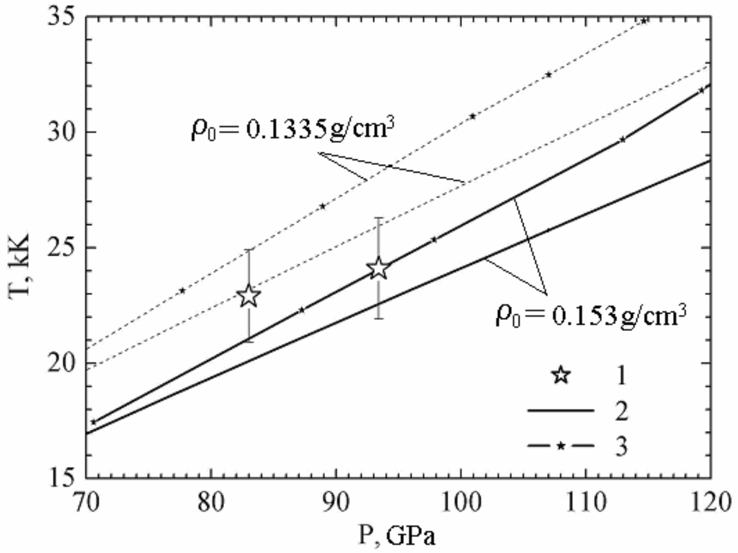

Figure – T-P dependence: 1 – experiment; calculation: 2 – model SAHA-IV, 3 – model MSK

CHARACTERIZATION OF LIQUID ARGON UNDER SHOCK COMPRESSION IN 125-515 GPa PRESSURE RANGE

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Investigation of thermodynamic and optical qualities for shock-compressed condensed inert gases is a field of interest because of its symmetric electron structure in atom and compact packing in crystalline state. That is why these substances are well-behaved for theoretic description of their qualities with following comparing with experiment.

In present work we represent new experimental data on shock compression, temperature and light absorption for liquid argon in a pressure range from 125 to 515 GPa.

To research qualities of liquid argon under pressures above 100 GPa in present work we used experimental devices consisted of semispherical generators of shock waves and cryogenic pans. Earlier in the same construction qualities of liquid shock-compressed xenon were investigated [1]. To obtain data on shock compression shock wave velocities in liquid argon and in screens of experimental devices were measured by electric pins and optical gauges. By registration of shock wave front irradiation we obtained data on temperature and light absorption.

During the experiments we have measured density ≈5 g/cm^3, temperature ≈31300K and absorption coefficients up to 180 cm^{-1} of shock-compressed liquid argon on basic Hugoniot up to pressures ≈233 GPa. After shock wave reflection from sapphire window we have registered density of compressed argon ≈5.8 g/cm^3 and 7.2 g/cm^3 under pressures 300 and 515 GPa. Basing on semi empirical models of equation of state we analyzed experimental and calculated data.

Reference [1]: M.V.Zhernokletov, R.I.Il’kaev, S.I.Kirshanov, et al. SCCM-2003, p.p.129-132.

Tailored Dynamic Thermodynamic Paths: Implications for Phase Transitions and Planetary Isentropes

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We will report a series of new dynamic compression experiments that can be tailored to reach previously inaccessible dynamic thermodynamic states beyond the principal Hugoniot and isentrope. In particular, we will discuss our progress on dynamic compression using prescribed impedance profile impactors in gas gun experiments. These impactors have been used in experiments demonstrating complex loading paths that include combination of shocks, quasi-isentropic compressions, controlled releases. The quasi-isentropic compression experiments last microseconds, and are capable of bridging the timescales of static experiments and current dynamic compression experiments. Using these techniques, we have carried out off-Hugoniot experiments on Al, Cu, and Ta. We also studied phase transitions in molten bismuth and water. We will also discuss the application of these techniques to study the timescale of phase transition and implications for experiments along the planetary isentropes.

[1] Work performed under the auspices of the U.S. DOE at the University of California/Lawrence Livermore National Laboratory under contract W-7405-ENG-48.

Electronic Structure Changes in Anthracene Crystals under Static and Shock Compression: Role of Nonhydrostaticity

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High pressure response of molecular crystals is not as well understood as the response of covalent or ionic crystals. Because molecular crystals are highly compressible, small variations in applied stresses result in large intermolecular changes. In addition, because of low symmetries resulting deformations, high pressure effects in these crystals are sensitive to nonhydrostaticity.

To understand the role of nonhydrostaticity on electronic structure changes in molecular solids, we examined anthracene crystals up to ~ 8 GPa under various loading conditions. The fluorescence and absorption experiments were performed to characterize differences in electronic structure of anthracene crystals under hydrostatic and nonhydrostatic (static and shock) compression. Under hydrostatic loading the changes in absorption and fluorescence spectra were gradual and reversible, and only red shifts are observed. In contrast, the onset of non-hydrostatic conditions generates several new features: (i) emergence of a new absorption band, (ii) deviation in absorption and fluorescence peak shifts, (iii) broadening of vibrational peaks, and (iv) occurrence of fluorescence with the excimer-like characteristics.

The spectroscopic results indicate the formation of new electronic states under nonhydrostatic conditions as a consequence of high stress and plastic deformation. The origin of new states is discussed and attributed to dimer-type defects formed in nonhydrostatically compressed (statically or shocked) anthracene.

Work supported by DOE and ONR.

Transient states of reconstructive phase transitions captured in shock recovery experiments

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Upon compression many materials undergo major reconstruction of their structure and bonding involving an increase in coordination of constituting atoms and change in bonding-character. While transforming, the materials pass through intermediate states, which are usually to fugitive to be captured and examined. Shock experiments allow in many cases for quenching such intermediates structural states. Recent developments in techniques of X-ray diffractometry allow for quantitative examination of structures of even very small amounts of shock-retrieved crystalline phases.

We discuss carbon and silica as examples of systems where we succeeded in quenching such interesting intermediate states of structure from shock-experiments. We present the structures of the retrieved new phases of carbon and silica and discuss them with respect to the transformation mechanisms. Further, we discuss states of disorder in some of these phases as being intrinsic to these transformation mechanisms.

Anisotropic Shock Propagation in Single Crystals

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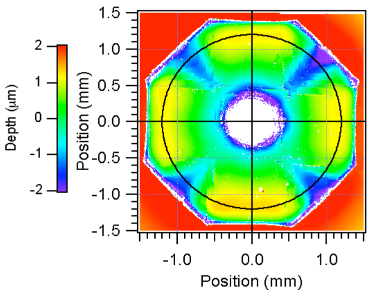
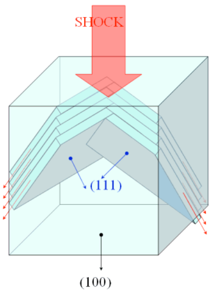
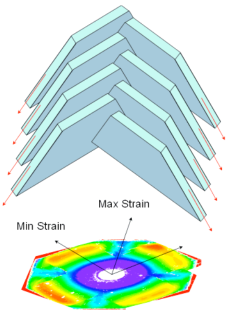
Convergent geometry or elastic anisotropy in single crystals causes non-planar acoustic waves to focus and/or form caustics [1,2]. For nonlinear waves the resolution of convergent geometry caustics has been studied, remaining unresolved, for nearly 50 years [1,3,4]. The case of nonlinear waves in elastically or plastically anisotropic crystals has not received similar attention. In fact, most single-crystal shock experiments have been performed in high-symmetry directions and the nature of shock propagation in low-symmetry directions remains largely unstudied.

We have propagated non-planar (divergent geometry), laser-driven shock waves through thick (~1 mm) single-crystals of diamond or silicon backed by an isotropic tungsten-carbide or stainless-steel backing plate. On recovery of the backing plates we observe a shallow depression showing evidence of anisotropic plastic strain with well-defined crystallographic registration. We observe 4- and 2-fold symmetric impressions for [100] and [110] oriented crystals respectively. For [100] oriented crystals the low-strain direction is toward the (111) slip planes as shown below. Various mechanisms for these observations will be discussed.







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High-pressure mineralogy: state of the art and future.

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Last decade has seen a tremendous improvement in the understanding of the interiors of the Earth and other planets. Many of these advances are due to better understanding of the micorscopic behaviour and physical properties of planet-forming materials at high pressures and temperatures. In this Lecture I will review several latest achievements, e.g.:

1. The discovery of the post-perovskite phase of $MgSiO_3$ [1,2].
2. The discovery of a new phase of alumina (Al_2O_3) and its potential geophysical implications [3].
3. Derivation of a thermal model of the Earth's mantle [4,5].
4. Studies of Fe at conditions of the Earth's core [6,7].

The major challenges, e.g. systematic exploration of new phases and studies of rheological properties [8], will be discussed as well.

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Absence of charge localization in compressed magnetite from first principle computations

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Magnetite (Fe_3O_4) is a magnetic mineral, of interest as a carrier of paleomagnetic data and for use in magneto-optical devices. Magnetite occurs in the inverse spinel structure: in this structure *n* tetrahedral sites (*t*) are occupied by ions with a nominal 3+ charge, while the 2n octahedral (*o*) sites are equally occupied by 2+ and 3+ ions. Magnetite is an antiferrimagnet with the moments of the *o* Fe having the opposite direction from those on the *t* site. Under ambient condition the two *o* Fe are equivalent, implying that nominal charges on this site can be written as 2.5+. Charge localization on the *o* site has been invoked both under low temperature (T), in order to explain the Verwey transition where magnetite transforms from a metal to an insulator, as well as a high pressure (P). While structural distortions and charge localization under low T have been explored extensively, charge localization under P has not attracted a comparable amount of attention. Using in-situ Mössbauer spectroscopy evidence for a transition with increasing P from Fe^{3+}(*t*) and 2 $Fe^{2.5+}$(*o*) through an intermediate state of Fe^{3+}(*t*) and Fe^{2+},Fe^{3+}(*o*), the inverse spinel, to normal spinel with Fe^{2+}(*t*) and 2 Fe^{3+}(*o*) has been found. Here we test the hypothesis of charge ordering as a function of P by means of density functional methods. We apply all electron computations (LAPW) with the generalized gradient (GGA) as well as LDA+U approximations to the exchange and correlation potential to investigate the electronic and magnetic structure of the three Fe sites in the structure, breaking the equivalency of the *o* sites. We monitor the magnetic moments and the electronic density states associated with them and evaluate the charge density with Bader charges. While formal charges can not be inferred from this, the Bader analysis should be sensitive to finding charge differences between the various sites. We are, however, not able to find any discernable charge localization, electronic or magnetic differences for the two *o* sites for compression range explored ($V/V_0>0.80$).

Ab initio treatment of minerals at high pressures and temperatures

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The mantle of the Earth extends from the depth of about 670 km to 2981 km. It consists mainly of $MgSiO_3$-perovskite, (Mg,Fe)O magnesiowüstite and $CaSiO_3$-perovskite. It is possible to calculate thermodynamic properties, structures and energetics of the separate minerals at extreme conditions of the mantle using *ab initio* methods. To get a better picture of the mantle it is necessary to not only look at chemically pure minerals, but to consider them as solid solution, as it is the probable case in nature.

The calculations are based on the generalized gradient approximation (GGA) [1] method and the projector augmented wave (PAW) method [2], which is a very accurate method for solving the total energy problem.

Using density functional theory the structure and the stability of the $CaSiO_3$ perovskite in the pressure range of the Earth's mantle (0-150 GPa) have been calculated [3]. Additionally we use the subregular solid solution model together with point defect calculations to model the solidus curve of the (Ca,Mg)-perovskite phase diagram at 25 GPa. This is a special case, because there is also a symmetry change from a tetragonal to an orthorhombic perovskite structure as you increase the concentration of Mg. This is the first work to treat this subject with ab initio methods.

Supercomputing facilities were provided by CSCS (Manno, Switzerland).

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Al, Fe incorporation into post-perovskite from first principles

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The phase transition of pure $MgSiO_3$ perovskite (*Pbnm*) to the post-perovskite (*Cmcm*) structure has been reported recently at pressures corresponding to the Earth's lowermost mantle [1-4]. We use ab initio calculations to assess whether this transition survives for more realistic mantle compositions containing significant amounts of Al and Fe. We estimate phase coexistence pressures as functions of minor element concentration, and from this we obtain the effects of Al and Fe on the depth and sharpness of the transition. For a pyrolitic mantle composition, and assuming all of the Al partitions into $MgSiO_3$, we find that Al preferentially partitions into perovskite, thus increasing the transition pressure (by approximately 5 GPa). The transition takes place over a depth range of width 225 km. Fe competes with Al by lowering the transition pressure, so that post-perovskite is likely to exist in the lower mantle; however, the transition is still smooth.

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HP-HT experimental study of uranium location in the Earth mantle

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The Earth's internal activity shows off through, among others, earthquakes, volcanic eruptions and continental drifts. These events are energetically related to the heat flux at the surface (~4.4 10^{13} W). Half of this power rises from the radioactive decay of U and Th. We hardly know partition coefficients for U and Th between the crust and the mantle. Also, we don't know which phases can host these two elements under the extreme PT conditions of the Earth's mantle. It appears essential to determine the location of these elements in the Earth in order to understand the thermal behavior of our planet.

We investigated the HP-HT behavior of potential U-bearing compounds in the lower mantle. Experiments were performed with a Multi-Anvil Press (MAP) and Laser-Heated Diamond Anvil Cell (LHDAC). Quenched MAP samples were analysed by Analytical Scanning Electron Microscopy (ASEM) and Electron Probe Micro-Analysis (EPMA). LHDAC samples were examined in situ by X-ray diffraction with a synchrotron source. We studied two types of starting materials: simple oxides like natural uraninite UO_2 and mixtures of Ca or Ca-Al silicates with uraninite UO_2.

UO_2 appears to display a new orthorhombic structure at pressure above 30 GPa and up to 80 GPa, different from the cotunnite structure expected for such a AO_2 compound. This orthorhombic structure is a sligth distortion of the cubic fluorite-type structure observed for UO_2 at lower pressure.

Among the HP-HT products of the mixtures of Ca and Ca-Al silicate with UO_2, we observe a new U-bearing phase with a stoichiometry close to $CaSiO_3$ and a perovskite-type structure which is stable at pressure up to 53 GPa. This phase is able to incorporate up to 3 at% of U. The importance of this new phase is discussed in the perspective of new geochimical and sismological models which propose dense and radiogenic layers in a heterogeneous lower mantle.

High pressure effects on microbial cell biology

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Research on the effect of high hydrostatic pressure (HHP) on cells and microorganisms has initially been driven to understand life in deep sea organisms or microbial inactivation in food processes. HHP exerts manifold effects on cells and microorganisms, leading to adaptation, stress response or cell death. It affects all levels of cellular physiology targeting cellular organization, transcription, translation, protein conformation, enzyme activity and membrane function. These effects result from the general thermodynamic property of high pressure to influence macromolecular interaction. Therefore, HHP can be used as a powerful tool to study these basic cellular functions and possibly tailor them to understand e. g. cellular regulation or signal transduction or use cells as factories apart from any food or deep sea related system.

To get insight in the mechanisms of the complex bacterial response to high pressure we have analysed *Lactobacillus sanfranciscensis* which is used in food biotechnology. HHP sensitive targets were identified in the (i) membrane physiology with fluorescence techniques, (ii) proteome with 2-D electrophoresis (iii) transcriptome with microarrays and real time PCR and (iiii) regulation with the development of a reporter system. More than 25 proteins were identified to be differentially expressed upon high pressure stress. In a transcriptome analysis about 8% of the investigated genes were affected in their expression. Most of them appeared to be up-regulated by 2-4 fold. These results were verified by real time PCR. For some genes up-regulated at proteome level, gene induction was shown (*clp*L/*gua*A/*gro*EL/*rbs*K), for others their response to high hydrostatic pressure at the transcriptome level seems to differ from proteome. The up-regulation of certain genes corroborates the hypothesis that the cell tries to compensate for pressure induced impairing of membrane transport and translation. The latter appears as a highly pressure sensitive process initiating changes in cellular physiology and stress response to maintain vital functions and repair.

Characterization of pressure-stabilized functional important protein states by high resolution NMR spectroscopy

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Abstract

The application of high hydrostatic pressure is of keen interest in un/refolding and misfolding processes of proteins. Multidimensional high resolution NMR spectroscopy is the only generally applicable method/technique to monitor pressure-induced structural changes at the atomic level in solution.

Up to now the application of most of the multidimensional NMR experiments is impossible due to the restricted volume of the high pressure glass cells which causes a poor signal-to-noise ratio. There are currently a number of approaches to overcome the filling factor problem, e.g. high strength single crystal sapphire cells, and ceramic cells.

To understand the effect of pressure on proteins, the pressure dependence of ^{1}H chemical shifts in random coil model tetrapeptides is necessary and was recently investigated. The results allow distinguishing structural changes from the pressure dependence of the chemical shifts. In addition, many buffer systems change their characteristica under the influence of pressure.

A number of proteins have been investigated by high-pressure NMR spectroscopy and display global differences in their sensitivity to pressure. The implementation of high pressure into NMR spectroscopy allows to shift the conformational equilibrium in these proteins and stabilize intermediate states important for function. Association/dissociation phenomena of proteins have been investigated as well.

Since high pressure was shown to populate intermediate amyloidogenic states of proteins the investigation of pressure on proteins involved in protein conformational disorders like Alzheimer's Disease (AD) and Transmissible Spongiform Encephalopathies (TSE) in combination with high resolution NMR spectroscopy is currently the only method to monitor and thus understand such transitions at the atomic detail.

Here we review the recent advances made in the methodology of high pressure NMR spectroscopy as well as novel results on protein aggregation and the stabilization of functional important intermediates.

Kinetics of the High Pressure Inactivation of Bacteriophages

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Bacterial fermentations in the fields of dairy technology and biotechnology require aseptic conditions to achieve the highest process safety. To ensure a high hygienic standard of the nutrient medium we have the options of heat treatment, microfiltration and high pressure treatment. Heat treatment is effective in terms of sterilization but valuable nutrients such as vitamins and functional substances may be destructed. Microfiltration is efficient in maintaining the nutrients and removing microorganisms but bacteriophages can pass (bacteriophages: 0.05 - 0.5 μm), which put the fermentation at risk. High pressure is known to inactivate pathogens while vitamins and enzymes mostly persist [1] but can bacteriophages be inactivated by high pressure? The kinetics of the high pressure inactivation of bacteriophages were to investigate in this study.

The lactococcal phage P008 which is wide-spread in dairy companies was chosen as the reference phage [2]. High pressure treatments ranged from 300-600 MPa at temperatures up to 70 °C. Phage counts were determined by the plaque assay.

The resultant kinetics were non-1st-order and exhibited a tailing. The kinetics were approximated by a nonlinear regression model which is based on the Eyring equation and the rate law of nth order [3]. The reaction order, n, the rate constant, $k_{p,T}$, and the volume of activation, $\Delta V^{\#}$ were calculated. From the kinetic data a pressure-temperature- (p,T-) diagram was established [4]. The experimental data as well as the p,T-diagram show that pressure and temperature act antagonistically when pressure and temperature are relatively high, i.e. for the effective inactivation of bacteriophages high pressure should be combined with low temperature. After all, high pressure has the potential to inactivate bacteriophages but further investigations on the relevant phage types and their kinetics is needed.

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High hydrostatic pressure treated tumour cells. – Cell death pathways and immunogenicity of treated cells.

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Today cancer causes the death of every forth human world-wide. The classical therapies for solid cancer have limitations in prolonging the live span of the patients. Therefore, new therapeutic approaches are urgently needed and vaccination against cancer with autologous tumour vaccines has shown promising results in animal experiments. Basically, autologous tumour cells are injected into the patient. For this purpose, they have to be inactivated before application. This strategy is dependent on an efficient inactivation of the cells, which is usually accomplished by gamma-irradiation. A new method for the inactivation of tumour cells is high hydrostatic pressure (HHP) treatment (> 100 MPa). A major issue of tumour cell inactivation is the preservation of their immunogenicity, which is strongly influenced by the pathway of cell death induced during inactivation. The aim of our studies was to analyse the HHP induced cell death pathways. We observed that treatment of tumour cells with pressure up to 100 MPa did not restrict the viability of the cells. However, a further increase of the pressure results in the death of treated cells. At 200 MPa, cells died in a way that is related to classical apoptosis with preservation of the selectivity of the plasma membrane, phosphatidylserine exposure, and morphological alterations. The HHP induced apoptosis proceeded faster than apoptosis induced by UVB irradiation. Cells treated with 300 and 400 MPa executed a necrotic death pathway. In contrast to alternative methods for the induction of necrosis (heat, detergent, oxidative stress), the nuclei of HHP treated cells were very efficiently degraded within a few ours of culture. Most importantly, both pressurized apoptotic and necrotic cells largely retained their humoral immunogenicity, when tested in C57/BL6 mice.

Functional food components prepared with assistance of high pressure treatment

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This paper reports on research results regarding the effect of preservation methods (heat pasteurisation, high pressure pasteurisation and freezing) of the vegetable juices on the content of health important chemical components (vitamins, polyphenols) and their anti-mutagenic activity. The chilled cruciferous vegetable such as cauliflower, broccoli, red cabbage and Brussels sprouts were used for single sort vegetable juices preparation. These juices contain potentially large number of glucosinolates and their enzymatic (myrosinase) decomposition products (isothiocyanates) that are regarded as anti-cancer anti-mutagenic agents provoking the decontamination processes in human body cells (chemoprevention). The main focus is devoted to the effect of preparation methods on sulforaphane in broccoli juice and the high pressure treatment (time and level of pressure) on the sulforaphane content in the juice. The anti-mutagenicity of these juices is compared and effect of preservation treatment is evaluated. These juices can be used as components of functional foods (fruit-vegetable juices) having preventative anti-cancer, anti-mutagenic effects.

Composition Fluctuations and Microdomains in Three-component Model Biomembrane Systems - The Effects of Temperature, Pressure and Lipid Composition

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The lateral organization of the constituents of biological membranes poses one of the major current problems in membrane biophysics. A particular question is related to the existence of lipid domains on the nm and micrometer length scale. Substantial evidence has also accumulated that points to the presence of distinct liquid-ordered lipid regions termed "rafts" in cell membranes. They are rich in sphingomyelin and cholesterol and are thought to be important for cellular functions, such as signal transduction and the transport of lipids and proteins. We studied the structure and lateral organization of several ternary lipid mixtures without and with incorporated peptides using small-neutron scattering (SANS) in combination with the H/D contrast variation technique and two-photon excitation fluorescence microscopy. The ternary mixtures DOPC / sphingomyelin / cholesterol (10-33 mol%) exhibit a power-law behavior of their SANS intensity with an exponent of 3.0 over an extended temperature range, indicating the existence of composition fluctuations, which correspond to space-filling droplets with a broad size-distribution ranging from about 20 to 200 nm. The heterogeneous membrane structure observed in this system thus contrasts with the characteristic shapes of gel-fluid type lipid domains, and can rather be described by coexisting liquid-ordered/liquid-disordered domains. Fluorescence microscopy was used for direct visualization of the lateral lipid organization and domain shapes including information on the lipid phase state in the micrometer range. By adding peptides (gramicidin, short lipidated peptides), drastic changes of the lateral organization of the membrane occur and, by a molecular sorting mechanism, new lateral structures may be induced. Moreover, pressure dependent FT-IR spectroscopy, SAXS and fluorescence microscopy experiments were carried out to reveal pressure dependent conformational and phase changes in these systems and to construct their corresponding temperature-pressure phase diagrams.

High pressure effects on the infectious prion protein

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Prion diseases are associated with the accumulation of a misfolded form (PrP^{Sc}) of the cellular prion protein (PrP^{C}). This misfolded beta-sheet rich aggregated pathogenic multimer seems to be the main component of the transmissible form. Suitable inactivation procedures are aggressive, with a consequent loss in quality and texture in the treated tissues. Therefore, our interest in assessing the effects of unconventional milder technologies on prion stability and prion infectivity arises from the necessity of providing alternative sterilisation procedures at risk materials.

Crude brain homogenates infected with the 263K strain of scrapie (PrP^{Sc}) and isolated prion proteins were heated and/or pressurised at 800 MPa at 60 °C for different holding times in different buffers and in water. Prion proteins were analysed on immunoblots for their proteinase K (PK) resistance, and in bioassays for their infectivity. Samples pressurised at initial neutral conditions and containing native PrP^{Sc} or the N-truncated PrP 27-30 were negative on immunoblots [1], a 6-7 $\log_{10}$ reduction of infectious units per gram was reported in PBS buffer after a two hour treatment [2]. A pressure induced change in the protein conformation of native PrP^{Sc} leading to less PK resistant and infectious prions was confirmed in all buffers tested at initial neutral conditions and in water.

However, opposite results were found after pressurising isolated prions at neutral conditions and after pressure treatment of native infectious prions at slightly acidic pH, arguing for the existence of pressure sensitive β-structures ($PrP^{Sc}_{\Delta Psen}$), and extremely pressure resistant β-structures ($PrP^{Sc}_{\Delta Pres}$).The distinct behaviour of native and isolated prions indicate differences in the protein structure that have not been taken into consideration before.

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Synergistic or antagonistic effects of combined high pressure subzero temperature microbial-inactivation: Involvement of thermodynamic properties of water

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High-pressure treatments necessary to reach high or complete microbial inactivation could be improved through the combination of high pressure with other physical parameters. Among the studies carried out on coupling effects, only a few have been interested in the synergy between high pressure and low temperatures, including subzero range [1-2].

This work was intended to study the coupling effect of subzero temperature and high pressure on microbial inactivation. A yeast (*Saccharomyces cerevisiae*), a gram positive bacteria (*Lactobacillus plantarum*) and a gram negative bacteria (*Escherichia coli*) were treated at different pressure levels (0.1 to 600 MPa, 0-60 min holding time), temperatures (from ambient to -20°C, without freezing) and water activity levels (from a_w 0.85 to $a_w \approx 1$). The inactivation and shape modifications of yeast spheroplasts and giant spheroplasts of *Escherichia coli* were also investigated.

Results show a non-monotonous pattern of microbial inactivation. In fact, synergistic and antagonistic interactions between subzero temperature and high pressure were observed. The type and magnitude of interaction was largely a function of pressure range, temperature, holding time and the type of microorganism. For example, for pressure between 150 and 300 MPa and a_w 0.992 a temperature of -20°C makes it possible to reduce pressure by about 100 MPa to achieve the same inactivation rate of *Escherichia coli* observed at 25°C. However, for pressure above 300 MPa, an antagonistic effect was observed and subzero temperatures seems to counteract the anti-microbial pressure effect.

The role of hydration conditions in the high pressure subzero temperature effects on microbial inactivation was investigated. Results argue in favor of the involvement of thermodynamic properties of water.

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Structural study of phase transformations in solid and liquid halogenides ($ZnCl_2$, $AlCl_3$) under high pressure

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The coordination changes in halogenide melts ($ZnCl_2$, $AlCl_3$) and P,T-phase diagrams of corresponding crystalline substances were investigated for the first time. $ZnCl_2$ substance at room pressure has tetrahedrally-coordinated structures in crystalline, glassy and liquid states. Crystalline $ZnCl_2$ at compression transforms to 6-coordinated modification. $AlCl_3$-substance is 4-coordinated in liquid state and 6-coordinated in crystalline state with the huge (90%) volume jump at melting. This substance was not studied previously under pressure. In present work we study P,T-phase diagrams of $ZnCl_2$ and $AlCl_3$, and their liquid short-range order structure at different pressures.

The transformation in crystalline $ZnCl_2$ occurs around 2.6-3.2 GPa at room temperature and around 2.3 GPa near melting curve (the triple point is located at 2.3+-0.2 GPa ; 650+-30C). $AlCl_3$ crystal does not change its structure up to 6.5 GPa. Heating to 300-350C at P>3GPa leads to the sub-structures of high-pressure phases formation in both substances. The melting was studied up to 4.4GPa (Tm~960C) for $ZnCl_2$ and up to 6GPa (Tm~1350C) for $AlCl_3$.

The quenching of liquid $ZnCl_2$ with cooling rates 10-100K/s at P>0.5GPa does not lead to the glass formation in contrast to room pressure behaviour. $ZnCl_2$ liquid at compression demonstrates strong decrease (or breakdown) of intermediate range order (IRO) in pressure range 0-1.5 GPa, remaining tetrahedrally-coordinated, and sharp first-order-like change of the structure to $ZnCl_6$-octahedron-based liquid around 3GPa, 800C. In $AlCl_3$ liquid also there is the breakdown of IRO in the pressure interval 0-2.5GPa and first-order-like coordination changes (4 - to 6-coordinated melt) around 4GPa, 1270C. Thus both liquid halogenids present the first example of the continuous breakdown of IRO at compression with the subsequent sharp liquid-liquid phase transitions.

Localization of 5f electrons and phase transitions in americium

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Density-functional electronic calculations have been used to investigate the high-pressure behaviour of americium. The phase transitions calculated agree with the recent sequence obtained experimentally under pressure [1]; double hexagonal close packed ($P6_3/mmc$) → face centred cubic ($Fm\overline{3}m$) → face centred orthorhombic ($Fddd$) → primitive orthorhombic ($Pnma$). In the first three phases the 5f electrons are found localized, only in the fourth phase (Am IV) the 5f electrons are found delocalized. The localization of the 5f electrons is modelled by an anti-ferromagnetic configuration which has a lower energy than the ferromagnetic ones. In this study the complex crystal structures have been fully relaxed.

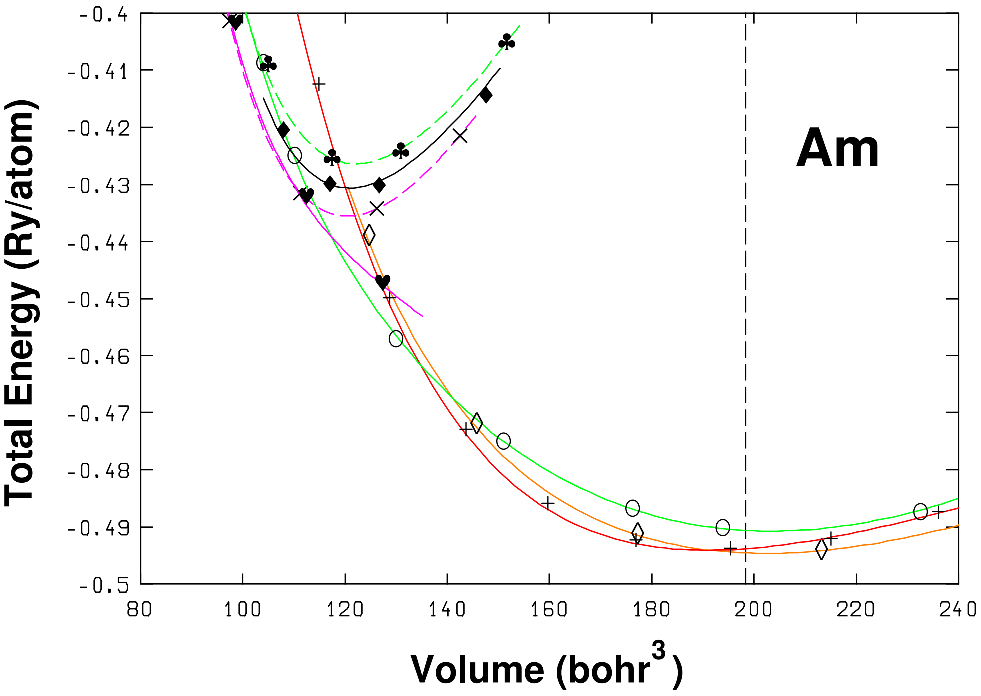

Figure 1. Total energies as functions of volume for Am, calculated in different crystal structures; dhcp (◊), fcc (+), Am III (o) and Am IV (♥) with an AFM configuration and Am III (♣), Am IV (×) and α-Pu (♦) assuming spin degeneracy. The room temperature equilibrium volume for Am is denoted by a vertical broken line.

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Pressure-induced electronic Mott transition in MnO

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Mott's seminal work on how insulating character may arise out of the electron-electron repulsion used a *3d* transition metal monoxide, NiO, as an example and suggested its pressure-induced metallization, the Mott transition [1]. Yet for 55 years the Mott transition in these archetypal Mott insulators MnO, FeO, CoO, and NiO has eluded detection at room temperature due to the high pressures required. Recent resistivity measurements using "designer" diamond anvils, however, have seen this insulator-metal transition in MnO, a five order of magnitude decrease in resistance between 90 and 106 GPa [2]. In this paper, we present x-ray emission spectroscopy and x-ray diffraction data which not only suggest that the Mott transition in MnO is a far richer phenomenon than just the onset of metallization, but that it also exhibits profound similarities to transitions in the lanthanides and actinides as has been predicted [3] and thus furthers our general understanding of electron-correlation driven phase transitions.

MnO is a paramagnetic (PM) insulator in the B1 (rock salt) structure at ambient pressure and temperature, transforms to an antiferromagnetic (AFM) rhombohedral distortion (denoted dB1) at 30 GPa, then to an unknown "intermediate" phase at 90 GPa, and then to the B8 (NiAs) structure at around 120 GPa [4]. In the present x-ray emission experiments (Fig. 1), we found that MnO undergoes at least two first-order electronic transitions: one at the onset of the B1 (PM)-dB1 (AFM) transition at 30 GPa and the other in the middle of intermediate phase at around 105 GPa. Furthermore, our subsequent x-ray diffraction experiments found that the intermediate phase is consisted of a mixture of dB1 (AFM) and B8 (PM) phases and the B8 (PM) phase further transforms to an iso-structural diamagnetic B8 (DM) at around 105 GPa.

The present spectral and diffraction data together with the recent resistance data [2] provide a coherent picture of the Mott transition in MnO, which concurrently manifests (1) significant loss of magnetic moment, (2) large isostructural volume collapse and (3) the insulator-metal transition. The magnetic and structural sequence we suggest is consistent with the available data for FeO [5,6] in a great geophysical importance and may shed light on the later *3d* monoxides as well. Furthermore, although similarities between the electron-correlation driven transitions in the *3d* monoxides and the 4*f*- and 5*f*-electron metals were predicted years ago [3], it is truly striking that these three signatures observed here for the archetypal Mott transition in MnO are *all* observed at the volume-collapse transitions in the lanthanide and actinide metals.

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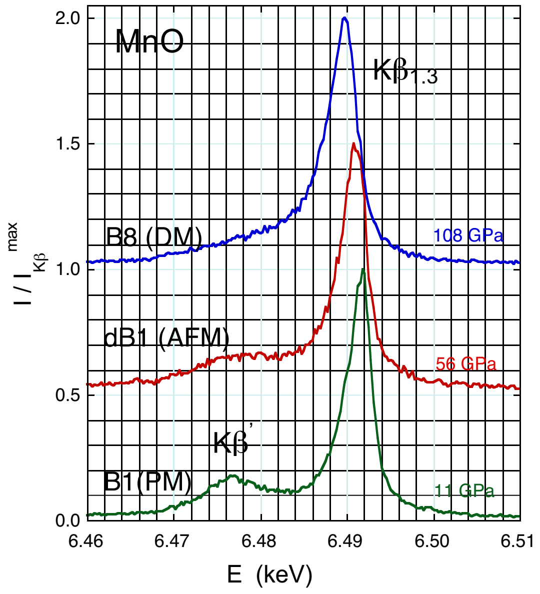

Figure 1: Mn K-edge x-ray emission spectra of MnO at high pressures showing a significant modification of magnetic moment evident from the changes in Kβ' as pressure increases. These spectral changes occur abruptly at 30 GPa and 105 GPa suggesting the first-order electronic phase transitions.

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Thermodynamic and electronic structure study of two pressure-induced stuctural phase transitions of $PdSe_2$: interconversion path and structural preferences between the CdI_2-, PdS_2- and pyrite-type structures.

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Under ambient conditions, $PdSe_2$ adopts the PdS_2-type structure (o-$PdSe_2$). Its crystal structure at high pressure (up to 30 GPa) was investigated at 20°C and at 300°C by X-ray energy-dispersive diffraction. Le Bail refinements and *ab initio* calculations evidenced a solid-solid phase transition to the pyrite-type structure (c-$PdSe_2$), strongly related to the o-PdS_2 (**Fig.1**).[1]

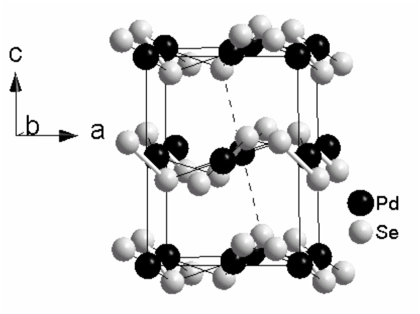

Fig. 1: perspective view of o-$PdSe_2$

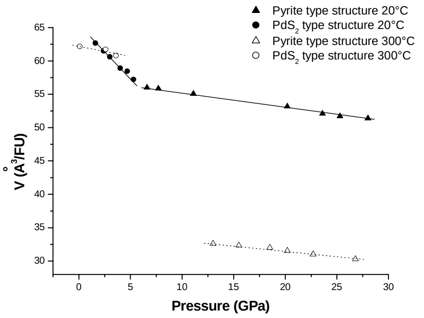

Fig. 2: plot of volume vs. pressure

Using the experimental data obtained at 20°C and 300°C, we examined the order of the $PdSe_2$ phase transition and its dependence on temperature. For this purpose, we calculated and analyzed the thermodynamical potential and the entropy generation by numerically calculating the equation of state. We also found that the cell volume of c-$PdSe_2$ was smaller at 300°C than at 20°C by nearly 40% (**Fig.2**). Such a dramatic decrease in the unit cell volume meant a strong reorganization of the bonding and was suggestive of an incoming phase transition. This possibility has been experimentally confirmed by fedgling high pressure experiments at ESRF. We surprisingly found that the new allotropic phase was a 2D CdI_2-type structure. It probed that all MSe_2 (M=transition metal) structures are linked. We evidenced the interconversion path between the 3 allotropes, explaining their relative stabilities on the basis of a thermodynamic and electronic structure study.

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The high-pressure phase diagram of the NH_3- H_2O system

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The ammonia-water system has been extensively studied by petrologists in the past decades below 0.2 GPa mainly because ammonia is a good inhibitor of clathrate formation. This system is now explored at larger pressures by planetologists because large amount of ammonia are supposed to be trapped in ices in the outer solar system and in geant ocean-exoplanets. In order to respond to this new interest, an accurate description of the ammonia effect on both the melting temperature and stability of high pressure ices is proposed.

The water rich region of the ammonia - water phase diagram presents at least six solid phases. The three characteristics of the diagram are: i) the melting temperature of ices decreases strongly when ammonia is added; ii) there is a peritectic curve corresponding to the reaction L+Ice ⇔ Dihydrate; iii) the eutectic curve (L⇔Dihydrate+Monohydrate) is located at very low temperature (180 K). Previous data are mainly located in the [0-300] MPa pressure range and in the water-rich domain (Fig. 1). Thus, except for ice I, ammonia effects on the melting temperature of HP ice polymorphs is not well known.

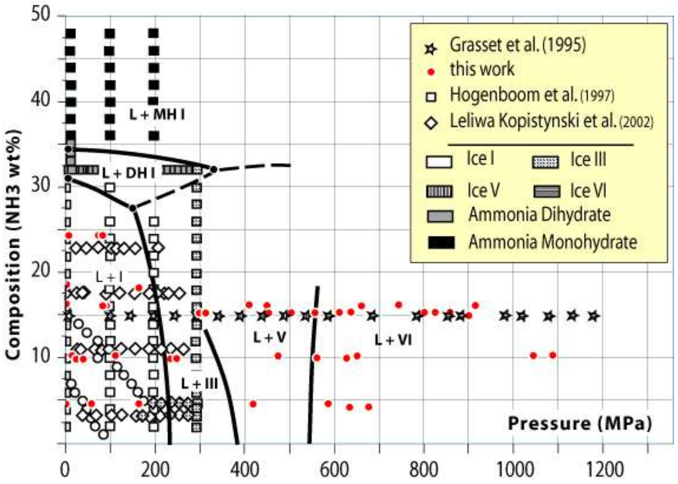

Figure 1: *Experimental data in the Pres.- Comp. space.*

New experiments have been carried out in an optical sapphire anvil cell coupled to a Raman spectrometer for adding data at high pressures. Based on previous and new data, a thermodynamical description of the different liquidii of the ammonia-water system will be proposed. It will be shown that the low pressure and water rich domain of the system is well constrained. Furthermore, the stability field of both high pressure ices and ammonia hydrates can be roughly defined. Implications of these results for studying internal structures of large icy satellites of Jupiter and Saturn and large planets of outer stellar systems will be shortly described.

KINETICS OF DYNAMICALLY DRIVEN POLYMORPHIC AND FREEZING PHASE TRANSFORMATIONS

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Dynamic quasi-isentropic compression experiments offer the unique opportunity for investigating structural phase transformations in condensed matter on time-scales of the order of 10e-9 - 10e-6s, bridging the shock compression and static high pressure regimes. We have observed evidence for polymorphic and freezing phase transitions in Bi, Pr and H_2O using these experimental techniques. The experimental results are interpreted using multiphase, thermodynamically consistent equations of state coupled with equilibrium hydrodynamic simulations and a nucleation and growth model. I will discuss the extracted kinetic timeconstants, critical exponents and activation energies obtained for the dynamic compression experiments and place them in the general context of phase transformation kinetics.

Crystal-Amorphous and Crystal-Crystal Phase Transformations via Virtual Melting

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Pressure-induced crystal (c)-amorphous (a) phase transformations (PTs) were considered in literature (e.g. for ice, quartz, high albeite, and jadeite) as a low temperature analog of melting along the metastable continuation of melting lines in pressure-temperature phase diagram. However, some contradictions were found concerning metastable melting hypotheses [1]. In this paper, a new mechanism of pressure-induced c-a and c-c PTs and internal stress relaxation via virtual melting (VM) induced by internal stresses was justified thermodynamically and kinetically. The energy of the internal elastic stresses, induced by large transformation strain for c-c PT, increases the driving force for melting and reduces the melting temperature; under certain conditions, a barrierless melt nucleation occurs. Melting releases the internal stresses and the unstable melt solidifies into the stable crystalline (above the glass transition temperature) or amorphous (below the glass transition temperature) phase. A short-lived unstable melt (transitional state) is called the VM [2]. VM removes interface friction, reduces kinetic barrier, increases atomic mobility, can reduce thermodynamic melting temperature and stabilize subcritical c nucleus or transform it to an amorphous nucleus. VM also resolves the contradictions mentioned in literature [1]. We combine VM, detailed stress analysis and nonequilibrium PT diagrams to develop new scenarios of c-a and c-c PTs. Results are applied for a new interpretation of melting, c-c and c-a PT mechanisms in ice Ih. *VM* is expected to be a main mechanism of amorphization in geological materials (e.g. α-quartz, coesite, and jadeite), in brittle semiconductors (e.g. Ge and Si), in materials leading to superhard phases (e.g. BN and graphite), as well as polymet, $Zn_{43}Sb_{57}$ and $Cd_{43}Sb_{57}$.

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Structure transition of Sc to 300 GPa

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It is well known that the stability of crystal structures of rare-earth metals is related to the *d*-band occupancy. Under high pressure, they exhibit a successive pressure-induced structure transitions with a systematic sequence of structure; hcp - Sm type–dhcp–fcc-distorted fcc–fcc. The sequence is caused by the electron-transfer from *s*-band to *d*-band (*s*-*d* transition).

Scandium (Sc) is the first member of the rare-earth elemental metals and its stable structure at ambient condition is hcp. Previous x-ray structural studies [1,2] reported that the hcp-Sc phase showed a phase transition around 23 GPa. However, according to the recent x-ray study [2], the crystal structure of the high-pressure phase (Sc-II) was explained as a pseudo-bcc structure with a distorted icosahedral clusters and did not correspond to any structures as mentioned above. Whether or not, Sc follow this systematic?

In this paper, the structural phase transition of Sc was studied at pressure up to 292 GPa and at 297 K, by powder x-ray diffraction experiments. Four structural phase transitions were observed around 23, 104, 140, and 240 GPa. The structure of the highest-pressure phase, Sc-V, was found to be a hexagonal lattice (S.G.:$P6_{1}22$ or $P6_{5}22$) consisted of 6-scrw helical chains (shown in Fig. 1),and this phase was stable up to 300 GPa. The lattice could be explained as a distorted face centered-cubic (dis.-fcc).

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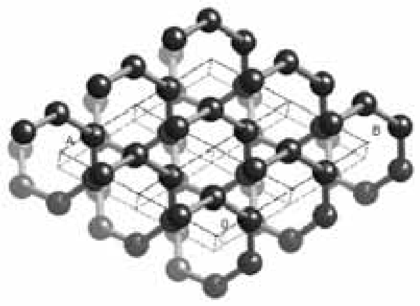

Fig.1 Structure model of Sc-V.

Transitional high-pressure diagrams of amorphous fullerene-based molecular and quasi-chain forms of carbon

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Due to the diversity of chemical bonds between carbon atoms (sp^1, sp^2, and sp^3 hybridized states), carbon allotropes are combined into a great family of materials. Whereas new crystalline, amorphous, cluster-based and nanocrystalline carbon phases are actively experimentally synthesized and theoretically developed, the high-pressure and/or high-temperature behavior of many carbon materials is still a grey area for researchers. In this respect, the influence of dimensionality and topology of covalent carbon networking on the structural stability and evolution of structure under extreme conditions needs to be recognized in many cases.

Here, using quenching experiments, *in situ* energy-dispersive x-ray diffraction in the cubic-type multi-anvil press at the Spring-8, and *in situ* optical measurements of absorption edge in the DAC, we present the study of transitional diagrams of two amorphous carbon materials, including molecular fullerite C_{2n} (mixture of fullerenes C_{2n} with varied size of fullerene buckyballs, $50<2n<170$) and quasi-chain sp^1-type form of carbon – cumulene carbyne. The measurements were carried out at high temperatures (up to 1000 °C) up to 9 GPa and at the room temperature up to 70 GPa. At pressures up to 9 GPa, the both studied materials demonstrate transformation to strongly disordered graphite-type states upon heating, whereas the pressure slightly influences on the scenarios of these graphitization processes. The both transformations are accompanied by semiconductor-to-semimetal transitions. I have been shown that carbyne is less stable with respect to high-temperature treatment, where graphitization occurs at 500 to 800 °C. The main stage of graphitization of fullerite C_{2n} takes place at 900 to 1000 °C as in the case of C_{60}. In contrast to molecular forms of carbon, like C_{60}, carbyne doesn't demonstrate a collapse of a semiconductor gap upon room-temperature pressurization, and its gap begins to increase at $P>20$ GPa after slight decrease at lower pressures.

Pressure Induced Phase Transitions in PbSnTe Alloy

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A study of PbTe:SnTe system under high compression has observed the structural phase transformations from the parental rocksalt (B1) type phase to finally most stable CsCl (B2) type structure. Three Body potential (TBP) approach [1], consists of long range modified Coulomb and three body forces and short range van der Waals and Hafmeister Flygare type overlap repulsive interactions, has been applied for the present investigation. In the present study the effect of van der Waals as well as three body forces have been analysed separately, which shows that the great influence of three body forces as well as short range van der Waals [2] as these materials are partially covalent compound. The computed transition pressures for the host binary compounds are in agreement to the observed results by other workers.

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Polymolecular high-pressure phase of nitrogen

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Recently, a distinct class of molecular phases of solid nitrogen has been discovered at high pressures and temperatures [1]. Optical measurements showed that one of the novel phases (θ) has very strong intermolecular interactions and infrared vibron absorbtion, which are strikingly different from all other known phases of N_2. We have performed x-ray diffraction studies on θ phase of nitrogen which show that intermolecular distances are significantly reduced compared to (epsilon/zeta)N_2 at the same pressures. These findings confirm a charge transfer from intra- to intermolecular bond, as deduced from optical measurements, and provide a microscopic basis for the observed high compressibility. These charge-transfer interactions connect nitrogen molecules in such a way that the chains of rings appear, forming a unit consisting of six nitrogen atoms (e.g. three N_2 molecules). Polynitrogen molecules have been of interest as possible high-energy-density molecules, with heat of formation of the order of few hundreds of kcal per mole [2]. N_6 molecules have been predicted to exist by theoretical investigations [3–5] and two of them, hexaazabicyclopropenyl and in particular hexaazadiazide are close to what we observe in θ phase. Also, solid hydrogen at high pressures pressures might undergo a phase transition to form termolecular complexes such as $(H_2)_3$ [6], before transition to the atomic or metallic phase at still higher pressures. The identification of this new structure of nitrogen casts new light on the nature of phase III of hydrogen.

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On the Nature of Solid Oxygen Beyond the ε–ζ Phase Transition

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Solid oxygen has been shown, unlike nitrogen and hydrogen, to undergo a transition to a metallic state at room temperature at 96 GPa [1,2]. The understanding of the mechanism of this insulator-metal phase transition is still controversial. The electronic transition to the metallic phase (ζ-O_2) was first shown to be accompanied by an iso-structural transition [3]. Weck *et al.* [4] have then shown, by single crystal X-ray diffraction, that the transition is not isostructural but of a displacive nature within the molecular plane of the ε-O_2 phase; the single crystal is even re-constructed above 110 GPa. However the structure of the (ζ-O_2) phase could not be refined. Yet, it has been shown that the x-ray data were not compatible with the various theoretical predictions. Furthermore, it was shown that metal oxygen is molecular but the magnitude of the wavenumber discontinuity of the vibron at the ε-ζ transition differs between the two Raman spectroscopy studies [4,5].

To further elucidate the nature of the ζ-O_2 phase, we have undertaken a study of dense solid oxygen under the best hydrostatic pressure conditions. In this communication, we report recent results of Raman spectroscopy experiments carried out on single crystals of oxygen imbedded and oriented differently in solid helium, across the ε-O_2 to ζ-O_2 phase transition and beyond, to pressures close to 140 GPa. Our results indicate, in agreement with those published [5], a significant decrease of the O_2 stretching vibration wavenumber at 103 GPa with respect of that extrapolated from the ε-O_2 phase and, in contrast, the appearance of a second Raman-active line at a wavenumber slightly above the former. The increase of pressure induces a gradual splitting between the vibron wavenumbers. We tentatively associate our observation with the displacive structural transition observed by X-ray diffraction. Finally, we report recent single crystal X-ray diffraction data, obtained at the ESRF.

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Pressure-induced hexagonal to cubic transition in the Yttrium and Rare-Earth trihydrides

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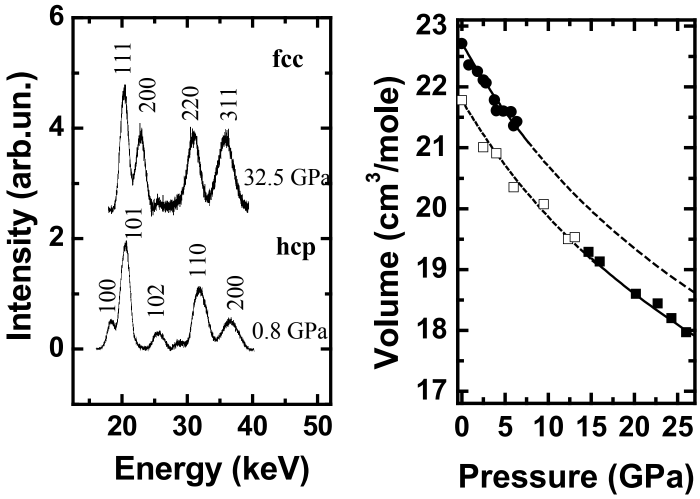
Since there is much interest in the physics of rare-earth hydrides after discovery of the ”switchable mirror” behaviour of Yttrium hydrides by Griessen’s group in 1996 [1], we have undertaken structural study of these hydrides under high pressure using Energy Dispersive X-ray Diffraction (EDXRD) mode in Diamond Anvil Cell (DAC). We have focused on the several rare-earth trihydrides (REH_3, RE = Sm, Gd, Ho, Er, Lu) [2,3] and YH_3 [4]. The **hcp** to **fcc** structural transformation have been observed for the all trihydrides investigated and the lattice parameters and parameters of equation of state (EOS) for both phases of each trihydride have been evaluated. Systematic classification of the phase transition has been established.



(a) (b)

Figure 1. The EDXRD patterns **(a)** and the pressure-volume relation **(b)** of HoH_3 are the typical examples for YH_3 and REH_3 family.

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Electronic properties of Jahn-Teller and photoluminescence systems under pressure.

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Photoluminescence (PL) properties of materials containing transition-metal (TM) ions depend on a variety of structural factors such as electronic structure, site symmetry and neighbouring atoms. These factors play a crucial role for the occurrence PL *i.e.* the PL quantum yield. This work investigates different mechanisms leading to non-radiative de-excitation processes and whether they can be modified by applying high pressure. In particular, the interest is focussed on non-radiative-multiphonon relaxation in TM impurities and PL quenching in concentrated materials, where exciton migration and subsequent transfer to non-PL centres take place. The former process is analysed in terms of the Dexter–Klick–Russell parameter Λ, defined as $\Lambda = \Delta E_s / E$ (ΔE_s and E are the Stokes shift and the PL-excited state energy, respectively), whose value scales with the quantum efficiency. Depending on the material, the PL onset is favoured for $\Lambda < 0.1 – 0.3$ [2,3]. The variation of E and ΔE_s with pressure for the Jahn-Teller Mn^{3+} [4] as well as Mn^{2+} and Cr^{3+} [5,6] in different coordination geometries will be presented and analysed.
The PL mechanism is quite different in concentrated materials such as MnF_2 (rutile-type structure) whose PL occurs in Mn^{2+}-perturbed traps after excitation migration. This work shows how pressure can either reduce the energy-transfer probability by structural modifications of the Mn-F-Mn exchange path or induce structural phase transitions providing more efficient PL sites. Interestingly, the present findings open new ways of achieving PL based on concentrated materials, particularly, in those cases where phase transformations show large hysteresis.

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Tailoring of photoluminescence of Czochralski silicon by high temperature - pressure treatment

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Dislocation related photoluminescence (PL) from silicon is promising for applications in Si based optoelectronics [1,2]. Dislocations are usually produced in Si (e. g. in oxygen containing Czochralski grown Cz-Si) by bending; the D1 dislocation-related line at 0.81 eV is typically of the highest intensity. Another way for producing dislocations is annealing of Cz-Si, especially under enhanced hydrostatic pressure (HT-HP treatment) [3]. The aim of present work is to explore potentials of the HT-HP treatment for tailoring of PL from Cz-Si.

Cz-Si with oxygen concentration of about 1.1×10^{18} cm^{-3} was subjected to annealing at 1000 K under 10^5 Pa for 20 h (to produce oxygen clusters), and next to the HT-HP treatment at 1170 - 1620 K under HP up to above 1 GPa, for up to 5 h. PL (excited by Ar laser, λ = 488 nm, T=7 K) of the HT – HP treated Cz-Si is strongly dependent on the treatment parameters. The D1 line is of the highest intensity for Cz-Si treated for 5 h at 1170 - 1230 K under 10^5 Pa - 0.01 GPa; similar treatment results also in appearance of PL at 0.84 eV (the D5 line). The treatments at 1230 K under 1 GPa or at 1400 K under 0.01 GPa result in strong PL peaking at 0.87 eV (the D2 line).

It means that the appropriate HT-HP treatment makes it possible to tailor PL from Cz-Si. This effect results from the treatment-induced creation of oxygen-containing precipitates affecting in turn production of dislocations and of other defects in Cz-Si.

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Band alignment in GaAs/GaInP heterostructures studied by low temperature photoluminescence under high pressure

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Heterojunctions in the GaAs/GaInP system have attracted recent attention because of their device applications but discrepancies exist between measurements such as band offsets even for similar growth conditions. Theoretical calculations show the band alignment to be dependent on CuPt-type ordering [1]. We report 11 K photoluminescence (PL) measurements of metalorganic vapor phase epitaxy grown GaAs/GaInP quantum wells at pressures up to ~5 GPa. Insertion of thin layers between the two material interfaces promotes a type-I band alignment [2]. In the absence of two thin GaP intermediate layers between the GaAs and partially ordered GaInP we observe no quantum well emission but an intense peak at ~1.46 eV. Its strong blueshift with increasing excitation intensity results in its becoming masked by GaAs related peaks. Selecting a photon energy that does not excite the GaInP layer weakens this emission peak. The use of low temperature allows us to study the nature of this emission at very low excitation powers to pressures well above the Γ-X crossover in GaInP. We see a *sublinear* shift with pressure towards higher energy close in behavior to that of the partially ordered GaInP layer and a consistent Γ-X crossover and associated drop in intensity. Our results clearly show that the true nature of this emission and the interface properties are only revealed at low excitation powers and arise from the GaInP layer, and strongly suggest that the 1.46 eV peak is a spatially indirect transition, GaInP(Γ_C)-GaAs(Γ_V), of electrons and holes separated at the interface in a type-II band alignment.

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Pressure-induced photoluminescence in MnF_2 at Room Temperature.

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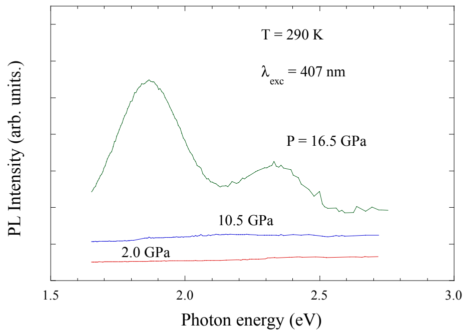
Photoluminescence (PL) and non-radiative processes yielding PL quenching in Mn^{2+}-doped fluorite crystals ($Ca_{1-x}Sr_xF_2$) mainly depend on the host site volume. The smaller the volume, the higher the PL efficiency [1]. Following this idea, we induced PL at room temperature (RT) in the non-PL Mn^{2+}-doped SrF_2 and BaF_2 by applying pressure [2].

On the other hand, the PL mechanism is quite different in concentrated materials such as MnF_2 (rutile-type structure) whose PL takes place in Mn^{2+}-perturbed traps after excitation migration. In this system, however, PL occurs only at low temperatures given that is quenched for T > 100 K [3]. In this work we demonstrate that non-PL MnF_2 can be transformed to PL MnF_2 by pressure. The pressure-induced PL correlates with the corresponding structural change sequence from rutile to cotunnite undergone by MnF_2 with pressure [4]. The PL appears for P > 14 GPa. The spectrum consists of two emission bands peaking at 2.34 and 1.87 eV which are likely associated with intrinsic Mn^{2+} and Mn^{2+} perturbed traps, respectively. Thus, pressure reveals as an efficient tool to reduce the excitation migration thus increasing the PL efficiency of the material. Interestingly, the present findings open new ways of achieving PL based on concentrated materials, particularly, in those cases where phase transformations show large hysteresis. We compare the present results with findings in MnF_2 nanoparticles as a function of temperature and pressure. Preliminary results show that particle-size reduction induces structural transformation towards high-pressure phases.



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Metallization of Silane at 100 GPa

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Silane has been studied to a pressure of 218 GPa using optical reflectivity and optical absorption . Above 100 GPa, there is a sharp jump in reflectivity and absorption, the effect being strongest at the lower energies.

At the same time, there is a large jump in R/V (where R is the molar refraction and V the molar volume). We are reminded that the Goldhammer-Herzfeld criterion for metallization is R/V -> 1 in the low energy (or long wavelength limit). In silane R/V makes a large jump from 0.44 at 93 GPa to 0.80 at 110 GPa both at 1.6 eV. Silver at atmospheric pressure and 1.6 eV has R/V = 0.91. Silane is clearly a metal above 100 GPa. As an alloy with a preponderance of hydrogen it may be a high Tc superconductor.

Oral

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Structure of intermediate high pressure phase of PbX compounds

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The lead chalcogenides PbX (X=Te, Se, S) are narrow-gap semiconductors (group IV-VI), which crystallise at ambient conditions in the cubic NaCl (B1) structure. It has been known for 20 years that they transform at 6, 4.5 and 2.2 GPa, respectively, to an intermediate phase, and at higher pressures (between 13 and 22 GPa) to the 8-fold coordinated CsCl (B2) structure. The intermediate phase has been referred to as being of the "GeS" type (B16, space group Pbnm) rather than of the "TlI" type as suggested for PbS and PbSe (B33, space group Cmcm), but there is evidence that this is incorrect [1,2]. This is also in contrast to computational results which affirm that all three systems PbTe, PbS and PbSe indeed adopt the TlI structure [3].

In this presentation, we report recent X-ray powder diffraction obtained at synchrotron sources on PbX compounds under pressure, that allowed us to solve the structure of the intermediate phase of PbTe, from simulated annealing techniques and Rietveld refinement : the phase transition at 6 GPa is not to the GeS (B16) or TlI (B33) type structures as previously reported, but to an orthorhombic Pnma structure, with cell parameters a=8.157(1), b=4.492(1), c=6.294(1) Ǻ at 6.7 GPa. This structure corresponds to a distortion of the low pressure NaCl structure with a coordination intermediate between the six-fold B1 and the eightfold B2 structure. These new results may modify the admitted paths of phase transitions between the B1 (NaCl) and B2 (CsCl) structures. We will also reconsider the intermediate high pressure phases of PbS and PbSe.

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Infrared properties of the quasi-one-dimensional superconductor β-$Na_{0.33}V_2O_5$ under pressure

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At ambient pressure β-$Na_{0.33}V_2O_5$ shows a quasi-one-dimensional metallic character at room temperature, which can be explained by its highly anisotropic crystal structure consisting of chains and ladders of VO_6 octahedra and chains of VO_5 square pyramids. Upon cooling it undergoes a metal-insulator transition at 135 K due to charge ordering on the V sites. The pressure-temperature phase diagram of β-$Na_{0.33}V_2O_5$ is remarkable, since it shows a superconducting phase for pressures higher than 7 GPa in direct vicinity to the charge-ordered phase [1]. The mechanism of the observed superconductivity and its relation to the charge ordering due to electronic correlations is not clear. Furthermore, electron-phonon interaction seems to play a role as well, influencing the conduction mechanism.

We carried out polarization-dependent reflectivity measurements in the midinfrared frequency range on β-$Na_{0.33}V_2O_5$ at room temperature as a function of pressure (<20 GPa). The results are discussed in terms of the conduction mechanism, pressure-induced structural changes, and charge ordering/redistribution.

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High Pressure Synthesis, Crystal Structure, Magnetic & Transport properties of Cr-doped strontium ruthenates, $SrCr_xRu_{1-x}O_3$

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In recent years, there has been considerable research interest in the ruthenate perovskites, due to the observation of a variety of interesting physical properties, including superconductivity in Sr_2RuO_4. The simple strontium ruthenate perovskite, $SrRuO_3$, which has an orthorhombic *Pbnm* perovskite structure has been of particular interest as it represents a rare example of a ferromagnetic *4d*-transition metal oxide, and exhibits a conducting behaviour best described as a "bad metal" [1].

We have prepared a series of strontium ruthenates in which the *4d* ruthenium is successively replaced by *3d* chromium. $SrCrO_3$ itself is a Pauli paramagnetic metallic conductor [2], and can only be prepared under high pressure conditions (60-65 kbar). We have used a range of high pressure synthetic techniques to obtain increased substitution of Cr^{4+} for Ru^{4+} in these $SrCr_xRu_{1-x}O_3$ materials, and have studied the crystal structure, magnetic and transport properties. Samples at $x \leq 0.2$ were synthesised in Edinburgh at 1100°C under ambient pressure conditions; samples with $0.2 < x \leq 0.6$ were synthesised in Madrid at 1000°C under 35kbar pressures; samples with $x > 0.6$ were synthesised in Munich at 1100°C and a pressure of 105kbar.

Two distinct structural phase transitions are observed with increased Cr-doping – from orthorhombic *Pbnm* to rhombohedral *R-3c*, accompanied by a phase coexistence, at $x = 0.15$, and from rhombohedral to cubic *Pm-3m* above $x = 0.5$.
Susceptibility measurements show the presence of an additional magnetic transition, above the Curie transition of $SrRuO_3$, at small levels of Cr-doping. At higher doping levels ($x \geq 0.5$), a single transition is again observed, but with a higher transition temperature than in $SrRuO_3$. Resistivity measurements show "bad metal" behaviour, with transitions to insulating states at low temperatures and medium *x* values.

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Structural Studies on Dy to 119 GPa and Applications to Lanthanide Systematics

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The Lanthanides, or Rare Earth Elements (REE), are known to undergo crystallographic as well as electronic structure changes with applied pressure. The trivalent REE have been shown to exhibit a sequence of structural phase transitions with increasing pressure (or decreasing atomic number): hcp → Sm-type → dhcp → fcc → dfcc. We have performed *in situ* x-ray diffraction studies on Dy to 119 GPa in a diamond anvil cell. Dy is shown to undergo the typical REE structural sequence, although a pristine fcc phase is not observed. This result is consistent with the observed narrowing of the fcc stability region for the heavy REE. In addition, at 73 GPa, Dy transforms from dfcc to a monoclinic structure in conjunction with a 6% reduction in volume. The observed volume change is similar to that observed in Ce, Pr, and Gd, and is attributed to delocalization of the 4-f electrons. Preliminary results on Tm indicate similar behavior, and will be discussed as available.

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Structure of Liquid Silver Halides at high pressures

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Pressure and temperature dependence of the structure of liquid silver halides AgX (X=Cl, Br, I) is investigated by a synchrotron x-ray diffraction up to 20 GPa by using SPEED1500 and MAX80 high-pressure apparatuses. The structure factor, S(Q), and the pair distribution function, g(r), of liquid AgI change drastically around 3 GPa and 11 GPa. At both pressures, the structural parameters, such as ratios in the position of the second peak to the first peak in S(Q) and g(r) abruptly change, as well as the significant increase in the coordination number. These show the existence of three stable liquid forms up to 20 GPa. The respective pressures where the drastic changes occur are almost the same as the transition pressures in the crystalline counterpart. The pressure-induced structural changes of AgX (X=Cl, Br, I) are compared and the pressure and temperature dependence of the structure of liquid silver halides are discussed.

The first-order phase transition-like phenomena in liquid silver halides are similar to those observed in liquid CdTe [1], while those are completely different from those in less ionic liquids, such as liquid Si[2], Ge[3], Sn[4], GaSb[5], InSb[6] and InAs [7]. The origin of the difference is discussed in the relation to the ionicity in the chemical bonds.

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High pressure study and electronic structure of the NiAl and Ni_3Al alloys

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Nickel aluminide intermetallic compounds, mainly NiAl and Ni_3Al, have been considered as promising high-temperature structural materials because of their high melting points, low densities and a good oxidation resistance. Ni-Al intermetallics are potential candidates as heat shields in chambers and gas turbines. Those materials suffer from brittleness. The Thermodynamic properties with advance first-principles approach where predicting the structural and physicals properties of the materials.

This study presents the room temperature crystallographic, metallurgical, and electronic properties of the Ni_3Al and NiAl compound, as a function of pressure. Both X-Ray diffraction (XRD) measurements and full potential linearized augmented plane wave (LAPW) calculations were applied. No phase transition was observed in the XRD measurements up to a pressure of ~30 GPa. Holzapfel equation was used to fit the volume-pressure curve to the equation-of-state, Fig. 1. The bulk modulus (B_0) at ambient pressure was calculated from the X-Ray data, sound-velocity and density measurements, and from the LAPW calculations.

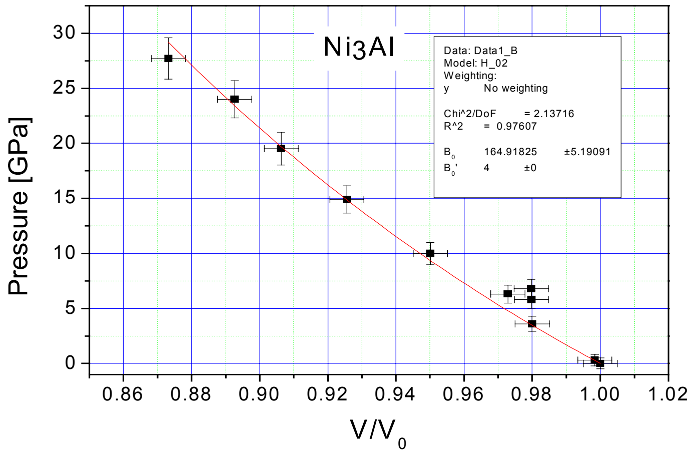

Figure 1. The volume-pressure curve of Ni_3Al fitted with The Holzapfel Eq.

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High pressure properties of carbon and silicon clathrates

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We propose to review the high pressure properties of carbon and silicon clathrates. Group IV clathrates are open-framework sp^3 based structures allowing for the ultra-degenerated intercalation of donor or acceptor atoms. Their physical properties are both governed by the sp^3 tetrahedral bonding and by the guest-host interactions. In spite of the important topological differences with respect to their diamond analogues, many of the clathrate physical properties as their low compressibility [1] or their superconductivity [2] can be interpreted in a common framework. On the other side, we have to consider the particular geometrical constraints of the hypothetical carbon clathrate structure to understand its exceptional ideal strength [3] that surpasses the one of diamond. The clathrate endohedral type of intercalation gives rise to the observation of a number of unique behaviours. We can underline the extreme high pressure stability [4], which can attain up to 4 times the one of the diamond phase for iodine intercalation, as well as their unique type of isostructural phase transformations [4,5].

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A failure wave phenomenon in brittle materials

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The impact loading of a glass and, probably, other brittle materials can be accompanied by an appearance of a failure wave. The failure wave is a network of cracks that are nucleated on the surface and propagate into the stressed body. It presents a mode of catastrophic fracture under high pressure that is not limited to impact events. One hopes that the investigation of failure wave in shock-compressed glasses will provide information about the mechanisms and general rules of nucleation, growth and interactions of multiple cracks. In the presentation, results of investigations of the phenomenon in different brittle materials are summarized and discussed. The failure waves were recorded in silicate glasses of different hardness, but were not recorded in hard single crystals and ceramics. A decrease of deviator stresses and vanishing of the tensile strength occur behind the failure wave front. It has been shown that the failure wave is really a wave process with a small stress increment, although its kinematics differs from that of elastic-plastic waves. The propagation velocity of the failure wave is less than the sound speed, it is not directly related to the compressibility but is determined by the crack growth speed. The propagation speed of the failure wave slightly depends on the stress above the failure threshold, and does not depend on the propagation distance. The glass surface plays an important role in the failure wave process because the surface is a source of cracks. Transformation of elastic compression wave followed by the failure wave in a thick glass plate into typical two-wave configuration in a pile of thin glass plates confirms the role of surfaces that distinguish the failure wave process and time-dependent inelastic compressive behavior of brittle materials. At peak stresses above the Hugoniot elastic limit, the failure wave process may occur at gradual compression as the stress grows above the failure threshold up to the stress at which plastic deformation begins.

The chalcogenide spinel, $CuIr_2S_4$, under high pressure

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Rare earth materials that exhibit mixed valence (MV) and display variety of phenomena due to the strongly correlated electrons are a widely investigated class of materials. Some transition metal chalcogenides exhibit MV and exhibit variety of phenomena like crystal structure transitions, insulator metal transitions (I-M), magnetic super conducting ordering etc. Among these compounds, recently, CuT_2X_4 (T=Rh/Ir, S/Se) are being investigated widely because of interplay of superconductivity T ionic state and an unusual low temperature insulating phase stabilized by doping, pressure, or low temperature.The thiospinel compound $CuIr_2S_4$ is metallic at room temperature and exhibits metal insulator transition with a transition temperature T_c=230K[1]. This is contrary to the normal trend of a low temperature metallic phase transforming to a high temperature insulating phase. Low temperature x-ray diffraction measurements shows that the metal insulator transition is accompanied by structural transition from the cubic to a monoclinic phase with a 0.7% reduction in volume[2]. Magnetic susceptibility measurements up to 1.0 GPa show that transition temperature increase with increasing pressure and the insulating phase do not have any localized spins[2]. In the cubic structure Cu atoms are tetrahedrally coordinated and Ir atoms are octahedrally coordinated with the S atom. In the ionic model evoked to explain the unusual behavior, a MV configuration for Ir ($Cu^{+1}Ir^{+3}Ir^{+4}S^{-2}{}_4$) is evoked. Thus insulating phase at low temperature can result from the charge ordering of two anions Ir^{+3} and Ir^{+4} along with Ir^{+4} polymerization [3]. The polymerization of Ir^{+4} (spin =1/2) to a state S=0 state is needed to account for the magnetic data. $CuIr_2S_4$ is the only example of a three dimensional structure with charge ordering and spin dimerization.[4] We have carried out the electrical resistance (R) measurements of $CuIr_2S_4$ up to 32 GPa at ambient temperature. The resistance increases gradually and reaches a value that is forty times the initial value around 15 GPa. Beyond 15 GPa the resistance decreases up to 32 GPa, with a change of slope near 25 GPa.. By 35 GPa, resistance recovers to that at the ambient condition. As there is no discontinuous change in R, there may not be any structural transition in this material. However, the reentrant metallic nature it exhibits under pressure is rare.It may be noted that the volume reduction under pressure may be brought about by the cubic to triclinic or a Ir^{+3} to Ir^{+4} conversion, in addition to the normal compression. Thus details of bond variation and equation of state behavior are important to understand the phenomena and are also useful inputs for any refinement of the model for I-M transition. Thus, in order to identify the structural basis of this behavior, x-ray powder diffraction measurements on $CuIr_2S_4$ under various pressures were also carried out. These results will also be presented.

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X-ray diffraction and Raman of GaP using a laser heated diamond anvil cell

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Understanding of the crystal structure systematic among III-V and II-VI semiconductors is of fundamental to semiconductor physics and has been well established using synchrotron x-ray diffraction at high pressures.[1] A recent phonon calculation suggests that the instability of the □-Sn structure, which was absent from the ionic compounds at high pressures stems from a soft phonon.[2] EXAFS data provided a value for the bulk modulus of GaP-I and the pressure-quenched sample was claimed as amorphous.[3] However, there was no EOS information for GaP-II, which is now firmly known as an orthorhombic metallic high pressure phase of GaP. The transition pressure of GaP-II also appears in conflict.

We measured x-ray diffraction of GaP at high pressures and high temperatures to better understand physics of III-V semiconductors, to determine first isothermal EOS of GaP-I and –II, and to examine further phase transitions.

The claim that GaP did not revert to the starting low-pressure phase after compression to 35 GPa may suggest intermediate phases. However, our Raman data shows that pressure quenched GaP appears to be highly strained GaP-I. X-ray diffraction also shows very broad peaks resembling GaP-I structure. At 23 GPa, we noticed a new peak starts showing and at 24 GPa, both I and II were identified in x-ray diffraction at ambient temperature. Finally at 34 GPa, GaP-II was the only phase recognized. When we laser heated GaP at 17 GPa to ~1800 K, we noticed a new phase mixed with GaP-I and the new phase was quenched to ambient temperature. When compressed to 22 GPa, the new high temperature phase disappeared. X-ray diffraction during laser heating at 22 GPa shows the same new phase with stronger intensity suggesting that the new phase is stable at high temperature. The new phase appears to be related to □-Sn structure.

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Solvothermal reactions: new trends in Materials Sciences.

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Solvothermal reaction can be described as a chemical reaction involving a solvent either in subcritical or supercritical conditions. Such a solvent can act as a chemical component or a fluid phase able through physico-chemical properties to modify the synthesis reaction.

During these last twenty years, solvothermal reactions have been used for developing different areas involving basis or applied researches. Several aspects will be presented

– in Materials Chemistry: (i) the synthesis of novel materials, (ii) the development of nanochemistry,

– in Materials Science: (i) new crystal growth processes, (ii) thin film deposition, (iii) sintering at low temperature.

In all these domains two main factors seems predominant: the improvement of the kinetics, (ii) the reduction of the required temperature compared to conventional processes.

Fluidised bed in supercritical phase

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In atmospheric conditions, fluidized beds are seldom used with particles belonging to the Geldart's classification C group. As a matter of fact, the expansion is not homogeneous if the particle size is below 20 µm, aggregates occur. However coupling with the supercritical carbon dioxide (SC CO_2), the particle fluidization seems to be favoured since, varying the CO_2 pressure and temperature, the medium density can be increased and the viscosity is still low.

First fluidization experiments were carried out with glass beads in order to verify whether standard relations can be applied in the supercritical domain. The high pressure fluidized bed (280 bar; 100 °C) with an inner diameter of 30 mm and a height column of 370 mm can be operated with a maximum CO_2 flow of 30 $kg.h^{-1}$ ·The pressure drop, that is measured by a 0-373 mbar pressure differential, in the fixed bed was compared with the Ergun equation whereas for the fluid velocity at the incipient fluidization, various equations, which take into account under pressure experiments, were studied. In SC CO_2, 150 µm glass beads behave like A group particles. At 80 bar and 40 °C, the minimum fluidization velocity is in good agreement with the Wen and Yu correlation with a mean gap of five per cent.

For smaller particles, new experiments are under process before proposing a general correlation. A hydrodynamic study of glass beads fluidization in supercritical conditions will be investigated thanks to the visualization of the fluidized bed through a specific quartz system.

The Development of Novel Methodology for Observing Discontinuous Behavior of Density of Compressed Gases by Light Scattering

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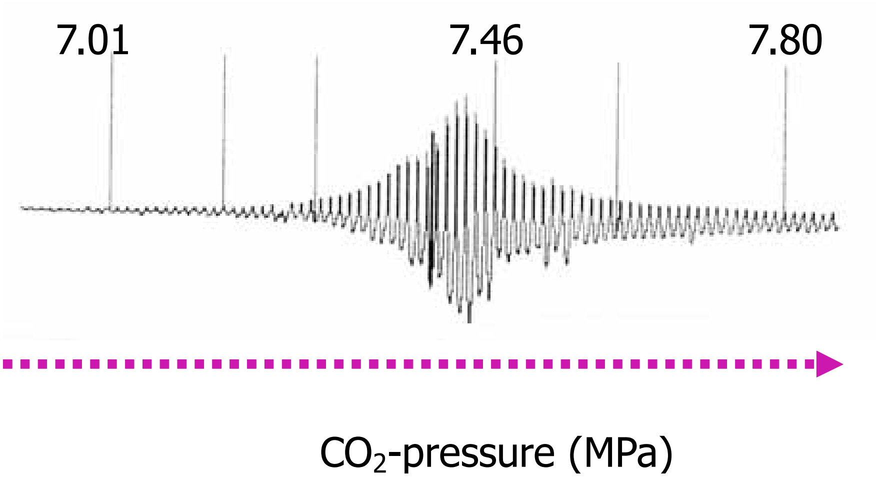
ABSTRACTS

A novel methodology for determining the discontinuous behavior of density of compressed gases has been developed based on light scattering method. This method is capable to quantitatively evaluate the degree of heterogeneity of the density of compressed gasses, carbon dioxide, ethane, ethylene or even their mixed gases, on its pulse pattern of UV or visible light scattering. A typical spectrum of carbon dioxide near the critical temperature (at 32.5°C) as a function of pressure is demonstrated below.



The maximum width of the pulse was observed at 7.36MPa, indicating its maximum heterogeneity. Also, a maximum of molar polarization has been observed at the same conditions using our different dielectric property measurement for determining molecular association, which detailed experimental data will present in the poster session at this conference.

In this paper, we will present detailed information of our new instrumentation with experimental data, and discuss potential research projects.

Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Controlling the selectivity of separation processes by pressure

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In order to utilize high hydrostatic pressure for selective separation processes, an automated high-pressure plant for a continuous flow through a fixed bed was designed and constructed. The plant is computer controlled and can be operated at pressures of up to 360 MPa.

The pressure influence on the adsorption and desorption behaviour of the surfactant Triton X-100 and tailor-made adsorbents [1] by means of isotherms and breakthrough curves, Fig. 1., were investigated.

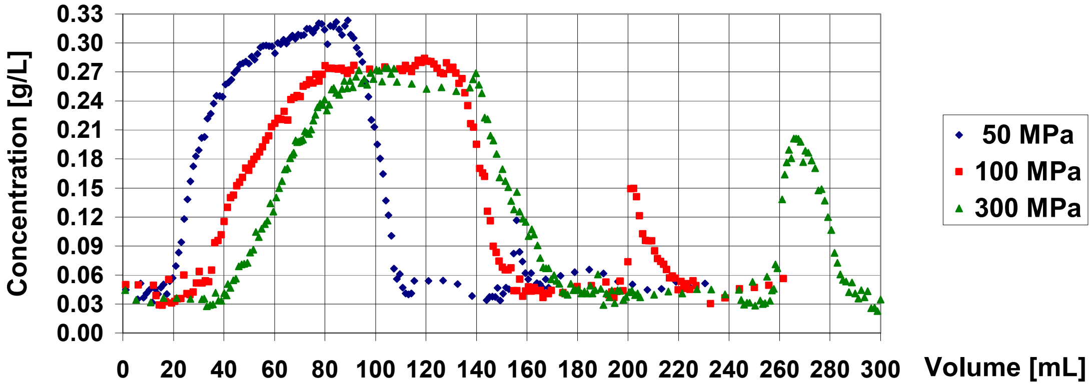

Fig. 1: Pressure-dependence of adsorption (breakthrough curves) and desorption of Triton X-100; adsorption at pressures indicated; desorption at 0.8 MPa

It was found that the adsorption equilibrium can be controlled by pressure. The utilized adsorbent was proofed not to adsorb any Triton X-100 at atmospheric pressure, which was used as a model substance for amphiphilic molecules such as glycolipides for pharmaceutical as well as process engineering use. A significant amount of Triton X-100 was adsorbed under pressure, the adsorption capacity increased with the pressure. After adsorption (breakthrough) and washing the fixed bed at 300 MPa, only by reducing the pressure to 0.8 MPa 75% of the initial concentration of Triton X-100 could be regained.

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The Use of Catalysts in Near-Critical Water Processing

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The use of heterogeneous catalysts in near-critical water processing provides many challenges of material stability in addition to the normal questions of chemical activity. Conventional catalyst materials developed in traditional organic chemistry or petroleum chemistry applications provide a source of information of materials with the required activities but often without the required stability when used in hot liquid water. The importance of the use of catalysts in near-critical water processing plays a particularly crucial role for the development of renewable fuels and chemicals based on biomass feedstocks. Stability issues include both those related to the catalytic metal and also to the catalyst support material [1]. In fact, the stability of the support is the most likely concern when using conventional catalyst formulations in near-critical water processing. Processing test results will be used to show important design parameters for catalyst formulations for use in wet biomass gasification in high-pressure water and in catalytic hydrogenations in water for production of value-added chemical products from biomass in the biorefinery concept. Analytical methods including powder x-ray diffraction for crystallite size and composition determination, surface area and porosity measurements, and elemental analysis have all been used to quantify differences in catalyst materials before and after use. By these methods both the chemical and physical stability of heterogeneous catalysts can be verified.

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Biomass gasification in supercritical water: Key compounds as a tool to understand the influence of biomass components.

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Energy produced from biomass may contribute in a considerable amount to the growing future energy demand. A large portion of biomass wastes is wet biomass containing up to 95 % water. This wet biomass causes high drying costs if classical gas phase gasification processes are applied. This can be avoided by conducting the gasification in supercritical water at pressures up to 30 MPa and temperatures around 600 °C, where hydrogen and carbon dioxide are the main products.

In order to optimize the gasification process in supercritical water an improved knowledge of the chemical reaction pathways is necessary. Therefore, experimental studies, in some cases combined with thermodynamic calculations or kinetic modeling, on model compounds such as glucose, glycerin, pyrocatechol, and methane as well as with biomass were conducted. From the model compounds, general characteristics of reactions steps could be derived, such as the dependence on temperature, pressure, residence time, heating rates, concentration etc. Selected “key compounds”, like phenols, furfurals and organic acids were identified and quantified, which are formed by different and characteristic reaction pathways. They can e. g. be used to compare results from studies with model compounds to those achieved by biomass conversion.

The different ingredients of biomass, like alkali salts or proteins influence the reaction significantly. The role of alkali salts is of special interest. In spite of the relatively high temperature the hydrothermal gasification is highly determined by chemical kinetics and the addition of alkali salts increases the hydrogen yield drastically.

From all these results a simplified reaction mechanism could be set up. The fundamental studies open the opportunity to identify some measures to be taken in order to increase of desired and to decrease unwanted products. These measures lead to an improved reaction engineering optimized towards a maximum hydrogen yield that will be presented, too.

Hydrogen and Methane Production from Biomass in Supercritical Water

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At supercritical water conditions (T>374 °C, p>22.1 MPa) biomass reacts with water to form a combustible gas rich in hydrogen and methane. The CO_2 formed can be separated from the product gas by a water wash column. Reactions are fast and almost complete gasification with high space-time yields can be achieved. Usage of heat exchangers is possible at supercritical water conditions. Compression work is low since only almost non compressible water slurry is pressurised. This leads to a highly efficient process also for educts with high water content [1].

Systematic experiments with corn silage in laboratory scale equipment show the dependence of the gasification yield from the temperature. Complete gasification is achieved at 700 °C, in residence times up to few minutes. Experiments in the new 100 kg/h continuous flow plant dedicated for the process of biomass gasification in supercritical water (acronym VERENA) show high thermal efficiency (~ 80%) for diluted educt streams (~ 10 wt% OM).

Conclusion: The comparison to the traditional gasification process shows several advantages for the hydrothermal gasification especially for wet biomass/organic waste feedstock. A gas rich in H_2 and methane (sum of both up to 80 vol %) can be produced in one process step, a high thermal efficiency of the heat exchanger (80 %) has been demonstrated and the soot and tar formation can be suppressed to less than 10% of the organic carbon.

The newest results from the experiments with corn silage planned to be performed in the pilot plant within the next weeks will also be presented.

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Efficient production of synthetic natural gas from biomass by hydrothermal gasification

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Objectives

This project aims at developing an efficient process capable of producing synthetic natural gas (SNG) from wet biomass waste streams by catalytic hydrothermal gasification. Biogenic SNG is a versatile “second generation” biofuel that can be used for electricity production, heating purposes as well as a clean fuel in natural gas vehicles. Several aspects important for the design of a miniplant, including feed preparation, biomass liquefaction, gas separation, and the influence of salts, will be discussed.

New Results

In an earlier publication [1] we reported the complete and tar-free gasification of wood slurries up to 30 wt% dry matter in a batch reactor using Raney® 2800 nickel as catalyst. New results from a continuous catalyst test rig using a concentrated wood model mixture revealed rapid deactivation of the Raney® 2800 nickel catalyst. Doping with small amounts of a noble metal improved the catalyst stability significantly. Several analytical methods (BET, XRD and TPO) were used to characterize the catalysts before and after use. Manure solids were also gasified in the batch reactor. The methane yield was lower than with wood due to the presence of salts.

Conclusions

A pronounced effect of different salts on the efficiency of the hydrothermal gasification was observed. More information on the interaction of specific salts with the catalyst are needed.

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Heat transfer to the turbulent flow of supercritical water where glucose oxidation is taking place

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Heat transfer to and from water under supercritical pressure is of practical importance when supercritical water technology is developed to commercialization. It is usual for a supercritical water process that heat requirement for achieving supercritical state is large and total energy efficiency for a plant is impractically low without heat recovery, or that recovery of heat from water under supercritical state leads to improvement of the system economy. Heat transfer characteristics of turbulent flow of water have been studied in 1960s and 70s, but it was only for the pure water system, and effects of neither solutes nor reactions taking place, which are essential for actual supercritical plants of recent interest, have been studied.

In this study, effects of chemical reaction on heat transfer characteristics were studied experimentally. As a model reaction, glucose oxidation was employed. Aqueous solutions of glucose and oxygen were mixed at the inlet of the tubular test section, and then heat transfer coefficient to the flow where glucose oxidation was taking place was measured by applying direct current to the section while measuring the surface temperature of the outer wall. Direct current application allowed the flow being heated at a constant heat flux. Inner surface wall temperature could be determined by solving Fourier’s equation through the tube wall. Bulk temperature of the fluid could be obtained from enthalpy increase of the fluid, which in turn was determined from the applied heat and heat released by the oxidation reaction. Heat transfer coefficient was calculated using this heat flux, inner surface wall temperature, and bulk temperature using Newton’s law of cooling.

As a result, effect of reaction was prominent in subcritical temperature range, causing large increase in heat transfer coefficient compared to pure water. This result is of importance in designing supercritical water gasification or oxidation plant in terms of heat recovery.

Stirred double shell reactor for waste treatment by supercritical water oxidation

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Summary

We developed a new apparatus with double entrance to treat organic waste with radionuclides in supercritical water. We demonstrate that an oxygen fraction higher than 10 v/v% and the dilution of waste with water/air mixture avoid the char production.

Moreover, we investigate hydrodynamics and heat transfer in SCWO processes with the industrial CFD software FLUENT.

Introduction

SuperCritical Water Oxidation (SCWO) is a very efficient to treat hazardous waste without emission of undesirable by-products such as NOx or SOx. However, this technology undergoes two well-known problems due to the operating conditions and the waste composition, which are corrosion and salt plugging. To overcome these problems, we developed a reactor design with both a double shell in titanium, which prevents corrosion, and a stirrer creating a turbulent flow, which prevents the sedimentation of inorganic compounds and enables better heat transfer. First results showed that this design is efficient enough in order to treat pure waste containing up to 50 wt% of salt and concentration up to 100g/L of chloride.

Experimental and results

This design is now adapted in order to treat organic waste highly contaminated by radionuclides in a glovebox. Safety constraints have led us to minimize the number of high pressure tubes entering the glovebox, and thus, the reactor is fed with a single water/air mixture flow which has to be split: one part is injected in the annular space where it is pre-heated before reacting, whereas a second part, which is kept cold, dilutes the organic waste in order to avoid the char production. An experiment design was performed which proves the importance of the role played by the fraction of water/air mixture introduced with the waste and by the oxygen fraction in the reactor on the char production. When the fraction of fluid is higher than 5 v/v% and the oxygen fraction is higher than 10 v/v%, no char is produced and all conversion yields are greater than 99.99 %.

Modelling

Furthermore, the study of hydrodynamics and heat transfer in SCWO processes is carried out using the industrial CFD software FLUENT so as to understand the physical and chemical phenomena involved. A kinetic model has been validated on a 2D geometry by comparison with experimental results on a tubular reactor; this model is currently implemented on a more complex 2D geometry modelling the double shell stirred reactor.

Energy Recovery from Wet Biomass Feedstock in Supercritical Water

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Energy recovery from biomass spares fossil fuels and, since it represents a CO_2 neutral energy feedstock, it can make an import contribution to climate protection. Large, till now on technical scale virtually unused resources are wet waste biomass with > 50 % g g^{-1} moisture, originating from the agricultural, the municipal and the industrial sector. Total oxidation of wet biomass in supercritical water seems to be a promising alternative to the conventional combustion with preceding drying of the biomass [1].

Above its critical conditions (i.e. 22,1 MPa and 374°C) water exists only as a fluid, the distinction between vapour and liquid vanishes and therefore the energy of vaporisation has not to be provided. In comparison to conventional processes an oxidation in supercritical water shows further advantages as extremely low levels of noxious emissions (NO_x, SO_2) [2].

To clarify the feasibility of such a SCWO (supercritical water oxidation) process, knowledge of the kinetics of biomass oxidation in sub- and supercritical water is helpful. As a model substance for cellulosic materials glucose was investigated, since under sub- and supercritical conditions the glycosidic link breaks easily [3]. Results of kinetic experiments at 24-34 MPa and 250-450°C are presented and different process designs of such a SCWO plant for wet biomass are discussed.

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Supercritical Hydrothermal Synthesis of Organic Inorganic Biomolecule Hybrid Nano Particles

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We have proposed and developed a new method of supercritical hydrothermal synthesis of metal oxide nanoparticles. Recently, we modified this method to synthesize organic-inorganic-biomolecule fused materials based on the methods of supercritical hydrothermal synthesis and organic synthesis reaction in supercritical water. By introducing organic species (aminoacids, carboxylic acids, amines, alcohols, aldehydes etc.) during supercritical hydrothermal synthesis, nanoparticles whose surface was modified with organic materials could be synthesized, which was probably due to the homogeneous phase formation of the supercritical conditions. Formation of 1-10 nm size metal oxide particles could be achieved, which has not been possible with other methods. Modification of bio-materials including amino acids or peptides is also possible. This type of surface modification allows the designer to incorporate unique characteristics of nanoparticles into their products, including perfect dispersion of inorganic nanoparticles in aqueous solutions, organic solvents or in polymers. This can be used for nanohybrid polymers, nano-ink, or nano-paints. Furthermo, biomodification of nanoparticles leads to form nanobiohybrid materials.

Synthesis of luminophores – powders in supercritical water fluid

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Under treatment of oxides or hydroxides of metals in supercritical water fluid occurs a solid-phase reorganization and ordering of oxides structure with formation of a powder of well edged single crystals. The adding into reaction medium of dopant as salt or oxide results in formation of crystals with uniform distribution of dopant ions. The doping of crystals allows to operate on optical properties of oxides. For example, thermovaporous treatment of aluminum hydroxide along with dopant at 400ºC and P_{H_2O} = 26 MPa results in formation of corundum (α-Al_2O_3) with an intensive luminescence at 694 nm (Cr), 678 nm (Mn, fig. 1), 614 nm (Eu), 356 nm (Ce). The synthesis of gahnite ($ZnAl_2O_4$) doped by Cr, Mn or Eu results in occurrence of a luminescence at 687, 659 and 612 nm accordingly. The yttrium - aluminum garnet ($Y_3Al_5O_{12}$) doped by Cr has luminescence bands about 688 nm, and in case of Nd at 1064 nm. Peculiarity of luminophores synthesized in water fluid is the presence in their structure of oxygen vacancies and residual hydroxyl groups. The doping ions will form the composite complexes with hydroxyl groups and oxygen vacancies. Due to formation of such complexes the temperature and pressure of water fluid during synthesis influence a state of dopant ions in forming crystals. The annealing of synthesized fine-crystalline oxides on air results in decomposition of complexes and change of luminescence (fig. 2).

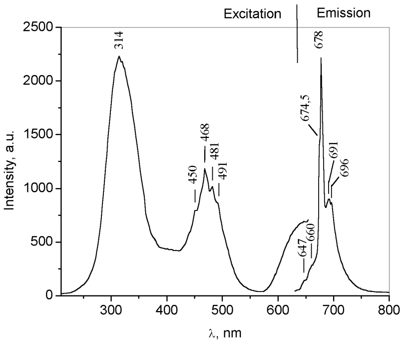

Fig. 1. Composite luminescence band (with basic maximum at 678 nm) of manganese ions in corundum and its excitation spectrum.

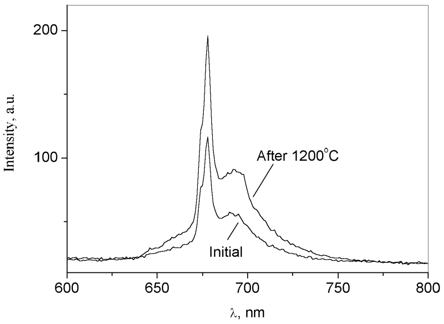

Fig. 2. Increase of luminescence intensity of corundum doped by Mn before and after annealing at 1200ºC.

Pseudomorphic Conversion of Mineral $SrSO_4$ to $SrCrO_4$ under Hydrothermal Conditions

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It is well known that mineral replacement reactions take place by a dissolution–reprecipitation process. Processes such as ion exchange and pseudomorphism are all linked by the common fact that mineral specie is replaced by a more stable phase under geological conditions. In the present work, we have investigated the feasibility for achieving the exchange of small $SO_4^{=}$ ions by large $CrO_4^{=}$ ions in natural celestite single crystals under hydrothermal conditions. Hydrothermal treatments were carried out by using a Teflon-lined stainless steel vessel. Experiments were performed at temperatures from 150 °C to 250 °C, for intervals from 1 to 96 h and filling ratios of 40 – 70 % of the autoclave volume. The CrO_4/SO_4 molar ratios investigated were 1, 2 and 5. The crystal structure of partially converted crystals was characterized by X-ray powder diffraction technique. SEM and EDX line scan analyses were conducted to reveal the morphology and chemical compositional aspects on the reacted crystals.

The results showed that the anion exchange of $SO_4^{=}$ ions by $CrO_4^{=}$ ions, partially proceeds on celestite crystals by a pseudomorphic process. The partially reacted crystals showed the formation of a thin layer, which matched the $SrCrO_4$ compound with monoclinic structure. The growth of the layer was further achieved by increasing the reaction temperature and the CrO_4/SO_4 molar ratio. In addition, EDX line analyses showed that the $SrCrO_4$ layer was formed by the mechanism of dissolution-precipitation of ion species. This layer was continuous and did not exhibited any etch pits, therefore, a further dissolution of the $SrCrO_4$ layer by the fresh ion exchange medium occurred during the long hydrothermal reaction intervals.

Hydrothemal Synthesis and Investigation of Aluminum Terephthalate

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Earlier we obtained terephthalates of the elements of I-II groups. Terephthalates of these elements can be obtained directly at temperatures not higher than 100^{o}C and normal pressure with interaction of a solution of ammonium terephthalate with the salts of the corresponding elements. Under analogous conditions we have obtained aluminum terephthalate in the amorphous state and it was identified on the basis of physical and chemical analysis (X-ray phase analysis, DTA, IR, element chemical analysis).

For more specific identification it is necessary to obtain not amorphous but crystalline aluminum terephthalate. For obtaining this compound the method of hydrothermal synthesis was used.

The process was carried out in the autoclave in temperature interval of 200 – 390^{0}C and under pressure of 1.6 - 25 MPa. As initial substances we used crystalline terephthalic acid (TA) and aqueous solutions of aluminum chloride.

On diffraction X-ray patterns we can fix the reflexes of a new substance which were not before encountered in the literature. The chemical composition of this compound corresponds to $Al_2(C_6H_4(COO)_2]_3.2H_2O$.

The obtained compound was investigated by IR, DTA methods.

Thermogravimetric study of obtained aluminum terephthalate indicates the similarity of results to terephthalates of I-II groups. On the X-ray patterns of the substance that obtained after heating to 900^{0}C wide lines corresponding to γ-Al_2O_3 are present.

IR studies of the samples treated at 500^{0}, 600^{0} and 900^{0}C indicate the formation of the molecules of water, located in the structure of the formed oxide. These water molecules are possibly formed because of the thermal decomposition of aluminum terephthalate.

Pressure measurements from Raman spectra of stressed diamond anvils.

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Problem of pressure measurements in a diamond anvil cell from Raman spectra of stressed diamond anvils have been studied. A splitting of the threefold-degenerate optic mode of diamond into singlet and doublet modes was observed in the Raman spectra from the stressed anvils. On the basis of the splitting effect quantitative relations between Raman spectra from the diamond anvil tip, stresses in the anvil tip and pressure in a sample have been considered [1]. The calibration of the Raman spectra against the sample pressure up to 220 GPa has been proposed. Experimental stress tensor study in the anvil tip permits comparison of the present data with theoretical calculations of diamond compressibility.

A correctness of pressure measurements procedure in the sample from high-frequency side of the Raman spectra profile has been studied on the base of the obtained results. Problems of the critical focus point shift from the culet and measurements stability and reproducibility are discussed. Data of the present study are in good correlation with recent experimental data of Ref. [2] (3 Mbar) and [3] (2.5 Mbar) as well theoretical calculations [4]. The obtained results demonstrate, that Raman spectra from the diamond anvil tip can be widely used for measurements of the normal stress in the sample (or pressure for the quasi-hydrostatic compression).

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New Anvil and Gasket Designs

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Mechanical stability and aperture in diamond cells can be significantly improved using conical supports for cone-shaped anvils. Because these anvils are machine-ground and smaller in diameter, they cost less than conventional anvils. The conical design allows for steel supports, which are significantly easier and cheaper to manufacture than tungsten carbide supports. Conical support also prevents seat damage upon diamond failure. An additional new feature of the anvils is the roughened outer portion of the culet, which increases friction between the anvils and the gasket. This increases the height to diameter ratio of the pressure cell and prevents bonding between gasket and diamond, which causes ring cracks during pressure release. The anvils have been extensively tested for culets ranging from 0.1 to 1 mm diameter up to megabar pressures. A new gasket design is also introduced. The stability of the gasket was significantly improved by filling laser-cut grooves with diamond powder. The procedure is straightforward and further increases the height to diameter ratios compared to pure metal gaskets. Example: For a 0.5 mm culet the the gasket height is typically 40 microns at 50 Gpa.

Neutron diffraction in 40 GPa - pressure range : a tool to study magnetic and crystal structures

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Neutron scattering is the powerful tool to study microscopic properties of condensed matters. It is the only direct way to determine spin arrangements and to study positions of light elements in structure. Recent progress in neutron diffraction experiments under pressures as high as 40 GPa at the Laboratoire Léon Brillouin is described. Original pressure cells use diamond, sapphire, moissanite and c-BN anvils. They are compatible with low-temperature equipments. Special focusing systems allow us to increase intensity by order of magnitude and therefore to study much smaller samples (0.01 mm^3) than conventional samples for neutron scattering experiments (0.1 cm^3). The techniques had been successfully used to study magnetic and structural phenomena in various compounds [1]. We focus on recent results obtained in high-pressure oxygen. At P=0, oxygen is the only elementary molecular magnet. At high pressure it becomes a metal and a superconductor [2,3]. Even though it was obvious that the magnetic interactions should play an important role in high-pressure oxygen, until now there was no any direct information on magnetic structure in solid O_2 under pressure. At the first time we studied magnetic ordering in the alpha- delta- and epsilon-O_2. New magnetic structure had been found in delta-O_2 at P=6 GPa [4]. The structure had unusual ferromagnetic coupling of the O_2 planes. A gradual weakening of magnetic interactions followed by a magnetic collapse was observed at higher pressures [5]. We discuss prospects for high-pressure neutron studies, including rotational ordering in solid oxygen and hydrogen and new pressure-induced magnetic phases.

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A New Opposed-Anvil type High-Pressure and High-Temperature Apparatus Using Sintered Diamond

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A new opposed-anvil type high-pressure and high-temperature apparatus was developed using sintered diamond as anvil material. This apparatus can generate up to at least 30 GPa and 1700 K. Compared to diamond anvil apparatus combined with laser heating, this apparatus has much larger sample volume and has higher stability in temperature. Compared to "Kawai-type" double stage multi-anvil apparatus, this apparatus requires much lower running cost and is easier to use. High pressure and temperature in-situ X-ray diffraction study can be performed when combined with synchrotron radiation.

Basic design is a "Drickamer-type" apparatus with a culet diameter of 3 mm. A combination of metal gasket and pressure transmitting medium made of diamond powder improved the stability of pressure generation dramatically. All the parts for heater, electrode, sample capsule, and so on, has either disc shape or a part of disc shape, and once all these parts are prepared, it is very easy to assemble them because all we need is to put all these parts by stacking them in a small central hall of the pressure transmitting medium. The detail of the apparatus and some examples of the performance will be described.

The Ruby Pressure Standard to 150 GPa

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A new determination of the ruby high-pressure scale is presented. We first review existing calibrations. The new ruby scale that we present is based on experimental data on materials in quasi-hydrostatic media (helium, hydrogen, or xenon) using all available appropriate measurements including those of Dewaele et al[1], Zha et al[2] and our own data. Calibration data extends to 150 GPa. A careful consideration of shock-wave reduced isotherms is given, including corrections for material strength.[3] The new calibration is $P=(A/B)\left[(\lambda/\lambda_0)^B-1\right](GPa)$, with A=1873.4±6.7 and B=10.82±0.14 where λ is the peak wavelength of the ruby R1 line. On the new scale at 150 GPa the pressure is about 13 GPa higher than on the old, so-called qausi-hydrostatic scale using argon for a pressurization medium.[4] Extrapolation to the 300-400 GPa region yield differences of over 20% in pressure. This research was supported by the NSF, grants No. DMR-9971326 and DMR-007182.

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DIAMOND AND cBN CRYSTALLIZATION: THERMODYNAMICS AND KINETICS

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Spontaneous crystallization of diamond and cubic boron nitride (cBN) takes place at high pressures and temperatures from melt solutions of systems, which contain carbon or boron nitride, in the thermodynamic stability regions of dense cubic phases. The solubility of the low-density phase (graphite, hBN) in the melt exceeds that of the high-density phase (diamond, cBN), therefore, in dissolution of the low-density phase, the solution reaches its supersaturation first of all in respect to the high-density phase. The thermodynamic incentive of the crystallization is the difference in chemical potential between the cubic and graphite-like phases μ_c-μ_h. In the equilibrium line between the graphite-like and cubic phases, the crystallization rate is zero. The stable liquidus of the dense phase in the phase diagrams of multicomponent systems is the necessary thermodynamic condition for spontaneous crystallization of the phase.

The crystal formation consists of nucleation and growth. In most cases, the cubic phase nucleation is heterogeneous. The probability of the formation of a critical-sized nucleus, and hence the nucleation rate, increases abruptly with decreasing surface energy at the melt-crystal nucleus interface. With a decrease in the surface energy, the crystal growth rate also increases. The nucleation rate depends exponentially on pressure. The pressure increase abruptly increases the formation rate of the phase of a lower volume. Thus, the negative difference of chemical potentials μ_c-μ_h is a necessary but insufficient condition for diamond or cBN spontaneous crystallization. Even the stable liquidus of the cubic phase in the phase diagram at high pressures does not ensure the spontaneous crystallization of the cubic phase in the presence of kinetic difficulties. The latter may involve (a) a low nucleation rate due to a high surface energy at the crystal–growth medium interface, or to low pressure, (b) a low growth rate of the cubic phase, due to a low difference in solubility between the cubic and graphite-like phases in the melt and low values of diffusion coefficients of clusters of carbon or boron nitride in the melt.

Various models are used to describe the crystallization kinetics. Based on the experimental data, the models allow one to estimate the activation energy of the crystallization process, to ascertain, what stage controls the process (diffusion delivery of the building material, or its integration into a growing crystal), to judge if the nucleation is a continuous process or it exhausts with time, and make a conclusion about the crystallization mechanism. The Avrami-Kolmogorov model has proved to be best suited to describe the process of the spontaneous crystallization of diamond and cubic boron nitride.

Potential super-hard phases and the stability of diamond-like B_nC_m structures

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Metastable complexes of diamond structured B-C-N complexes are now established with the recent synthesis of the metastable material BC_2N[1]. The precursor to the BC_2N super-hard phase has a graphitic structure with the same stoichiometry. Claims that such a material is the second hardest material to date have inspired further studies of hard materials having a potential diamond-like structure and quite recently a B-C phase has been synthesized[2] and where an extreme hardness was also claimed.

The properties of some potential super-hard diamond like boron carbon phases are examined using ab-initio computational modelling. Both the bulk and shear modulus show a steady decrease with boron concentration. The electronic density of states suggest that each of the materials has a strong conducting character. Two specific phases, namely BC_3 and BC_7, are singled out and their possible graphitic precursor phases considered. Finally energies of the graphitic phases are related to the super-hard phases with the same stoichiometry.

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Cubic boron nitride crystallization in fluid systems – in situ studies

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According to the equilibrium phase *p*,*T*-diagram of BN suggested by Solozhenko in 1988 [1], at ambient pressure cubic boron nitride (cBN) is the thermodynamically stable BN polymorph up to 1600 K. However, low-pressure crystallization of cBN in the region of its thermodynamic stability is kinetically restricted. For a rich variety of systems, the threshold pressure of cBN spontaneous crystallization is about 4 GPa irrespective of the temperature. Early in the 90s, Solozhenko *et al.* [2,3] found that synthesis of cubic boron nitride in the presence of supercritical fluids results in drastic reduction of the threshold pressure of cBN formation.

Present work is the first attempt to study *in situ* the crystallization of cubic boron nitride from BN solutions in supercritical N–H fluid at pressures up to 5.2 GPa and temperatures up to 1600 K using angle- and energy-dispersive X-ray diffraction with synchrotron radiation.

In cooling of the BN solution in supercritical N–H fluid, the disappearance of short-range order in the solution is observed which is accompanied by the precipitation of solid phases (cBN or hBN and BN–NH_3 intercalation compound depending on the pressure, temperature and concentration). Spontaneous crystallization of cubic boron nitride has been observed down to 1.9±0.2 GPa, which is the lowest pressure of the cBN crystallization reported so far. Based on the results obtained, the BN–NH_3 hypothetical quasibinary section of the phase diagram of the B–N–H system at 4 GPa has been constructed.

A comparison between diamond and cBN crystallization has shown that for the fluid-containing systems the position of the low-temperature boundary of cBN formation in the *p,T*-diagram of boron nitride is defined either by the line of the incongruent melting of the BN compound with the solvent, or by the kinetics of the cBN nucleation and crystal growth. The position of the high-temperature boundary of the *p,T*-region of cBN crystallization is always defined by kinetics factors.

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Strain-Induced Disorder, Phase Transformations and TRIP in Hexagonal Boron Nitride under Compression and Shear in a Rotational Diamond Anvil Cell: In-Situ X-ray Diffraction Study and Modeling

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It is known that plastic shear significantly reduces the phase transformation (PT) pressure when compared to hydrostatic conditions. Here, a paradoxical result was obtained: PT of hexagonal hBN to superhard wurtzitic wBN under pressure and shear started at the same pressure ~10 GPa as under hydrostatic conditions. To resolve the paradox and to quantitatively study the basic physics and mechanisms, a simultaneous in-situ X-ray diffraction study and modeling of the disorder (the turbostratic staking fault concentration) and PT in hBN were performed. Under hydrostatic pressure, changes in the disorder were negligible. Under compression and shear, a strain-induced disorder was revealed and quantitatively characterized. The strain-induced disorder, in turn suppressed PT; this resolves the paradox. During the strain-induced PT, existence of transformation-induced plasticity (TRIP) was proved. The degree of disorder is suggested as a physical measure of plastic straining which also allows us to quantitatively separate the conventional plasticity and TRIP. TRIP exceeds the conventional plasticity by a factor of 20. In comparison with hydrostatic loading, for the same degree of disorder, plastic shear indeed reduced the PT pressure by a factor of 3-4, as well as caused a complete irreversible PT. Coupled strain-controlled kinetic equations for disorder and PT were derived. The analytical solutions confirm our conclusions and resulted in some predictions. Also, conditions for quasi-uniform pressure distribution were predicted and achieved experimentally. A homogeneous pressure self-multiplication effect was revealed.

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High-pressure synthesis of high purity single crystal of cubic and hexagonal boron nitride and their band-edge natures

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Cubic and hexagonal form of boron nitride(BN) single crystals were synthesized by using temperature gradient method under high pressure. Compounds of alkali metal and/or alkali earth metal- boron nitride were used as solvent for the crystal growth[1]. The quality of these single crystals was studied with respect to their optical properties , etch-pit density and SIMS analysis. Recovered crystals exhibited variety of colors and crystalline natures. Nearly colorless cubic BN crystals obtained by using Ba-BN solvent system revealed that superior characteristics showing optical properties of band-edge nature as well as lower etch-pit density of the order of 10^4/cm[1,2].

Furthermore, high quality single crystal of hexagonal BN were also grown by using Ba-BN solvent under HP/HT. The crystals exhibit the band-edge optical nature of direct wide-band gap semiconductor with Eg:5.9eV. Evidence for room temperature ultraviolet lasing at 215nm by accelerated electron excitation is provided by the enhancement and narrowing of the longitudinal mode, threshould behavior of the excitation current dependenceof the emission intensity, and a far-field pattern of the transverse mode[3,4].

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New Bulk Superhard Semiconducting C-B Composite

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A bulk composite material has been synthesized from graphite-like BC_3 at 20 GPa and 2300 K using a multianvil press in the form of well-sintered 8-mm^3 cylinders. The material consists of intergrown boron carbide B_4C and boron-doped diamond with 1.8 at% B. The material exhibits semiconducting behaviour and has hardness comparable with that of single-crystal diamond. Synthesis of composite ceramics with hardness approaching that of diamond suggests that new superhard materials could be not only among monophases. Combination of semiconducting properties and extreme hardness makes the synthesised material potentially important for precision (for example, electroerosion) machining, electrochemical, and electronic (high-power, high-frequency) applications.

Pure Phases of C_3N_4 Synthesized at High Pressure and High Temperature

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Since A. Y. Liu and M. L. Cohen predicted that beta phase of C_3N_4 may be comparable to diamond in hardness [1], and then D.M.Teter and R.J.Hemley predicted that cubic phase of C_3N_4 will be harder than beta phase C_3N_4 and a particular challenger to diamond [2], thousands of laboratories around the world launched into preparation of beta and cubic phase of C_3N_4 by use of various experimental metholds [3]. Unfortunately, they failed to get pure phases of C_3N_4 with stoichiometric ratio. We have obtained pure phases of graphite phase, beta phase of C_3N_4 synthesized from carbon-natrogen organic compounds as stating material with different catalysts under high pressure and high temperature. We also got beta phase and cubic phase of C_3N_4 starting from its graphite phase by use of laser heating method at high pressure and high temperature in DAC. Phase transitions from graphite phase C_3N_4 to beta phase C_3N_4, and from beta to cubic C_3N_4 under high pressure and room temperature have been investigated by XRD and electrical resistance measurement up to 104 GPa. A phase transition of C_3N_4 looks like an electronic phase transition from direct band gap to indirect band gap by ab initio calculation of energy band at 40 GPa.The physical properties of C_3N_4 will be reported in present paper.

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Structure of Liquid Water up to 6.5 GPa and 672 K

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The local structure of liquid water has been and still is the subject of discussion [1 and references therein]: (i) many of the theoretical concepts of water base upon two-state models, (ii) local inhomogeneities in the liquid phase have been proposed and (iii) the relationship between the amorphous ice phases and the liquid remains unclear. We have extended the pressure range of previous diffraction studies by more than a factor four. Our study along the melting line of ice VII reveals pronounced structural changes induced by pressure. We discuss details on the experimental aspects [2] and on the method of *Empirical Potential Structural Refinement* (EPSR) [3], which allowed us to extract partial and angular averages from a single neutron scattering experiment without isotope substitution. Our experimental findings are compared to classical and *ab-initio* molecular dynamics calculations [4] and preliminary conclusions are drawn.

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High-pressure High-temperature liquid carbon dioxide

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Carbon dioxide is a simple system widely studied because of its importance in life and geological sciences. Despite its simplicity, it shows several high-pressure polymorphs quenchable at room temperature and its phase diagram isn't still fully characterized especially at high temperature [1,2,3,4]. This work deals more specifically with the properties of liquid carbon dioxide at high pressure and high temperature. We have measured the melting curve separating the liquid from phase I (the dry-ice cubic structure) from 300 to 800 K by visually monitoring the solid/fluid equilibrium inside a diamond anvil cell and identifying the solid phase by Raman scattering. Our data are in good agreement with those from Bridgman to 366 K[5] but deviate from the work of Grace and Kennedy [6] for temperatures greater than 370 K. The only recently measured melting point by Iota and Yoo [1] is in fact well inside the liquid domain. We also redetermined the I-IV transition line and found it quite different from the one of Ref. [1], whereas consistent with the melting curve data. Brillouin scattering and refractive index measurements have been performed on the high-temperature liquid in order to obtain the sound velocity along several isotherms and then to calculate the equation of state of liquid CO_2 to 8 GPa and 700 K.

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New High P-T Phase Diagram of Oxygen

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High *P*-*T* Raman measurements and optical observations of solid and fluid oxygen in the 300-1250 K and 8-25 GPa range led to discover a new molecular phase η and strikingly unusual behavior of the melting curve. Three triple points were also identified along the *P*-*T* phase boundaries of the new phase. The direct measurement of the melting curve greatly extends previous optical investigations. We find the melting temperature is much higher than that inferred from the existing phase diagram (e.g., 400 K higher at 25 GPa). Measurements in the vibron and in the lattice frequency regions reveal the extent of orientational order disorder and persistence of strong intermolecular interactions in the high *P*-*T* phases [1].

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High-Pressure High-Temperature Amorphous Ice.

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Properties of H_2O at elevated pressure and temperature are of fundamental importance in both condense matter physics and planetary sciences. The pressure-temperature phase diagram of water ices is extremely complex and various solids forms of H_2O have been and still are the subject of intense experimental and theoretical investigations. Ice Ih is the first system which was observed to amorphize under pressure. Several glassy and amorphous ices (including low-density (LDA) and high-density (HDA) amorphous forms) were observed to exist metastably at pressures below ~1.5 GPa and low temperatures. We studied behaviour of H_2O in externally heated diamond anvil cells (DACs) at pressures up to 50 GPa and temperatures to 1150 K combining visual observations, Raman spectroscopy, and X-ray powder diffraction. Above 30 GPa and 950 K, using visual observations and Raman spectroscopy we found an X-ray amorphous phase clearly distinct from liquid water. The new material reversibly transforms to Ice VII and can be obtained on cooling or compression of liquid water suggesting that the high-pressure high-temperature amorphous phase may be thermodynamically stable.

Dynamic ionization and superionic state of water under extreme conditions

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The behavior of water at extreme conditions of pressure and temperature is of profound importance to the planetary and geosciences, fundamental chemistry, environmental science, and biology. A superionic phase has been theoretically predicted above 20 GPa and at 2000 K [1], but has not been confirmed in more recent calculations [2]. Experimental studies include shock wave data to 26 GPa [3] and observations of the melting line up to 90 GPa [4-6], but no in situ characterization of water at extreme conditions is reported above 22 GPa.

Raman spectroscopy in a laser heated diamond anvil cell and first principles molecular dynamics (MD) simulations have been used to study water in the temperature range to 1500 K and at pressures to 56 GPa. We find a substantial decrease in intensity of the O-H stretch mode in the liquid phase with pressure and a change in slope of the melting line at 47 GPa and 1000 K. In agreement with these observations, theoretical calculations show that water beyond 50 GPa consists of very short lived (<10 fs) H_2O, H_3O^+ and O^{2-} species and that the mobility of the oxygen ions decreases abruptly with pressure, while hydrogen ions remain very mobile. We suggest that this regime corresponds to a superionic state, while water above the melting curve is dynamically ionized.

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Observation of metallic helium: Equation of state and transport measurements under astrophysical conditions.

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The equation of state and opacity of warm dense helium ($1 < \rho < 10$ g/cm^3, $0.5 < T < 5$ eV) is essential for addressing a variety of astrophysical problems, such as the cooling rate of white dwarfs or the miscibility of H/He in the interior of giant planets. High-pressure experimental data on dense helium are sparse, and in particular none exist in the region of direct astrophysical relevance: models used by the astrophysical community have been calibrated on a small number of gas-gun measurements much below 1 g/cm^3 [1]. It has recently been shown that by coupling static- and dynamic-compression techniques, it is becoming feasible to recreate the conditions of giant planetary interiors in laboratory [2]. We present accurate pressure, temperature, density, and reflectivity measurements of helium using quartz as a reference material for impedance matching. We compressed helium to over 1.2 g/cm^3, and reflectivity data at these conditions show that helium is not a clear dielectric fluid but reflects like a metal. The pressure for this transition is almost independent of temperature, as would be expected for pressure-induced ionisation, but it occurs at pressures 1-2 orders of magnitude lower than theoretically expected for the $T = 0$ K solid or fluid [3]. These measurements also have implications for the phase diagram of helium, including the presence of a maximum on the melting line or the existence of a plasma phase transition.

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New transformation of ice in aqueous RbCl solution to a high-pressure phase at low temperature

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In previous reports [1, 2], we found that the ice phase in aqueous LiCl solution (LiCl・$12H_2O$) transforms to an amorphous phase at 500 MPa, as in the case of pressure-induced amorphization of ice I_h to a high-density amorphous ice (HDA)[3], whereas that the ice phase in aqueous KCl solution transforms to a crystalline ice VII’ phase (the frozen-in disorder of ice VII) at 800 MPa. Since salts are considered to not dissolve interstitially in the ice lattice, it is very intriguing that the results show differences depending on the salts.

In this study, the changes in *in situ* Raman spectra of ice in aqueous RbCl solution (RbCl・$12H_2O$) have been measured as a function of pressure at liquid nitrogen temperature (77 K). Here we show that the ice in aqueous RbCl transforms to ice VII’ phase at 800 MPa. It is well known that the aqueous LiCl solution is a good glass former, but aqueous solutions of alkali halide, such as KCl, RbCl, etc., except for Li-salts, do not become amorphous state with a standard cooling rate of ～ 10^3 K/min [4]. Therefore, there might be tendencies that the aqueous salt solution to form a glassy state upon cooling becomes an amorphous phase on compression, while that the aqueous salt forming a crystalline state on cooling at a normal pressure transforms to a high-pressure crystalline ice phase, such as ice VII’.

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Infrared and X-ray Diffraction Study of Symmetric Hydrogen Bond Formation in the Methane Clathrate

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The recent study of the methane clathrate under pressure has revealed two new structures in addition to the well known structure I clathrate. The highest pressure structure resembles a filled ice lattice and is denoted MH-III. This structure has been shown to be stable to pressures near 50 GPa. The open structure and consequent high compressibility of this clathrate means a centro-symmetric hydrogen bonds could be obtained at lower pressures than are required for the stable ice ice VIII phase in the pressure range above 2 GPa. In this study, we carried out infrared studies at ambient and low temperatures on mixtures of H2O and D2O in order to characterize this formation the centro-symmetric hydrogen bond. These studies were complemented by detailed theoretical calculations of the behavior of the MH-III clathrate using ab initio techniques.

Pressure influence on magnetism in uranium intermetallics

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The complex evolution of 5f-electron magnetism within U intermetallics is controlled by interactions of the U 5f electrons with valence electrons of ligands. The 5f electron orbitals are extended in space and therefore their overlap with the neighboring U 5f-orbitals and the non-U ligand valence electron wave functions (yielding a considerable 5f-ligand hybridization). These mechanisms play a dual role in determining 5f-electron magnetism in U intermetallics. The only "clean" way how to control the interatomic distances is realized by external pressure acting on the studied material. Good knowledge of the compressibility, which is frequently anisotropic, is crucial for detailed microscopic interpretation of data. These aspects will be systematically demonstrated by experimental results available for several prominent representatives of the large family of U intermetallics. Special aspects of for different types of pressure experiments (hydrostatic pressure, uniaxial stress) will be also addressed. A more general scenario relating the electronic structure and the 5f-electron magnetism will be finally presented.

Pressure-Driven Orbital Reorientation and Band Gap Closure in Transition-Metal Perovskites

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Orbital ordering, fluctuation, and excitation phenomena in transition metal perovskites have been investigated in recent years both experimentally and theoretically. In this context, rare-earth titanates with three nearly degenerate $3d(t_{2g})$ orbitals, which are occupied by a single electron, have been of particular interest. We address here the question of how robust the orbital ordering is in $YTiO_3$, and show that it can be tuned by the application of hydrostatic pressure. By means of synchrotron x-ray powder diffraction we investigated the crystal structure of $YTiO_3$ up to 30 GPa. The evolution of the distortion of the TiO_6 octahedra indicates a pressure-driven spatial reorientation of the t_{2g} wavefunction at around 10 GPa. We will discuss this observation in comparison with experimental results on the related compounds $LaTiO_3$ and $LaMnO_3$. In addition to the structural aspects, we have investigated the pressure-induced charge delocalization and metallization in these three perovskites by synchrotron infrared micro-spectroscopy in the mid- and far-infrared spectral ranges. The optical band gap shift in $YTiO_3$ and $LaMnO_3$ under pressure was determined quantitatively. The combined results on the structural, orbital and electronic changes under pressure give new insight into the physics of these materials.

This work was performed in collaboration with Y.-L. Mathis, B. Gasharova, and D. Moss (ANKA, Karlsruhe, Germany); M. Amboage and M. Hanfland (ESRF, Grenoble, France); O. K. Mel'nikov and A. Ya. Shapiro (Russian Academy of Science, Moscow, Russia).

Tuning of superconductivity and magnetic order of heavy fermion $CePt_3Si$ by substitution and pressure

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$CePt_3Si$ is a novel unconventional superconductor (SC) which undergoes a transition into an antiferromagnetic ground state at T_N ~ 2.2 K and exhibits superconductivity below 0.75 K. $CePt_3Si$ crystallizes in the tetragonal structure P4mm which lacks a center of inversion. Large values of H_{c2}' ~ -8.5 T/K and $H_{c2}(0)$ ~ 5 T were derived, referring to Cooper pairs formed out of heavy quasi-particles. The mass enhancement originates from Kondo interactions with a characteristic temperature T_K ~ 8 K. $CePt_3Si$ follows the general features of correlated electron systems and can be arranged within the Kadowaki-Woods plot next to the unconventional SC UPt_3. NMR and µSR results show that both magnetic order and SC coexist on a microscopic scale without having spatial segregation of both phenomena. The absence of an inversion symmetry gives rise to a lifting of the degeneracy of electronic bands by spin-orbit coupling. As a consequence, the SC order parameter may have uncommon features as indicated from a very unique NMR relaxation rate $1/T_1$ and a linear temperature dependence of the penetration depth λ.

The aim of the present work is to trace the evolution of superconductivity and magnetic order upon the application of hydrostatic pressure; changes originated by hydrostatic pressure will be compared with results of measurements performed on substituted samples, where the exchange of elements, such as Si/Ge causes chemical pressure effects.

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Pressure-induced magnetic phase transitions in selected lanthanide and actinide compounds

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The ground state properties of *f* electron compounds depend critically on the competition between different interactions, whose balance can be strongly modified by an external perturbation, such as pressure, magnetic field or a change in the chemical composition. Pressure, in particular, offers a direct way of changing the interatomic distances without artificially altering the electronic structure of a compound. Its effect can be dramatic and have severe consequences on the electronic and magnetic properties of 4*f* and 5*f* systems, as will be shown by selected examples of Sm(4*f*) and U(5*f*)- based compounds. In the case of SmS, which is a divalent (and therefore non magnetic) semiconductor at ambient conditions, pressure induces first an isostructural transition to a semiconducting intermediate valent state (v~2.7), followed by the closure of the charge gap and the onset of long range magnetic order. On the contrary, in the Kondo insulator UNiSn, where the U(5*f*) moments are ordered at ambient conditions, pressure induces first a complete metallisation at ~9 GPa and then (~18 GPa) a collapse of the magnetic order. These results will be presented and discussed in the framework of theoretical models taking into account the competition between the RKKY exchange interaction, the Kondo effect and the degree of hybridisation of the *f* electrons with those of the outer shells.

Structural and vibrational properties on $CuFeS_2$ under pressure

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An insulator-metal transition is one of the interesting properties in strongly correlated electron systems. At ambient pressure, $CuFeS_2$ is an antiferromagnetic semiconductor. As indicated by high-pressure resistivity measurements at room temperature [1], it undergoes the insulator-metal transition at 6.5 GPa with increasing pressure. Furthermore, the antiferromagnetic order disappears at this transition [2].

In the present study, we have measured X-ray diffraction and ^{57}Fe nuclear resonant inelastic scattering (NRIS) of $CuFeS_2$ under pressure using synchrotron radiation at SPring-8. The X-ray diffraction data were collected at room temperature with angle-dispersive techniques and an image-plate detector on BL10XU. For ^{57}Fe NRIS, the pulsed synchrotron radiation was monochromatized by the high-resolution monochromator on BL09XU. The ^{57}Fe NRIS spectra were measured by tuning the highly monochromatized X-ray beam in an energy range of about 60 meV.

Since a halo-like pattern is observed in the X-ray diffraction data above 7.1 GPa, $CuFeS_2$ undergoes a pressure-induced crystal-amorphous transition. ^{57}Fe NRIS spectra under pressure consist of large center peaks originating from elastic scattering and sidebands resulting from inelastic scattering with the annihilation and creation of phonons. The inelastic components in the spectra extract lead to the partial phonon densities of states (DOS) assuming a harmonic lattice model. There are three peaks at 10, 22 and 43 meV in the extracted partial phonon DOS below 5.5 GPa. The lowest peak originates from the acoustic phonon branches and other two peaks come from optical branches. Above 7 GPa, the acoustic and optical phonon branches are overlapped.

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Pressure-induced quantum instability in highly correlated f-electron systems

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There have been a lot of investigations about the instability of electronic state under high pressure in the highly correlated electron systems including 4f or 5f electrons. In the materials showing such properties, some physical quantities such as electrical resistivity, specific heat, magnetic susceptibility and so forth, show large deviations from the normal Fermi liquids(FL). These phenomena have been called as non Fermi liquid (NFL) properties, which is related to the instability of quantum electronic state or quantum phase transition(QPT). In the present work we will describe some examples mainly for the following materials, in which the NFL or FL state shows an instability to give rise to QPT under high pressure.

(1) $CeAl_3$:

This material is considered as a prototype of heavy Fermion, in which a large value of Sommerfeld coefficient and large value of T^2 term in the electrical resistivity have been found. These properties are affected significantly by applying high pressure. At high pressure around 10 GPa, this compound shows a crossover in the electronic state from HF to normal metal or intermediate valence state.

(2)$Y_{0.8}U_{0.2}$ Pd_3:

This has been well known as a typical example of NFL. The effect of pressure has been investigated by many authors below 2 GPa. Recently we found that this NFL state is unstable and the FL state is recovered at high pressure of about 6 GPa. We suggest that this transition is a kind of QPT induced by high pressure.

Other examples showing interesting electronic properties under high pressure will be briefly introduced for the materials including f electrons.

Pressure Stimulated Charge-Crossover in Transition-Metal Oxides and Hydroxides

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Mössbauer spectroscopy, x-ray diffraction (XRD), and electrical resistance (R(P,T)) studies were applied to investigate the high properties of the Mott insulator antiferromagnetic layered $Fe(OH)_2$ and $CuFeO_2$. In $Fe(OH)_2$ an unforeseen process by which a gradual Fe^{2+} oxidation takes place, starting at ~8 GPa reaching 70% Fe^{3+}-abundance at 40 GPa. Based on XRD and R(P,T) data it is unequivocally concluded that this non-reversible process, $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$, results in Fe^{2+} converting into Fe^{3+} with no structural transition. The "ousted" electrons form a deep band within the $Fe(OH)_2$ high-pressure electronic-manifold becoming weakly-localized at P > 50 GPa. This process is attributed to an effective ionization potential created by the pressure-induced orientation deformed $(OH)^{-1}$ dipoles and the unusual small binding energy of the valence electron in $Fe^{2+}(OH)_2$.

Magnetic properties of the 2D spin-frustrated $CuFeO_2$ delafossite have been studied up to 100 GPa. The partially disordered spin arrangement at ambient pressure in the 11 – 16 K range, transforms with pressure to a long-range ordered "5-sublattice" phase with a distinct T_N, a similar role played by external magnetic field in neutron studies. This phase gradually substitutes for the "4-sublattice" magnetic ground state present at ambient pressure, reaching 100% at 19 GPa. The twofold increase of T_N at 19 GPa is explained in terms of the unusual increase of the intra-planar direct exchange $J_{||}$ caused by the anomalous anisotropic compression of $CuFeO_2$ in which *c/a* increases with pressure. With further pressure increase at ~ 30 GPa, about half of the Fe^{3+} and Cu^{1+} ions undergo a *reduction-oxidation*1 transition: $\left(Fe^{3+}, Cu^{1+}\right) \xrightarrow{P} \left(Fe^{2+}, Cu^{2+}\right)$ explained by pressure-induced *band overlap*. New magnetic sublattices are formed composed of $Fe^{2+}(S=2)$ and $Cu^{2+}(S=1/2)$ enhancing dramatically the T_N. At 50 GPa both Fe ions undergo a spin transition and finally at 80 GPa a *Mott* transition into a metallic state takes place.

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High pressure transport and AC calorimetric studies of some correlated electron systems

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Some recent results are presented:

1) For the first time, the specific-heat anomaly in the overdoped range of a single crystal of the high-temperature superconductor $YBa_2Cu_3O_7$ has been studied under high pressure, up to 10 GPa, using AC calorimetry. The evolution of the specific-heat jump, as well as the bulk T_c, are consistent with a pressure-induced increase of the charge-carrier concentration n_h by about 0.02.

2) The pressure range of the non-Fermi liquid (NFL) region of MnSi has been investigated by resistivity. In contrast with predictions of the current model, the exponent n=3/2 is stable from p_c = 1.46 GPa up to 4.5 GPa and even at 8 GPa, the Fermi liquid relationship $\rho = AT^n$ with n=2 was not still recovered.

3) For the element Fe, NFL behaviour as revealed by resistivity variation with n=5/3 extends above the entire spin-mediated superconducting region. [1] At p = 31 GPa, where T_c vanishes, the A coefficient has decreased by around 50%, indicating a threshold value of A for superconductivity.

4) The high pressure superconductivity of $CeCu_2Si_2$ can be understood via an attractive interaction driven by charge fluctuations around a first order transition, with a critical endpoint at sufficiently low temperature. [1] It is noteworthy that superconductivity can develop despite huge residual resistivities, of the order of the Ioffe-Regel limit.

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Nanocarbon materials under high pressure

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Nanostructured carbon materials, namely fullerenes and carbon nanotubes, have produced significant excitement in the field of high pressure science in this decade. An important feature of this class of materials is that they have well defined nanostructures as well as free void formed in the assembled solids. These two features provide a large variety of freedom in properties of nanocarbon solids. In this paper, I will describe several peculiar aspects of high pressure behaviours, which are ascribed to the freedom in fullerene and carbon nanotube solids.

Pressure-induced intermolecular bond switching was discovered more than ten years ago, and this phenomenon produced a large variety of polymeric forms of fullerenes [1]. Nowadays, one-, two-, and three-dimensionaly polymerized C_{60} have been isolated, as well as dimers C_{120}. Furthermore, *in-situ* x-ray diffraction experiments uncovered the reaction process from the two-dimensional tetragonal polymer of C_{60} to a three-dimensional polymer *via.* a first-order irreversible transformation at P = 24 GPa [2].

Intercalated fullerides also display rich variety of phase transitions at high pressure. Particularly, the covalent bonds between intercalated metals and carbon atoms cause unique structural changes in rare earth doped fullerides. A pressure-induced orientational transition associated with the change of bonding nature will be presented in the rare-earth doped fullerides $Sm_{2.7}C_{70}$ [3].

Finally, the high pressure behaviour of double walled carbon nanotubes (DWNT) is reported. A Raman experiment showed that the outer tubes act as a protection shield of pressure for the inner tubes, whereas the latter increase the structural stability of the outer tubes upon pressure application [4].

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Behavior of Structural Metastability in Nanocrystalline FeS

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Iron sulfide (FeS) has attracted great interest in recent years because it is an important material for the Earth and space science. Nanocrystalline FeS coated with polyvinyl alcohol (PVA) is prepared from $FeCl_2$ and Na_2S aqueous solution via the chemical precipitation synthesis process. We find that crystal structure of nanocrystalline FeS prepared by this method is similar to the high-pressure phase of its bulk materials at high pressure around 6 GPa. This phenomenon can be explained by comparing the energetic height of nanocrystalline FeS in microcosmic mechanisms with that of bulk material. And energetic height in transition pressure was influenced by crystal size. This suggests that nanocrystalline FeS has a metastable, high-energy structure.

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High pressure induced polymerization of C_{60} nanorod

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C_{60} is one of the most important member in the carbon family due to its unique structure. Linking nearest neighbor C_{60} in fcc lattice can lead to at least three polymerized crystal structures under high temperature and high pressure below 6 GPa, including orthorhombic (linear-chain), tetragonal and rhombohedral structures. As a novel material, one dimensional nanometer scale C_{60} nanorod has been attracted much attention. Synthesis of high crystalline C_{60} nanorod with various structures is a challenging topic in this field. So far, there is no report on C_{60} nanorod under high pressure.

In the present work, we report a simple solution- grown method for synthesis of C_{60} nanorod, characterized with AFM, TEM and Raman spectroscopy. The C_{60} nanorods were then polymerized under high pressure. Nanorods deposited on Mo or glass substrates were loaded into the pressure cell and were treated at different high pressure and high temperature over 1h. Teflon pressure cell contained internal ovens and several thermocouples for temperature measurement and pressure calibrator. low-viscosity silicone oil was used as pressure medium to ensure hydrostatic conditions. High pressure treated samples were characterized by Raman spectroscopy and AFM. The results indicate that C_{60} nanorods survived from high -pressure treatment. At pressure of 1.5 GPa and temperature of 573 K, C_{60} nanorod forms an orthorhombic polymeric structure; At 2 GPa and 700 K, C_{60} nanorod forms an tetragonal polymeric structure.

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PHYSICAL PROPERTIES OF CARBON NANOSTRUCTURES DERIVED FROM FULLERENE C_{70} AT HIGH PRESSURE

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It has been well established that application of high pressure to C_{60} at elevated temperatures results in formation of one-dimensional (1D) and two-dimensional (2D) polymeric structures comprised of covalently bonded buckyballs [1]. Nevertheless, numerous attempts to polymerize the next simplest fullerene, C_{70}, have generally been inconclusive and yielded only dimers (C_{140}) [2,3] until the polymer was finally synthesized at hydrostatic pressure in the form of zig-zag chains [4]. Here we present the results of a wide range of experimental studies (Raman, FTIR and NMR spectroscopy, thermal conductivity, high resolution dilatometry) of C_{140} and 1D polymeric C_{70}. We show that the type of nanostructure (dimers vs. chains) formed during polymerization of C_{70} at high pressure strongly depends on the structural state of the source material. In a separate set of experiments dedicated to study of the kinetics of de-polymerization of C_{140} and 1D polymeric C_{70}, we revealed a tremendous difference in the relaxation times for the process in these systems which we tentatively associate with the difference in entropy change during de-polymerization.

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Superhard nanocluster-based materials synthesized from single wall nanotubes

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Results of structure and mechanical properties studies (Raman, TEM, X-ray, NanoScan) of different nanocluster-based materials synthesized from single wall carbon nanotubes (SWNT) with mean tube diameters 0.7, 0.9 and 1.2 nm are presented. Samples of SWNT were compressed in shear diamond anvil cell (SDAC) up to pressure 65 GPa. In SDAC controlled shear deformation is applied to the sample under pressure by a rotation of one of the anvils around an axis of load. The application of shear deformation decreases the hysteresis of phase transformations and makes it possible to obtain a homogeneous phase.

Two different types of phases have been studied. High-pressure phases synthesized at pressure above 35 GPa compose from cross-linked (by presumably sp^3 bonds) nanometer-sized graphene flakes. The cross-linked flakes create nanoclusters with size correlated to nanotube diameter. The flakes could create both linear and onion-like structures. The second type of phases synthesized at pressure 15 to 35 GPa are cross-linked nanotubes described earlier [1]. Pressure stability of nanotubes depends on nanotube diameter. Remarkable fact is that 1.2 nm diameter nanotubes still exist after pressure 40 GPa, while nanotubes of lesser diameter (0.7 and 0.9 nm) was not revealed in the samples structure after compressions (combined with shear deformation) to 35 GPa.

All the phases synthesized from SWNT have extremely high hardness comparable or even harder then c-BN. In present study hardness was measured using NanoScan measurement equipment. Obtained hardness measurement results agree well to previous data obtained with Nanoindentation System [1].

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Resonant Raman spectroscopy of single wall carbon nanotubes under pressure

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Due to their unique one dimensional structure carbon nanotubes are expected to stand up, through pressure application, strong geometrical changes that preserve their nanostructured character. This has motivated an important number of experimental investigations including compressibility[1], X-ray[2] and neutron diffraction[3], Raman spectroscopy[4], as well as an important number of theoretical works predicting pressure induced polygonization or ovalisation, including or not *sp*^{3} bonding between the tubes. In spite of these efforts, we are far from having a clear image of the exact nature of phase transitions taking place under pressure on carbon SWNT and of the shape changes associated. Motivated by these considerations, we take profit of the resonant selectivity of Raman spectroscopy to separately study the high pressure evolution of bundles of metallic and semiconducting carbon nanotubes of 1.3±0.2 nm in diameter, by working at two different excitation wavelengths. We perform Raman experiments on metallic (excitation wavelength 632.8 nm) and semiconducting (excitation wavelength 514.5 nm) single-wall carbon nanotubes up to 40 GPa[6] using Argon as pressure transmitting media. The effects of high pressure on Raman response of SWNT are discussed in the poster.

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20th AIRAPT and 43th EHPRG Meeting

The properties of nano BaTiO3 ceramics fabricated by high pressure

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Abstract

Barium titanate ($BaTiO_3$: BT) is one of the most extensively studied ferroelectric materials. It is well know that the successive phase transitions of $BaTiO_3$ bulk crystal occur at three temperatures in the near 403K (T_c), 298K ($T_{t\text{-}o}$) and 183K ($T_{o\text{-}r}$). Above the Curie temperature, the structure of $BaTiO_3$ is cubic and paraelectric. Below Tc, the structure is slightly distorted and three ferroelectric polymorphs appear continuously depending on temperature. It is generally observed that the phase transition temperature of $BaTiO_3$ crystal strongly depends on its grain size, and the T_c shifts to lower temperature, the $T_{t\text{-}o}$ and $T_{o\text{-}r}$ to higher temperature with reducing grain size. Since it is difficult to process the nanocrystalline powders into high quality dense bulk products that retain the original nanocrystalline grain size, the crystal structure of nanocrystalline $BaTiO_3$ ceramics is still a controversial topic.

By applying pressure during sintering, high density ceramics can be fabricated due to the pressure induced increase of the densification driving force. On the other hand, the growth rate is dramatically reduced under high pressure because of the decrease of diffusivity with pressure. So high pressure sintering can be an optimal approach to obtain nanocrystalline ceramics.

In this presentation, we report that high quality nano $BaTiO_3$ bulk of high density and homogeneous grain size could be prepared from the 10nm $BaTiO_3$ raw powder by using a specified high pressure sintering route, i.e. the three-step method. The obtained 28nm $BaTiO_3$ bulk retains original nanocrystalline grain size. X-ray diffraction pattern and Raman spectrum at various temperatures indicated that successive phase transitions certainly occurred in nano BaTiO3 ceramics.

Key words: $BaTiO_3$; High pressure; Nanocrystalline ceramics

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A theoretical study on high-pressure shifts of the R lines of Cr^{3+} ions in gallium garnets*

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The ground state of Cr^{3+} ions in gallium garnet crystals is the $^4A_2$ and the first excited state can be the $^4T_2$ or the ^2E depending on the crystal-field strength [1]. There exist the theoretical difficulties of the high-pressure shifts of the R lines ($^2E \to {}^4A_2$ transition) of Cr^{3+} ions in several gallium garnets, such as $Gd_3Sc_2Ga_3O_{12}$, $Gd_3Ga_5O_{12}$, $La_3Lu_2Ga_3O_{12}$ and so on [2]. From the standardized crystal-field theory, the energy of the ^2E level for this ion is as follows [3]

$$E(^2E) \approx 7.9B + 3.05C - 1.8B^2 / Dq$$

where *B* and *C* are the Racah parameters and *Dq* the crystal-field parameter. Obviously, the increase of the crystal field strength (i.e., *Dq*), due to the increase of the pressure, should lead to an increase of the energy of the ^2E level. However, the luminescence experiments for Cr^{3+} ions in above gallium garnets find that the measured R lines first increase, then level and finally decrease under pressure [2]. One assumes that it is due to an enhancement of the so-called nephelauxetic effect, which reduces the interelectronic repulsion described by *B* and *C* [2]. However, there is few of the quantitative study on this effect, to the best of my knowledge.

Recently a series of theoretical studies based on a molecular-orbital model well deals with the optical and magnetic experiments for Fe^{2+} and Cr^{2+} ions in semiconductors [4]. The molecular orbitals of the central transition metal ions in crystals are given by

$$\Psi_i = N_i(\phi_{di} - \sum_j \lambda_{ij}\chi_{ij})$$

where ϕ_{di} and χ_{ij} are the *d* orbitals of the central transition-metal ion and the appropriate symmetry orbitals of the ligands, respectively, λ_{ij} the admixture coefficients, N_i the normalization constants being dependent on the distance r between central ion and ligands. And the *B,C* and *Dq* are accordingly as

$$B_i = N_i{}^4 B,\ \ C_i = N_i{}^4 C,\ \ Dq_i = N_i{}^2 Dq.$$

One should note that in this model, the parameters B_i, C_i and Dq_i are dependent on r, i.e., not only Dq_i but also B_i, and C_i should change with the increase of the pressure, and this change of B and C is just the nephelauxetic effect expectancy. Adopting this model, the presently theoretical results are in agreement with the luminescence experiments [2]. This shows that a molecular-orbital model can well deal with the luminescence properties of Cr^{3+} ions in gallium garnets, and the model seems to take into account the contribution from the nephelauxetic effect at a different angle.

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Keywords: high-pressure spectroscopy; gallium garnets; Cr^{3+} ions; molecular-orbital model

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Stabilization under high oxygen pressures of unusual oxidation states of transition metals in perovskite lattice: a model for studying electronic phenomena through Mössbauer Spectroscopy

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High oxygen pressures is an important tool for stabilizing the highest oxidation states of transition metal M^{n+}.

When the formal oxidation state n+ increases the energy level of the d orbitals of M^{n+} decreases. Consequently the charge transfert phenomenon can take place ($M^{n+}\!-\!O \Leftrightarrow M^{(n-1)+}\!-\!O\underline{L}$, L being an electron hole on oxygen).

In the case of a anisotropic electronic configuration as high spin Fe^{4+} or low spin Ni^{3+} different electronic phenomena are induced: insulator→metal transition ($t_{2g}^{6}e_{g}^{1} \rightarrow t_{2g}^{6}\sigma^{*1}$), disproportionation ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$)…

Recent investigations underline that Mössbauer Spectroscopy can be a fruitful tool for studying such phenomena.

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Equation of state and pressure-induced polymorphism of $ZrSiO_4$

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In this contribution, we present the results of a combined experimental and theoretical investigation aimed to determine equation of state parameters and phase stability thermodynamic boundaries of $ZrSiO_4$ polymorphs. Experimental unit-cell data have been obtained for a powdered sample in a diamond-anvil cell using energy-dispersive synchrotron X-ray diffraction in the pressure range 0 – 47 GPa. Total energy calculations have been performed within the density functional theory at LDA and GGA levels using a plane wave-pseudopotential scheme. Our quantum-mechanical simulations explore the two observed tetragonal structures (zircon and scheelite) as well as other potential post-scheelite phases. We find a very good agreement between our experimental and calculated pressure-volume values for the low-pressure phase of $ZrSiO_4$ in terms of the bulk modulus and linear compressibilities. Our results also allow to clarify some of the discrepancies found in very recent theoretical and experimental studies. The zircon-scheelite thermodynamic phase transition is computed around 5 GPa. No other post-scheelite phase is found stable above this pressure though a decomposition into ZrO_2 (cottunite) and SiO_2 (stishovite) is predicted at about 6 GPa. These two transition pressure values are well below the experimental ranges detected in the laboratory, which is in concordance with the large hysteresis associated with these transformations. Under a martensitic perspective, we examine both a low symmetry (monoclinic) unit cell and a direct $I4_1/a$ pathway (due to the group-subgroup relationship between zircon and scheelite structures) to describe the transition phase mechanism. A preliminary evaluation of the Gibbs energy profile along these transition paths is also reported.

Structure, stability, and electron density of Al lattices in the light of the model of anions in metallic matrices

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The model of anions in metallic matrices is a new interpretative tool of the structure and bonding of inorganic crystals under both normal and extreme conditions. In this model, the metallic sub-lattice of the solid plays an essential role as it is considered to be the building block of the crystal, the formation and the positions of the anions in the lattice being driven by the electronic and geometrical structure of the metallic matrix. The crystalline bonding is described in terms of metallic atoms that transfer their valence electrons to inter-metallic positions inducing the localization of the non-metallic species and the subsequent formation of anions at those sites. The non-metallic element localizes the electron density enhancing its value with respect to the pure metal and, thus, the anions act as chemical pressure agents. The model provides a rational explanation of the particular structures shown by crystalline solids covering the limitations of the traditional view. Taking the metallic sub-lattices of AlX_3 (X = F, Cl, OH) crystals as illustrative examples, we aim to provide a theoretical interpretation of the model of anions in metallic matrices and, in particular, of the link between chemical and hydrostatic pressures. To this end we have carried out accurate quantum-mechanical calculations within the framework of the density functional approximation, as implemented in standard solid state computational packages. We present the results of: (i) energy-volume curves, (ii) pressure effects on elastic constants, and (iii) analysis of the electron density within the formalism of the atoms in molecules theory of both the pure lattices and the compounds. Equations of state parameters and stability conditions are determined for cubic, rhombohedral, hexagonal and monoclinic Al structures. The bonding features and the electron charge localization in the Al lattices is discussed in relation with the positions of the X atoms in AlX_3 crystals. Overall, we found a successful application of the model of anions in metallic matrices in these compounds.

First-principles study of the modulated structure of solid iodine in the phase-V

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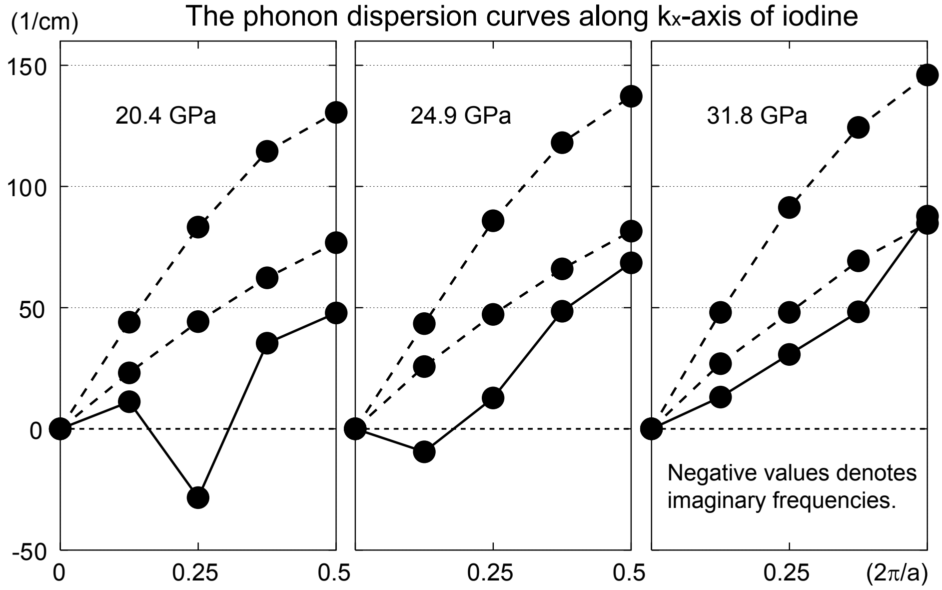
A new phase (phase-V) found by Takemura et al.[1] in the pressure range from 23 GPa to 30 GPa is studied through the phonon properties by means of the density functional theory (DFT) with the pseudopotential and plane wave basis[2]. Experimentally, an incommensurately modulated structure of the FCO and the pressure dependent modulation wave vector has been reported for this phase.

Our phonon calculations show that the FCO iodine is unstable with respect to the atomic displacements with a particular modulation wave vector in the pressure region of the phase-V. The amplitude of the modulation agrees well with the experiments. The pressure dependence of the unstable modulation wave vector is also in conformity with the experimental results. We find also that the similar instabilities appear in solid bromine and chlorine under high pressure.



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Pressure induced Superconductivity in Iodine

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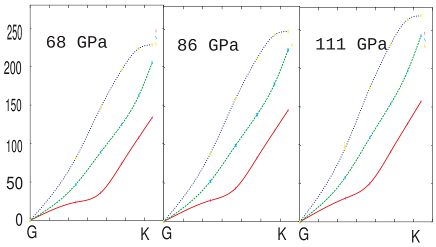
The superconducting transition temperature of Iodine in the FCC phase is calculated using *ab initio* methods based on the density functional theory, in which the lattice dynamics is carefully analyzed and some phonon softening is found near the Gamma point.(Fig. 1) In our study, we used the packaged codes FP-LMTO and ABINIT. The calculated T_cs are much higher than those reported earlier[1] and in the range of the experimental values[2]. The higher T_c values in the present study partly comes from the soft phonon modes near the Gamma point.(Fig.2) The pressure dependence of the T_c, however, still contradicts very recent experimental results[3] in the pressure region from 68GPa to 111GPa.(Fig.3)



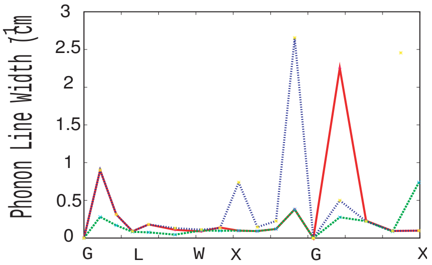


Fig.1 Phonon Softening along the sigma line (Frequencies in cm^{-1})

Fig. 2 Phonon line width at 68 GPa (in cm^{-1})

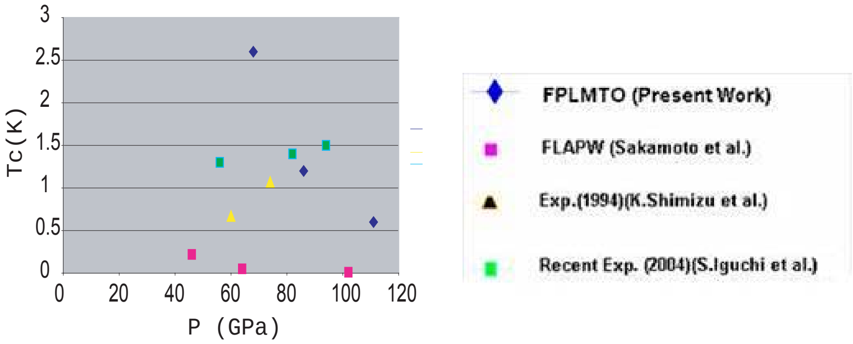


Fig. 3 Comparison of T_cs

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Equation of state experiments using directly laser-driven terapascal shocks

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Abstract

In this report, some studies about laser equation of state (EOS) have been presented, which were carried out on SG-Ⅱfacility recently. After the parameters of lens-array (LA) used in beam smoothing were optimized, which based on the character of the near-field distribution of SG-Ⅱlaser beam, the spatial uniformity of the output laser on the target surface became more and more better, and then a good planar shockwave in target could be formed, moreover the region of shock planarity was about 650~750 μm. The wedged-target experiments indicated that the shockwave was steady enough during the target thickness range in which the shock velocity measured. On this base, the shock adiabat of copper and aluminum was measured experimentally with the targets of Al-Cu impedance-match and Cu-Al impedance-anti-match respectively. The targets consisting of a base, with steps of a known EOS material and of the materials of unknown EOS were irradiated by one beam ~300J, 0.53μm wavelength, 1ns near-trapezoid laser pulse from the SG-Ⅱ facility. Optical streak camera monitored emission while shock breakout from the base and steps rear surface and shock velocities were calculated from the transit times across the known-height steps. The obtained data which the pressure were up to 2 TPa agreed with that got from chemical explosive, gas gun, and underground nuclear test, etc.

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Thermodynamic Regularities in Compressed Liquids

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This work analyse the behaviour of several thermodynamic properties: the thermal expansion coefficient (α_p), the isothermal compressibility (κ_T), the reduced bulk modulus (B), and the isobaric heat capacity (C_p), for a great number of liquids at high pressures. The thermodynamic behaviour of the liquid state is by far the most difficult to understand and to predict, due to the inherent complexity of this state of matter and the diversity of molecular interactions. More often than would be desirable, the pressure and temperature dependencies of the derived properties are imposed by the algebraic form of the equation of state (EOS), resulting in a severe lost of information contained in the original results. The analysis of EOS models in terms of derived properties such as α_p or κ_T has interesting advantages, since both are related to the first derivatives of the (p,V,T) equation of state, and both can be accurately measured over wide ranges of pressure and temperature with several experimental techniques [1]. Recently, we have analysed the pressure behaviour of the α_p isotherms for a number of different liquids [2].

The aim of this work is therefore to analyse the behaviour of the thermophysical properties at high pressures for a number of liquids of different nature. The liquids included into our analysis have been selected to meet two criteria: 1) available experimental data over wide ranges of pressure and temperature (from the melting point up to the critical point), and 2) liquids composed of molecules with different geometries and interactions. The obtained results provide us insight in developing equations of state models.

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Ab initio Study of the Pressure-induced Isostructural Phase Transition in Osmium

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Recently, Occelli *et al.* [1] performed the accurate measurement of the equation of states (EOS) of Os to 75 GPa using angle-dispersive x-ray diffraction. A discontinuity in the first pressure derivative of the c/a ratio around 25 GPa was identified, signalling an electronic topological transition (ETT) in this pressure range. They suggested that the energy band of Os at high-symmetry L point might drop below to Fermi level, resulting in a topological singularity of Fermi surface, thus it is responsible for the observed ETT.

In this work, the EOS, electronic bandstructure, Fermi surface, and lattice dynamics of Os have been studied as a function of pressure by *ab initio* calculations. The current theoretical study reproduced successfully the experimentally observed anomaly in c/a ratio around 25 GPa. Analysis of the calculated results of the electronic bandstructure and Fermi surface with pressure, it was concluded that the energy band at high-symmetry L point doesn't drop below to Fermi Level up to 80 GPa under study. Therefore, we eliminated the L-point driven mechanism of this ETT proposed by Occelli *et al.* [1]. Lattice dynamical calculations showed that the phonon frequencies for optical and acoustic modes increased with increasing pressure. No softening phonons were observed in the pressure range around 25GPa, where ETT is expected to occur. A more detailed study is needed to further probe the mechanism of the ETT in Os.

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Equation of State for Vanadium under Hydrostatic Conditions

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The pressure dependence of the superconducting transition temperature T_C of vanadium (V) has been investigated in several works. Ishizuka et al [1] observed characteristic behavior of T_C. The value of T_C is 5.3 K at atmospheric pressure and linearly increases with pressure. It reaches 17.2 K at 120 GPa. With further increase in pressure from 120 to 150 GPa, T_C approaches a constant value [1]. The crystal structure of V is reported to be *bcc* from ambient pressure up to 150 GPa [2]. First-principles calculation predicts a structural transition around the pressure [3].

In order to study the structural stability of the *bcc* phase at ultrahigh pressures, we have performed angle-dispersive powder x-ray diffraction experiments up to 214 GPa at room temperature at the Photon Factory, KEK. Helium was used as a pressure medium up to 60 GPa. Pressures were determined on the basis of the ruby pressure scale. For pressures above 100 GPa no pressure medium was used. Pressures were determined by the equation of state of Pt in this case.

The *bcc* phase was stable up to 214 GPa without any transition. The bulk modulus and its pressure derivative were obtained by fitting the present data to the Birch-Murnaghan equation of state. We will discuss the comparison of the equation of state for the same group element niobium.

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Mechanical Behavior of Diluted Magnetic Semiconductors under high compression

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We have investigated the pressure dependence of mechanical properties of some diluted magnetic semiconductors. Under high pressure, these systems undergo a structural phase transformations from its original rocksalt (B1) type phase to the most stable CsCl (B2) type structure. For the present investigation, a Three Body potential (TBP) approach [1], consists of long range modified Coulomb and three body forces and short range van der Waals and Hafmeister Flygare type overlap repulsive interactions, has been. In the present study the effect of van der Waals as well as three body forces have been analysed separately, which shows that the variations of second order elastic constants [2] C_{11} and C_{12} as a function of pressure shows almost similar trend where as C_{44} opposite to them. The role of Mn on variations of C11, C12 and C44 has also been observed before and after the phase transitions.

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Bulk modulus of Os by experiments and first-principles calculations

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Cynn *et al*. [1] performed powder x-ray diffraction experiments on osmium, and reported that the bulk modulus of Os is 462 GPa, exceeding the value for diamond (443 GPa). Since such a high value of bulk modulus is uncommon for metals, the report stimulated further experimental and theoretical studies. Takemura [2] carried out powder x-ray diffraction experiments on Os by using a helium pressure medium, which offers excellent quasihydrostatic conditions. By fitting the Birch-Murnaghan equation of state to the pressure-volume data, the bulk modulus of Os was determined to be 395(15) GPa, which is smaller than that for diamond [2]. It should be noted that Cynn *et al*. used argon as a pressure medium, which is known to develop sizable nonhydrostatic stress at high pressures. Independent powder x-ray diffraction experiments by Occelli *et al*. [3], also with the He-pressure medium, gave a value of 411(6) GPa, similar to the result by Takemura.

Early first-principles calculation by Joshi *et al*. [4] yielded comparable values of bulk modulus both for Os and diamond. More recent calculation by Hebbache and Zemzemi [5], on the other hand, suggests that the bulk modulus for Os is larger than that for diamond, at least at small compression. We have computed electronic structures of Os by FLAPW method. We compare calculated bulk modulus with all the experimental and theoretical ones, and discuss how we can understand the discrepancy.

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Effects of Pressure on the Electronic Spectra of Cyano-anthracene and related molecules

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This theoretical study investigates the effect of pressure on 4-(10-cyano-9-anthracenylmethyl)-N, N-dimethylanaline and similar molecules to understand how electron transfer processes can be modified under extreme conditions. The current study combines classical molecular dynamics simulations with quantum calculations to characterize the role of charge transfer and electronic level crossings that can be induced by application of pressure. Molecular dynamics is used to predict the change of molecular conformation defined by the change of the angle between the cyano group and the carbon atom on the anthracene component. The pressure effect on charge transfer states is also predicted for this set of molecules.

ON KINETIC COEFFICIENTS OF SOLID AN A RAGION PHASE TRANSITIONS

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Polymorphous and superconductive transitions in solids tape place in the finite interval of temperature and pressure. In a region of transformation at a fixation of external conditions there is quickly established the stable metastable state, where both phase co-exist and the substance may be considered as two component system. A variant of approximation of the effective medium is used for mathematic description of phase transitions according to data for kinetic coefficients (an application of this method is possible far from the percolation threshold) and percolation theory, which in asymptotically precise. One supposes the coefficients taking into account a configuration of dielectric (low conductive) phase 1 and metallic (high conductive) phase 2, are different for different phase and depend upon a transformation degree. There is used the threshold value ν_c=0.17, at which an infinitely extended region of the space is appeared to be available for infinite movement of charge carriers and critical exponents of electrical conductivity t=1.7, ν is relative volume fraction of phase 2. It is obtained correlations correspondingly bound effective values of the specific resistanceρ, thermal conductivity λ, thermal electric power Q from ν and relations of kinetic coefficients in low and high conductive phases. The relative volume fractions of phases, effective value ρ_c at $\nu=\nu_c$, critical index t for $0<\rho_2/\rho_1\leq 1$ are estimated. In particular, on the dielectric side $\rho_c/\rho_1 \cong 0.22\sqrt{\alpha}$ at $0\leq\rho_2/\rho_1<0.1$. The pressure P=P$_c$, where $\nu=\nu_c$, is offered to define as a pressure the phase transition. There are analyzed the experimental data for dependency of electrical and thermal conductivity, and thermal electric power in high temperature superconductors (HTSC) $YBa_2Cu_3O_x$ and in semiconductors n-InAs and n-GaAs in the transformation region. A phase composition is calculated in HTSC on temperature dependence λ(T) below the critical temperature, where ρ=Q=0. The volume fraction of superconductive phase increases in the neighborhood of transition threshold by ~10% at pressure rise from atmospheric to 1 GPa and dT_c/dP=0.3 K/GPa).

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Molecular dynamic program for simulation of molecular nitrogen N_2 properties under high pressure

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Molecular dynamic simulation program has been developed which can be used to model the static and dynamic properties of molecular nitrogen (N_2) under high pressure. The dynamics of the N_2 molecules accounts precisely both translational and rotational degrees of freedom. The rotational motion of the N_2 molecule is approximated assuming constant moment of inertia of the nitrogen molecule.

The program fully accounts anisotropic N_2-N_2 interaction potential. N_2-N_2 interaction potential has been based on the results of high precision Hartree-Fock ab initio quantum mechanical calculations of van der Avoird et al [1]. The seven parameter potential form, fully accounting rotational symmetry of the N_2-N_2, using 6-j Wigner symbol, thus preserving full rotational symmetry of the system, was used [1].

Various numerical algorithms were tested, with respect to energy preservation during the simulation. It has been shown that Verlet algorithm was not preserving the energy for the standard timestep, equal 5 $*10^{-16}$ s. Runge-Kutta fourth order method was able to preserve the energy within 10^{-4} relative error, but it requires calculation of the force four time for the timestep and therefore it is inefficient. A predictor-corrector method of the 4th order was found to be efficient and precise [2] and was therefore adopted for the simulation of the molecular nitrogen properties at high pressure.

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Ab initio calculations of a new phase of Fe_5Si_3 with the structure of cations in the garnet $Fe_5Si_3O_{12}$

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Iron silicides have interest because its promising optoelectronic applications. From a geological point of view they have also interest because they are considered as important components of the outer core. Finally, from a crystallochemical point of view, these phases have interest because some of them produce oxides in which the Fe:Si stoichiometry is maintained. This is the case of Fe_5Si_3 which, by oxidation, produces the garnet $Fe_5Si_3O_{12}$ whose Fe_5Si_3 subarray differs from that of the alloy itself. As in some cases, the cation array of the oxides reproduces the structure of high pressure phases of the alloy [1-3], it may be possible that at high pressure, the Fe_5Si_3 alloy could undergo a phase transition to a structure, which may reproduce that of the cation array in the garnet. Previous experimental studies up to 30 GPa showed no structural change [4]. For this reason we have undertaken the present theoretical study, to see whether the the structure of the cation array in the garnet might be a stable one for the Fe_5Si_3 alloy.

The study has been carried out theoretically by means of *ab initio* total energy calculations in the framework of the density functional theory, (DFT). The theoretical results reproduce very well the structural parameters and the equation of state (EOS) of the low pressure phase. We also study the relative stability of different structures candidates to the high pressure phase. The results presented here indicate that this is a plausible structure for the high pressure phase of iron silicide and provide a new example of the equivalence between oxidation and pressure.

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Multi-Phase Equation of State for Water at High Pressures and Temperatures

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A thermodynamically complete model of semiempirical equation of state for matter with taking into account the polymorphic phase transformations, melting, evaporation, dissociation and ionization effects is proposed. Equation of state for water is constructed on the basis of the model developed, and calculations of thermodynamic characteristics of the ice, water and steam phases over a wide range of temperatures and pressures are carried out. The critical analysis of calculated results in comparison with a set of available static and shock-wave experimental data is made. The resulting multi-phase equation of state in a tabular form can be employed effectively in numerical simulations of hydrodynamic processes in matter under extreme conditions of high pressures and temperatures.

An Am IV type structure in plutonium at high pressure

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The ambient temperature α-phase of plutonium metal has a monoclinic structure with 16 atoms in a cell of space group $P2_1/m$. On heating to its melting point of 913 K, it exhibits five more phases. However, under high pressure, only one phase transition has been reported in literature. Akela et al alluded to a monoclinic to hcp transition under pressure in a publication in 1988 [High Pressure Res.1 (1988) 91]. However, Dabos et al [J.Alloys Compd.190 (1993) 237], in a study up to 62 GPa, showed that α – Pu transforms at 37 GPa to a hexagonal structure in space group $P6_3/m$ with Z=8.But the total energy calculations, using the full-potential linearized-augmented-plane-wave (FPLAPW) method by Penicaud [J.Phys:Codens.Matter 14 (2002) 3575], show that the total energy of this phase is always higher than that of the α-phase and instead suggests under pressure a sequence: α- Pu → Am IV → bcc. Am IV is a four atom distorted α – U structure occurring in elemental Am at 16 GPa. I have reinterpret the data of Dabos et al and find that indeed Am IV (Pnma) cell is the correct structural description for the high pressure phase in Pu The structures of both the high pressure Am IV type phase and α-Pu ,the 0.1 MPa phase, are shown to have a distorted hcp topology along their b-axis and only small movements of atom will be needed to bring about the transformation between the two structures. The upturn in the atomic volume of Pu at 0.1 MPa can also be rationalized on the basis of this proposal

Exploring the structure of the P-IV phase for phosphorus by using metadynamics

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We have theoretically explored the structure of the intermediate phase of phosphorus P-IV, which is the most stable in the pressure range from 107 to 137 GPa [1], by using the first-principles metadynamics simulation [2,3]. In spite of the small simulation cell, we obtained a new structure at 120 GPa starting from the simple cubic structure. We performed a simulation determining the X-ray diffraction pattern of the obtained structure, for which relative positions of large peaks of roughly accord with those of experimental result. (Fig. 1)

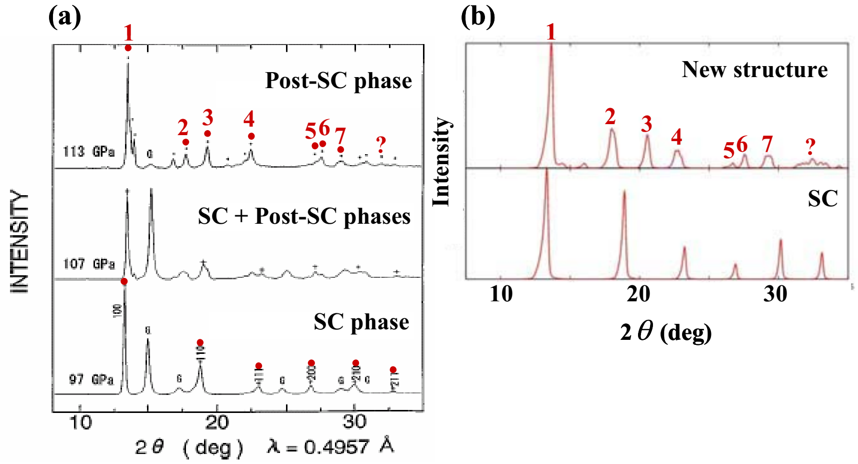

Fig. 1. The comparison of (a) experimental x-ray diffraction patterns [1] for the simple cubic structure (SC) and the structure of the phase P-IV (Post-SC phase) with (b) simulational x-ray diffraction patterns (RIETAN2000) for SC and the new structure.

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Hugoniot Anomaly in ZnS : A Theoretical Study

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In dynamic high pressure measurements upto 135 GPa, Uchino et al. (J.Phys. Chem. Solids 60, 827, 1999) observe anomaly in the Hugoniot behaviour of ZnS between 75 to 99 GPa and associate it with melting and decomposition. In their static high pressure study upto 96 GPa, Desgreniers et al. (Phy.Rev.B 61, 8726, 2000), report the existence of diffraction lines apart from those of rocksalt structure from 65 GPa onwards, after the initial structural transition from zinc blende (B3) to rock salt (B1) structure in ZnS. Emergence of prominent peaks corresponding to Cmcm structure were observed at 96 GPa, however, the authors could not estimate the atomic positions of the Cmcm phase due to lack of sufficient data.

In the present study we have analysed the cause of this anomaly in the Hugoniot of ZnS using FP-LAPW method within Generalised Gradient Approx. Also, analysed is the stability of its various phases and computed the amount of distortion in the cell and atomic positions of rocksalt phase leading to Cmcm phase, at 96 GPa.

We find the B3 to B1 phase change around 16 GPa in agreement with recent pseudopotential calculations of Lopez-solano et al (Phys. Stat. Sol. (b), 235, 452, (2003)) and Qteish and Munoz (Phys. Stat. Sol. (b), 223, 417(2001)), and various experimental studies. Our calculations at 96 GPa for the Cmcm phase at various values of b/a and fractional co-ordinates show that the energy of the Cmcm phase with b/a = 1.015 and atomic positions (0, 0.7 (Zn), 0.25) and (0, 0.2 (S), 0.25) is minimum and is even lower than that of the rocksalt phase, in agreement with Desgreniers et al. The value of K_0 (K_0 ‘) for the B3 and B1 phase is determined to be 71.26 (4.32) and 87.17GPa (4.32), respectively.

Our temperature estimate from the calculated P-V isotherm and the Gruinesen ‘γ ’ derived from it, is around 4350K at 75 GPa. Moreover, from the pseudopotential calculation of Lopez-solano et al, there is no discernible change in the curvature of P-V curve around B1 to Cmcm phase change, implying hugoniot anomaly may not be associated with structural transition. Hence, we agree with Uchino et. al. that the shock anomaly in ZnS (T_m = 2100) above 75 GPa could be due to melting and/ or decomposition under shock conditions.

Ab initio Total Energy and Phonon Calculations of hcp Co up to 250 GPa Pressure

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Cobalt being the metal following iron in the periodic table, is potentially important for the properties of the earth's core which is believed to be composed of iron dominated alloys. Goncharov et al[1] have recently studied the elastic and vibrational properties of Co up to 120 GPa and found that under pressure the elastic properties of hcp Co depart from the normal behavior well below (80 GPa) the transition pressure (105-150 GPa) for hcp to fcc phase. They also found an abnormal decrease in the E_{2g} mode frequency, which suggests the approach of a lattice instability due to the collapse of the magnetic moment. We have carried out total energy and phonon frequency calculations of hcp Co under pressure using pseudopotential based Plane Wave Self-Consistent Field (PWSCF)[2] programs. For the exchange-correlation terms we have used generalized gradient approximation. We have optimized the hcp structure both with respect to volume and *c/a*. For higher compressions we kept *c/a* constant.

Our calculated equilibrium properties of hcp-Co are in good agreement with the available experimental results. We found that hcp to fcc transition pressure is around 125 GPa compared to experimental pressure range of 105 to 150 GPa[3]. Our calculations show that the hcp magnetic moment falls with pressure and around 100 GPa, the rate of fall increases, whereas for fcc phase it decreases slowly up to 100 GPa and then suddenly falls to zero. Our calculated E_{2g} phonon frequency at ambient pressure of 141.5 cm^{-1} compares well with the experimental[1] value of 132 cm^{-1}. We have found that the frequency of the E_{2g} mode increases linearly with pressure. However the slope of the variation changes discontinuously near 80 GPa. Thus we have theoretically verified that the observed lattice instability at high pressure, well below the pressure range of hcp to fcc phase transition, is due to the onset of more rapid magnetic collapse at high pressure.

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Shock-wave Reduced High Pressure Equations of State of Al, Cu, Ta, and W

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We have generated 300-K isotherms to pressures as high as 300 GPa for Al, Cu, Ta, and W. Hugoniot data were reduced to isotherms using calculated thermal pressures from Wang et al.[1] For these four metals, available experimental results permitted corrections of Hugoniot data for shock-induced strength as a function of shock pressure. This is the first time that such corrections have been made for isotherms and so the isotherms better correspond to hydrostatic conditions. The isotherms are presented in the Vinet form along with isotherms for Mo and Au and Pt. These isotherms can be used for performing calibrations of pressure scales using the x-ray marker method and have been utilized in a recent improved determination of the ruby pressure scale.

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High Pressure Effects on the Crystal and Magnetic Structure of $Pr_{1-x}Na_xMnO_3$ Manganites (x = 0.2, 0.25)

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The crystal and magnetic structures of manganites $Pr_{1-x}Na_xMnO_3$ (x = 0.2, 0.25) have been studied by means of neutron diffraction at high pressures up to 8.5 GPa in the temperature range 4 – 300 K. At ambient conditions these compounds have an orthorhombic structure (sp. gr. *Pnma*) and undergo a charge ordering below T_{CO} ~ 220 K followed by an onset of the pseudo-CE type antiferromagnetic (AFM) state below T_N ~ 170 K. This state has two magnetic sublattices formed by ordered Mn^{3+} and Mn^{4+} ions corresponding to propagation vectors q_1 = (0 0 ½) and q_2 = (½ 0 ½). In addition to the majority pseudo-CE type AFM phase, in $Pr_{0.8}Na_{0.2}MnO_3$ there is about 10 % of the ferromagnetic (FM) clusters forming charge-disordered spin-glass regions. The formation of the FM clusters is largely suppressed in the sample $Pr_{0.75}Na_{0.25}MnO_3$.

Under high pressure $P \approx 2.6$ GPa, in both $Pr_{0.8}Na_{0.2}MnO_3$ and $Pr_{0.75}Na_{0.25}MnO_3$ a suppression of the initial charge ordered pseudo-CE type AFM and the onset of the layered A-type AFM state with a propagation vector q = (0 1 0) was observed [1]. In $Pr_{0.8}Na_{0.2}MnO_3$ the magnetic moments are oriented within the [0 1 0] crystallographic planes and in the $Pr_{0.8}Na_{0.2}MnO_3$ they are slightly inclined towards the *b*-axis. The possible reason for stabilization of the A-type AFM phase is the compression anisotropy which leads to the apical contraction of MnO_6 octahedra under high pressure and creates favorable conditions for appearance of the $d(x^2-y^2)$ orbital polarization, prerequisite for the A-type AFM order. The work has been supported by the Russian Foundation for Basic Research, grant 03-02-16879.

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High Pressure Effects on the Crystal and Magnetic Structures of $La_{0.7}Sr_{0.3}CoO_3$

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The magnetic, transport and electronic properties of cobaltites $La_{1-x}Sr_xCoO_3$ have been extensively studied with a growing interest from 1950s until now [1, 2]. At ambient pressure, a parent compound $LaCoO_3$ is a nonmagnetic semiconductor at low temperature and undergoes a phase transition to a paramagnetic insulating state near 100 K and paramagnetic metallic state at about 500 K. These transitions are usually related to a change of the Co^{3+} spin state from a low spin (LS) state (t^6_{2g}, S = 0) to intermediate spin (IS) state ($t^5_{2g}e^1_g$, S = 1) and from IS to high spin (HS) state ($t^4_{2g}e^2_g$, S = 2), respectively. Partial substitution of La^{3+} by Sr^{2+} leads to the appearance of ferromagnetic metallic state in $La_{1-x}Sr_xCoO_3$ for $x > 0.18$. Recent investigations of the magnetization, susceptibility and resistivity of $LaCoO_3$ [1] and $La_{0.82}Sr_{0.18}CoO_3$ [2] indicate the suppression of the IS state and stabilization of the LS state of Co^{3+} ions under high pressure.

In order to study the crystal and magnetic structures and the stability of different spin states of Co^{3+} ions in $La_{0.7}Sr_{0.3}CoO_3$ at high pressure, neutron diffraction measurements were performed in the 0 – 4 GPa pressure range and 16 - 300 K temperature range. The crystal structure of $La_{0.7}Sr_{0.3}CoO_3$ remains rhombohedral (sp. gr. R-3c) over the studied pressure range. The Curie temperature decreases with increasing pressure from T_C = 200 K (P = 0 GPa) with dT_C/dP = -6 K/GPa indicating the suppression of the IS state of Co^{3+} ions. The Co-O bond length decreases nearly linearly and the Co-O-Co bond angle increases with a pressure increase.

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Doping and pressure dependence of the optical properties of quasi-one-dimensional $LaTiO_{3.4}$

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The perovskite-related compound $LaTiO_{3.4}$ shows a quasi-one-dimensional metallic character, which can be explained by its crystal structure consisting of chains of TiO_6 octahedra [1,2]. Based on temperature-dependent optical studies, a conduction mechanism involving polaronic quasiparticles was recently suggested [2].

To clarify the importance of polarons in $LaTiO_{3.4}$ polarization-dependent infrared reflectivity measurements were carried out as a function of doping and pressure. Besides the conduction mechanism, the issues of pressure-induced dimensional crossover and pressure dependence of phonon modes will be discussed.

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Electronic effects in $Hg_{1-x}Cd_xSe$ single crystals in vicinity of phase transition under hydrostatic pressure up to 2 GPa

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In the present work the (i) thermoelectric, (ii) galvanomagnetic – GM and (iii) thermomagnetic – TM (longitudinal and transverse Nernst-Ettingshausen) effects were investigated in single crystals of gapless semiconductors $Hg_{1-x}Cd_xSe$ (x=0, 0.03, 0.07) at hydrostatic pressure conditions up to 2 GPa (Fig). The TM as well as their pressure behavior are known to be preferable in compare with GM ones for analysis of electron structure and charge carriers scattering mechanisms [1].

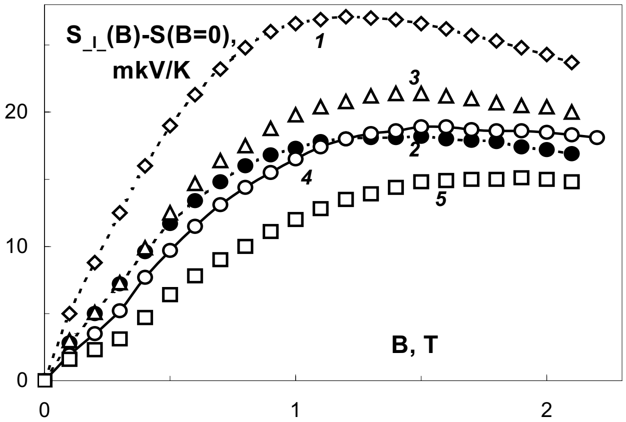

Fig. 1. Dependencies of transverse Nernst-Ettingshausen effect in $Hg_{1-x}Cd_xSe$ (x=0.03) on magnetic field ***B*** at different pressures, GPa: ***1*** – 0.04, ***2*** –0.216, ***3*** – 0.535, ***4*** – 0.858, ***5*** – 1.28.

HgSe underwent the structural phase transition into the widegap semiconductor cinnabar phase at relatively low pressure *P*=0.8 GPa [2]. Cd-substitution in cation sublattice increases greatly stability of initial zinc blende lattice and shifts the phase transformation into cinnabar structure to higher pressures [3]. For ternary $Hg_{1-x}Cd_xSe$ compounds the values of concentration, mobility and scattering parameters of charge carriers have been obtained and analyzed from the above effects up to phase transition points 1.4–1.7 GPa. The work was supported by the RFBR – Gr. No. 04-02-16178, and by the INTAS (Ref. Nr. 03-55-629).

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High-pressure thermopowers of ZnTe, ZnSe and ZnS single crystals

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In the present work the thermoelectric power (Seebeck coefficient) *S* and electrical resistance *R* were investigated in ZnTe single crystals in pressure *P* range of 0-20 GPa. By the *R*(*P*) dependencies the phase transitions in ZnTe [1] (zinc blende → cinnabar → *Cmcm*) were observed. At the *S*(*P*) dependencies of ZnTe the anomaly drops were observed both at increasing and at decreasing pressure circles. So, thermopower´s sign even changed during the return circle (see figure below). The observing anomalies is related by authors to a transition in intermediate phase, probable with NaCl lattice. A comparison with investigated earlier high-pressure thermopowers of other zinc chalcogenides (ZnSe, ZnS) [2] was performed.

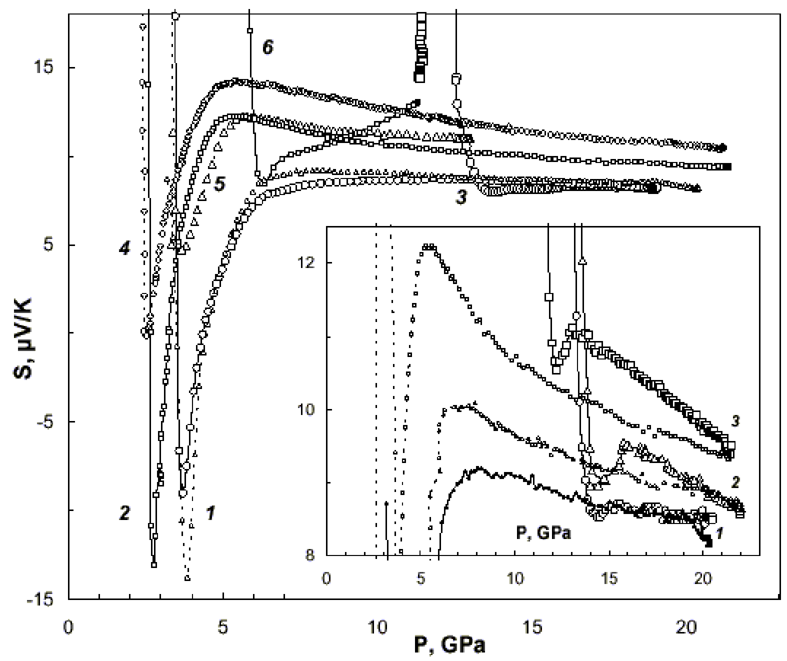

Fig. 3. The "drops" of thermopower *S* for ZnTe at *T*=295 K in enlarged scale obtained at decreasing of pressure *P* for samples 1 (***1***, ***2***) and 2 (***3***, ***4***, ***5***, ***6***). The decreasing cycles were started from different values of pressure (11-21 GPa), that resulted in variation of *S* drops. At the insert the similar *S* peculiarities are shown for sample 1 at consequent cycles (***1***, ***2***, ***3***) of *P* increasing (big) and decreasing (small symbols).

The work was supported by the Russian Foundation for Basic Research (Gr. No. 04-02-16178) and by the INTAS (Ref. Nr. 03-55-629).

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Thermoelectric properties of Ce at ultrahigh pressure

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In the present work for the first time the thermoelectric power *S* of Ce have been studied in a pressure *P* range 0-20 GPa. The study has revealed a non-monotonic character of *S*(*P*) reflecting changes in electron structure both due to phase transitions above ~ 1, ~ 5 and ~ 12 GPa from *fcc* (γ) into modified *fcc* structure (α), *bcc* monoclinic (α'') and tetragonal phases (ε), respectively and also due to the electron bands moving in the phase stability regions. The thermopower's sign kept positive for whole pressure range studied. The dependence of *S*(*P*) obtained is compared with the published electron structrure calsulations for different phases of Ce [1]. It has been shown an advantage of the thermopower technique in comparison with resistivity one in studies of phase transitions and electron structure of high-pressure phases of materials like Ce with complicated electron structure, where *s*-, *d*-, and *f*- electron bands contribute in total conductivity.

The work was supported by the INTAS (Nr. 03-55-629) and RFBR (Gr. No. 04-02-16178).

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Thermoelectric properties of narrow-gap PbTe-based semiconductors in region of pressure-induced phase transition

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Narrow-gap semiconductor PbTe being the best thermoelectric material in a region of average temperatures (600-1000 K). High-pressure thermopower $S(P)$ of *n*-type PbTe has been recently established [1] in a pressure range up to 30 GPa. But behaviour of $S(P)$ for *p*-PbTe as well as influence of impurities of different Groups were unknown up to now. So, in the present work a high-pressure behaviour was investigated of thermoelectric and electric properties of *p*-PbTe-based compounds (see figure).

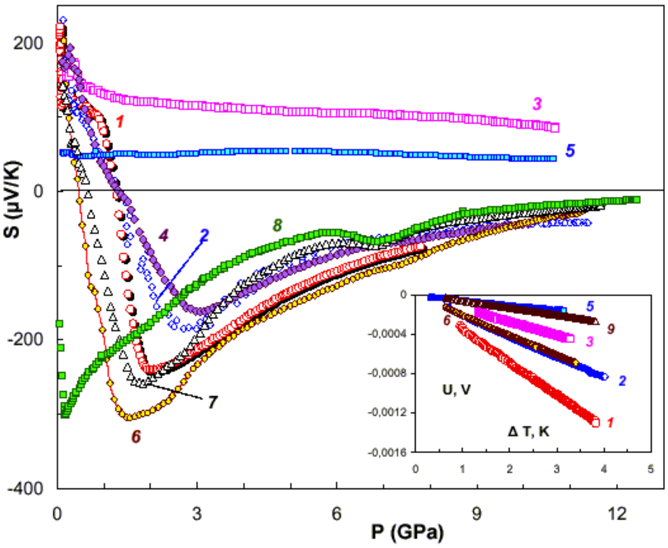

Fig. 1. The dependencies of thermopower (Seebeck coefficient) on pressure obtained at T=293 K for single crystals of: ***1*** – $Pb_{1-x}Si_xTe$ (x=0.00005), ***2*** – $Pb_{1-x}Ga_xTe$ (x=0.001), ***3*** – $Pb_{1-x}Sn_xTe_{1-y}$ (x=0.285, y=0.182): Si ~ 10^{-3} at. %, ***4*** – $Pb_{1-y}Te$ (y=0.182): Si ~ 10^{-3} at. %, ***5*** – $Pb_{1-x}Sn_xTe$ (x=0.29), ***6*** – $Pb_{1-x}Mn_xTe$ (x=0.05), ***7*** – $PbTe_{1-y}$ (y=0.182), and ***8*** – n-PbTe polycrystal. The insert shows the dependencies of thermoelectric voltage U on thermal difference ΔT at the same samples, ***9*** – $Pb_{1-x}Sn_xTe_{1-y}$ (x=0.285, y=0.182).

The work was supported by the RFBR – Gr. No. 04-02-16178, US CRDF – Gr. No. TGP-1125, and by the INTAS – Ref. Nr. 03-55-629.

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High-pressure thermopower of Si wafers suffered to hydrogen implantation

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In the present work the Czochralski grown Si single crystals implanted with the different fluences of H^+ ions, were investigated. Ions had energies ranged in 3–24 keV, which corresponds to ion project range up to 0.22 μm. The ion fluences were inside of $2*10^{13}$ – $3*10^{17}$ cm^{-2} diapason. The thin plates ~40x200x200 μm were cut with the assistance of ultrasound setup from the wafers surface containing an H^+–implanted layer. The comparative high-pressure thermoelectric characterization have been performed up to 20 GPa of the above plates and the samples prepared from the bulk Si crystals for comparison. Some difference was observed of thermoelectric power dependence on pressure for these two kinds of samples in the semiconductor-metal phase transition region under pressure. Both before and after ultrahigh pressure treatment the crystal structure of the samples were controlled with assistance of ultra soft X-ray $L_{2,3}$ spectroscopy. The features of amorphyzation were noted for the samples suffered to ultrahigh pressure treatment. The influence of H^+ implantation on thermoelectric properties and X-ray $L_{2,3}$ spectra of Si wafers is discussed in the work.

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Dependence of high-pressure thermoelectric and mechanical properties of Cz-Si on nitrogen doping and *P*-*T* pre-treatment

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Czochralski grown Si single crystals (Cz-Si) with nitrogen concentration of about 5×10^{14}cm^{-3} (Cz-Si:N is applied in modern microelectronics), as grown and *P*-*T* pre-treated up to 1400 K under hydrostatic pressure up to 1 GPa (resulting in oxygen precipitation) have been investigated in a sintered diamond chamber up to 20 GPa. Microhardness value was also measured. A shift has been established of semiconductor-metal transition pressure (P_t) to the higher magnitudes. A correlation between the values of transition pressure P_t and mechanical properties of Cz-Si:N has been detected. An influence of N on behaviour of thermoelectric properties of Cz-Si:N and P_t as well as mechanical properties is discussed in the work.

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Electrical properties of lithium up to 100GPa

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Li undergoes several structural transitions under high pressure. Neaton and Ashcroft [1] predicted that the compressed Li might form pairs of atoms, and that this paired atom phase is semi – insulating. The superconductivity of Li has been observed above 25 GPa up to 85 GPa and the T_c reaches 20 K (48 GPa) which is the highest observed of any elements [2, 3, 4]. In order to search for the predicted paired atom phase and superconductivity under high pressure, we performed the electrical resistance measurements by using a diamond anvil cell. To prevent leaking of Li from sample chamber, we improved the arrangements of gasket and made it possible to carry out the electrical resistance measurements under pressure up to 100 GPa. The electrical resistance was measured by four probe method with the deposited electrodes on the surface of the diamond anvil. We have succeeded to pressurize and measure the electrical resistance of Li up to 97 ±3 GPa. The superconductivity was observed at 97 ±3 GPa (T_c ~ 10.2 K). No clear evidence of metal to insulator transition that indicates the appearance of paired atom phase was observed. Figure 1 shows the pressure dependence of T_c obtained from our previous works and this work.

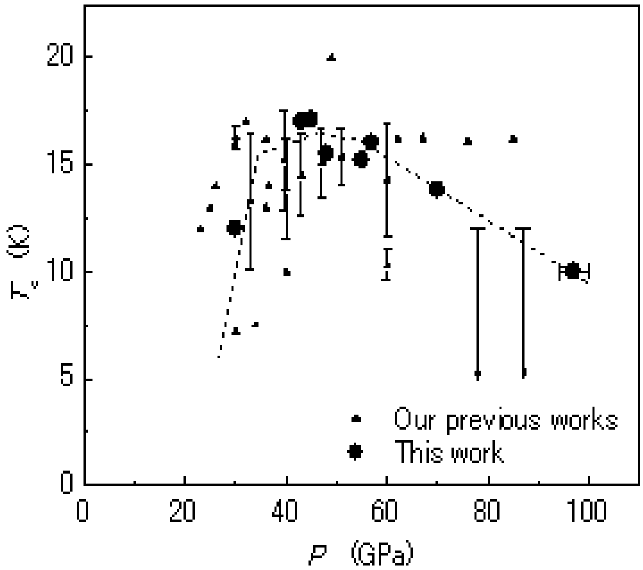

Fig.1 Pressure dependence of T_c

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High pressure phase transitions in $ZrMo_2O_8$ and $HfMo_2O_8$: an electrical conductivity study

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Over the last few decades investigations on frame work structured materials of the type MX_2O_8 (M = Zr, Hf and X = W, Mo) have drawn considerable interest due to their negative thermal expansion behaviour, which may have important technological applications in *e.g.* composites with tunable thermal expansion [1]. Also $ZrMo_2O_8$ has shown promises for possible use in nuclear fuel processes, as ion-exchangers and catalysts [2]. Therefore high pressure studies of these materials have acquired a significant importance for both basic and applied sciences. In fact high pressure investigations on many of the above materials have revealed the existence of a number of phase changes and amorphization; both reversible and irreversible [1].

$ZrMo_2O_8$ and its isostructural compound $HfMo_2O_8$ stabilize in a trigonal symmetry (α-phase) at ambient condition. High pressure structural investigations on α-$ZrMo_2O_8$ has shown two successive phase transformations: α - δ (monoclinic) phase at 1 – 1.1 GPa and δ - ε (triclinic) phase at 2 –2.5 GPa followed by amorphization above 10 GPa [3]. α-$HfMo_2O_8$ has been found to transform to a 20% denser monoclinic (β) phase at 2.15 GPa and 560°C [1]. But to our knowledge no other reports on the high pressure studies of α-$HfMo_2O_8$ are available till date. In order to gain more insight about the phase transitions and to obtain its significance, we carried out high pressure ac and dc resistance measurements on $ZrMo_2O_8$ and $HfMo_2O_8$ respectively up to 5.5 GPa, which is reported here.

High pressure ac (~1% accuracy) and dc (~0.1% accuracy) electrical resistance measurements were carried out up to 5 GPa in a modified pressure cell of the toroid anvil apparatus. For $ZrMo_2O_8$ slope changes and anomalies are observed in both the ac and dc resistance data at about 0.95 GPa and 2 – 2.5 GPa, which are related to the already reported high pressure structural transitions. Similarly for $HfMo_2O_8$, slope changes and anomalies are observed at about 1.1 GPa and 2.1 GPa. This apparently indicates structural phase transitions in $HfMo_2O_8$ similar to those observed in $ZrMo_2O_8$. For both the compounds, the activation volumes at room temperature are obtained by analyzing the conductance data in terms of the pressure dependent activation volume model [4]. The ac resistance data in both the samples are found to be strongly frequency dependent and show a transition between two power law regimes marked by a cross over frequency. This behaviour is associated with the strong lattice responses to the movement of the ions.

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Keywords: *High pressure, Phase transition, Negative thermal expansion, Conductivity*

Pressure dependence of the Curie temperature in Fe-Pd Invar alloys

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Fe-Pd alloys with Pd-concentration around 34 at.% are known to show so called Invar anomaly. Those alloys show very low or rather negative thermal expansion below the Curie temperature. This anomaly is caused by the compensation of the normal thermal expansion with the lattice contraction due to the decrease of the spontaneous magnetisation with increasing temperature through the large positive magneto-volume coupling. The magneto-volume anomaly is a common character in three typical Fe-base Invar alloys; Fe-Ni, Fe-Pd and Fe-Pt. To investigate the magneto-volume effect, it is the most direct way to observe magnetic properties under high pressure. In Fe-Ni Invar alloys there have been accumulated numbers of data, while in Fe-Pt Invar alloys only a few are available. In Fe-Pd Invar alloys no high pressure data is available above several GPa.

By using a cubic anvil press, measurements of temperature dependence of AC-susceptibility in Fe-Pd Invar alloys were made under high pressure up to 8GPa. The Curie temperature decreased 200 K under the maximum pressure. It was found that the decreasing rate is almost the same in three Fe-base Invar alloys. The low-temperature high-pressure magnetic phase found in Fe-Ni [1] and in Fe-Pt Invar alloys [2] was not observed in Fe-Pd Invar alloy. This fact may be related to the relatively higher Curie temperature in Fe-Pd alloy than in other two Invar alloys.

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Excitation and pressure effects on photoluminescence from silicon-based light emitting diode material

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The development of efficient silicon-based optoelectronic devices operating at room temperature is of fundamental importance. Silicon, however, is an indirect band-gap material, making it fundamentally a poor emitter of light. The controlled introduction of dislocation loops into silicon wafers by ion implantation and subsequent annealing modifies its indirect band structure [1]. This "dislocation engineered" material has been used to produce light-emitting diodes that operate efficiently at room temperature [1]. We investigate the nature of photoluminescence (PL) at around 1140 nm from this boron-implanted material using diamond anvil high-pressure cell techniques up to about 4 GPa. The integrated PL intensity increases with increasing temperature in the same manner as the electroluminescence (EL) [1]. The observed tendency is typical for the PL spectra excited especially at shorter wavelengths. We can extract the distinct effects of dislocation loops on the PL properties by selecting laser excitation wavelength and therefore changing penetration depth from the surface. With increasing pressure, the observed emission peak at room temperature shifts to lower energy at a rate of -14 meV/GPa. The value of this shift agrees with earlier optical absorption measurements on the indirect band gap of silicon [2], confirming that the emission is closely related to this indirect transition.

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Critical behaviour of bipolaronic transition in magnéli phase Ti_nO_{2n-1} (n=4 and 5) under hydrostatic pressure

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We observed critical behaviours in magnéli phase Ti_nO_{2n-1} (n=4 and 5) under hydrostatic high-pressure. Ti_nO_{2n-1}, which contains two Ti^{3+} and (n-2) Ti^{4+} ions per unit formula, shows the transitions from a metal to bipolaronic insulators. The theoretical studies have suggested the appearance of a superconductivity[1] which is related to the Bose condensation of bipolarons. Because of the insulating ground state, no superconductivity is observed in magnéli phase Ti_nO_{2n-1}. The bipolaronic insulating phase is suppressed by applying pressure[2,3] and the high temperature metallic state becomes stable down to low temperature[3]. Acha *et al.* have explored in ‘metallic’ Ti_4O_7 under pressure[3] but the superconducting state was not observed down to 1.2 K. However, the possibility of the superconducting state of Ti_4O_7 still remains in the experimental conditions of ‘more hydrostatic’ pressures or ‘lower’ temperatures. Therefore, we measured the electrical resistivity of Ti_4O_7 up to 4 GPa by using our new pressure cell which is originally developed by Nakanishi *et al.*[4]. This pressure cell is small enough to cool down to cryogenic temperature by dilution refrigerator.

At 4 GPa, Ti_4O_7 represents the metallic behaviour down to 280 mK. The residual resistivity ratio (RRR) is ~230 which suggests that the quality of sample is very high and the homogeneity of pressure is good enough. The superconductivity is not appeared in this measurement. To see the detail of the critical behaviour, the measurement under wider pressure variation in Ti_4O_7 and Ti_5O_9 is going on.

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20th AIRAPT and 43th EHPRG Meeting

THE ELECTRICAL CONDUCTIVITY OF INFINITE LAYER $CaCuO_2$ UNDER HIGH TEMPERATURE AND HIGH PRESSURE

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Infinite-layer $CaCuO_2$ (IL $CaCuO_2$) is the simplest copper oxide containing [CuO2] plane. Investigating the electronic properties of IL $CaCuO_2$ under high pressure are beneficial to understanding the physical origin of the Tc enhancement with increasing pressure in cuprate high Tc superconductors (HTS). The in-situ electrical resistance measurement of IL $CaCuO_2$ was performed for the first time as a function of both temperature and hydrostatic pressure utilizing a 6-8 type high-pressure apparatus. The temperature dependences of resistance can be fitted by the $\ln R \propto T^{-1}$ from the thermal activation mechanism in the whole measured temperature ranges. The relationships of resistance versus pressure at variant temperature revealed that there was an abnormal hump occurring around 8 GPa with increasing pressure. This is considered to relate to an electronic structure transition resulted from the anisotropic compression of the IL $CaCuO_2$ unit cell under high pressure. The band calculation with the local density approximation combined with the on-site Coulomb interaction U also shows the similar evolution of the band gap with increasing pressure.

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20th AIRAPT and 43th EHPRG Meeting

Structure Properties of $A_2CuO_2Cl_2$ under High Pressure

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$A_2CuO_2Cl_2$ (A=Ca, Sr, Ba) as the parent compounds of high Tc superconductors (HTS) have attracted much attention because their compositions are chemically simple having the single-layer [CuO_2] plane structures without apical oxygen[1]. $A_2CuO_2Cl_2$ system with apical chlorine has been proposed to be a candidate of HTS, and they are ideal systems to investigate the role of apical oxygen atoms in HTS. We have studied the structure and electrical properties of oxychloride compounds $Ca_2CuO_2Cl_2$, $Sr_2CuO_2Cl_2$, and $Ba_2CuO_2Cl_2$ with K_2NiF_4-type structure under high pressure up to 30 GPa at room temperature using diamond anvil cell. The equations of state of the compounds were obtained from the V/Vo-P relationship. Based on the Birch-Murnaghan equation, bulk modulus B_0 of $Ca_2CuO_2Cl_2$, $Sr_2CuO_2Cl_2$, and $Ba_2CuO_2Cl_2$ were calculated. It is found that with increasing the ionic radius at A site the B_0 gradually decreases from $Ca_2CuO_2Cl_2$ across $Sr_2CuO_2Cl_2$ to $Ba_2CuO_2Cl_2$.

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Magnetization of MnO and FeO at high pressures: a powder neutron diffraction study.

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A neutron powder diffraction study of MnO and $Fe_{0.92}O$ was held at high pressures (up to 5 GPa) and low temperatures (down to 1.5 K). Neutron diffraction measurements were performed at LLB G6 cold-neutron diffractometer with a constant wavelength of 4.741 Å, equipped with a liquid He cryostat. Measurements at high pressures were performed in a sapphire anvils high-pressure cell, pressure calibration was based on a ruby fluorescence scale. Magnetic reflections (1/2 1/2 1/2) and (3/2 1/2 1/2) for MnO and (3/2 1/2 1/2) for $Fe_{0.92}O$ were clearly observed below the Néel temperature (T_N), allowing us to determine temperature dependence of magnetization at various pressures (Fig. 1). Measurements of MnO were performed at 0 and 5 GPa, and of $Fe_{0.92}O$ at 0, 3.6, and 5 GPa. The resulting data at $T > 0.5{*}T_N$ were fitted to the simple exponential function $\frac{M}{M_0} \sim \left(1 - \frac{T}{T_N}\right)^{\beta}$, where M is the magnetic moment at a given temperature, M_0 is the magnetic moment at zero temperature, and ß is the critical exponent. For MnO the Néel temperatures were determined to be 120 K and 200 K and ß was determined to be 0.20 and 0.73 for 0 and 5 GPa respectively. For $Fe_{0.92}O$ T_N rises from 205 K to 254 K and to 310 K while pressure rises from 0 to 3.6 and to 5 GPa; ß exponent changes from 0.47 to 0.57 and up to 0.76. These results imply that a critical ß value of 1 will be reached at about 8 GPa for MnO and at about 10 GPa for $Fe_{0.92}O$.

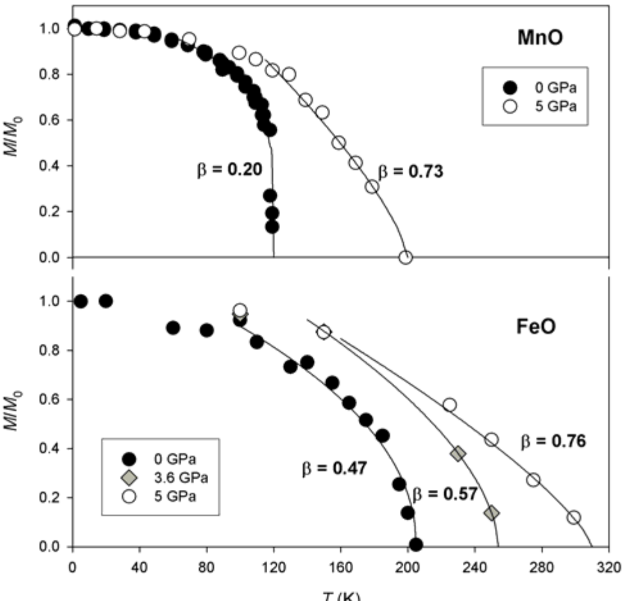

Figure 1. Magnetization of MnO and $Fe_{0.92}O$ at different *P,T* conditions.

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Gallium-induced resonant level in $Pb_{1-x}Sn_xTe$ under pressure

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It is known that doping of $Pb_{1-x}Ge_xTe$ with gallium leads to appearance of two different impurity levels E_{Ga1} and E_{Ga} in the energy spectrum of alloys [1]. In particular in PbTe deep level E_{Ga1} lies slightly above the middle of the gap while level E_{Ga} - on the background of the conduction band. However, we are still lacking of information on these impurity levels in other PbTe-based alloys and under pressure. In order to reveal the impurity-induced resonant level E_{Ga} and to obtain the diagram of the energy spectrum reconstruction under pressure the galvanomagnetic effects ($4.2 \leq T \leq 300$ K, $B \leq 0.1$ T) in the n-$Pb_{1-x}Sn_xTe$:Ga (C_{Ga}=0.2-2.2 mol.%) alloys under variation of matrix composition (x=0.09-0.21) and under hydrostatic compression up to 16 kbar have been investigated .

The measurements performed have shown that in all samples and in the whole investigated pressure range temperature dependencies of the resistivity ρ and the Hall coefficient R_H have a “metallic” character, indicating an existence of the resonant gallium level E_{Ga}, which stabilizes the Fermi level in the conduction band. Under pressure the increase of the free electron concentration due to transition to the gapless state and flowing of electrons from the resonant level to the conduction band takes place. Using the values of the Hall coefficient at helium temperature in the frame of two-band dispersion law we have calculated the pressure dependencies of the Fermi level and the free electron concentration. The results obtain allow us to determine the position of resonant impurity level and to construct the energy diagram of its movement relative to the principal band edges. It was shown that under pressure this level slightly shifts upward with the rate approximately 1 meV/kbar and its energy position relative to the middle of the gap remains practically unchanged.

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Influence of pressure on electrical propeeties $AgPbSbS_3$

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The resistance of complex chalkogenid $AgPbSbS_3$ at pressure 10-45GPa was investigation in the work.

High pressure up to 50 GPa has been generated in the diamond anvil cell with anvils of the "rounded cone-plane" type [1]. The electrical properties of the samples were investigated by method of impedance spectroscopy in the frequency range of 1Hz-800 kHz on an IM6 Zahner Electric installation.

The synthesised compound $AgPbSbS_3$ has monoclinic symmetry with lattice constant a=0.752 nm; b=1.334 nm; c=0.589 nm; β=91,17° [1]. At normal pressure $AgPbSbS_3$ is ionic conductor.

The godographs of an impedance at pressure 15GPa-50GPa were received. The dependencies of conductivity on frequency are investigated. The hysteresis of conductivity is investigated at the gradual unloading of the sample. Influence of borders of the electrode / sample was analyzed at various pressure.

The resistance of the sample decreases with decreasing of pressure. The dielectric tangent do not change practically with change of pressure. Phase transitions in compound $AgPbSbS_3$ in the investigated region of pressure were not found.

The researches are executed at partial financial support CRDF (Ek-005-X1), grant CRDF and Ministry of education of Russian Federation (BRHE, Post Doctoral Fellowship, award EK-005-X1, annex 7, No Y1-05-09).

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The $YBa_2Cu_{2.5}Mn_{0,5}O_9$ and $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$ oxides at high pressure investigation

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The properties of oxides $YBa_2Cu_{2.5}Mn_{0,5}O_9$ and $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$ were investigated by the method of impedance spectroscopy at pressures 15GPa-50GPa at T=300K.

High pressure up to 50 GPa has been generated in the diamond anvil cell with anvils of the "rounded cone-plane" type [1]. The electrical properties of the samples were investigated by method of impedance spectroscopy in the frequency range of 1Hz-800 kHz on an IM6 Zahner Electric installation.

At normal pressure the oxides $YBa_2Cu_{2.5}Mn_{0,5}O_9$ and $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$ are superconductors with temperature of transition 67K and 62K accordingly. The specific conductivity at T=300K is 3.98 μS/m for $YBa_2Cu_{2.5}Mn_{0,5}O_9$ and 0.87 μS/m for $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$.

The hodographs of the impedance $YBa_2Cu_{2.5}Mn_{0,5}O_9$ and $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$ were investigated at pressure 15GPa-50GPa at temperature 300K. The dependencies of conductivity from the frequency are analyzed.

The following conclusions were made:

There is a convertible phase transition at pressures 38-40 GPa in the compounds $YBa_2Cu_{2.5}Mn_{0,5}O_9$. There are convertible phase transitions in the compound $YBa_2Cu_{2.5}Mn_{0.5}S_{0.5}O_8$ at pressure 30-32 GPa and 36-38 GPa.

The replacement of a part of oxygen by sulfur results in displacement of region of phase transition in the region of lower pressure and to occurrence of additional phase transition.

The researches are executed at partial financial support CRDF (Ek-005-X1), grant CRDF and Ministry of education of Russian Federation (BRHE, Post Doctoral Fellowship, award EK-005-X1, annex 7, No Y1-05-09).

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TEMPERATURE DEPENDENCES OF RESISTANCE $AgGeSbS_3$ AT PRESSURE 10-45GPa

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In the present work the investigated of resistance $AgGeSbS_3$ were spent at pressure 10-45GPa in the region of temperatures 78K-400K. The chamber of high pressure with carbonado-diamond anvil cell was used for generation of pressure up to 50Gpa.

At normal pressure the compound $AgGeSbS_3$ is an ionic conductor. The region of temperatures of a beginning of the ionic transport is 150K-200K, the part the ionic transport is 99,8%.

At increase of pressure (P) there is a change of the region of temperatures of a beginning the ionic transport T_i. The dependence $T_i(P)$ is not monotonous. Dependence of resistance from temperature is also not monotonous. At loading and unloading the sample the hysteresis of resistance is found out. The regions of existence in a sample of phase transitions are determined. The change of energy of activation of conductivity with increase of pressure is analyzed. The temporary dependence of resistance is investigated at different pressure.

The work are executed at partial financial support CRDF (grant Ek-005-X1), grant CRDF and Ministry of education of Russian Federation (BRHE, Post Doctoral Fellowship, award EK-005-X1, annex 7, No Y1-05-09).

Pressure induced non-collinear magnetic structures in Fe-based intermetallics

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The pronounced magnetovolume effects (anomalous decrease of magnetization and large anisotropy of a lattice compressibility) in R_2Fe_{17} (R = Y, Ce, Lu) intermetallics result in a suppression of their ferromagnetic ground state with increasing pressure [1-3]. Combined magnetization and neutron diffraction measurements under hydrostatic pressure were concentrated on Y_2Fe_{17} that is considered as a representative of the Fe-sublattice in all the R_2Fe_{17} compounds. The ferromagnetic phase of Y_2Fe_{17} with Fe-moment in ***ab***-plane is transformed into incommensurate helical structures (similar to that described in [1]) at pressure above 1 GPa at 5 K. The critical pressure is 0.35 GPa or 0.4 GPa in the case of Lu_2Fe_{17} and Ce_2Fe_{17}, respectively. The helical structures were described by propagation vector $\tau = (0,0,\tau_z)$ with a complex character of temperature dependence of τ_z [2]. The ferromagnetic state is restored by a metamagnetic transition with the large field hysteresis, however, magnetization is not saturated even at field 5 T under pressure.

The hexagonal crystal structure of R_2Fe_{17}, as a natural multilayer system, can be described by Fe-layers perpendicular to the ***c***-axis accompanied by dumbbell Fe-pairs between them. The shortest Fe-Fe distances give rise to negative exchange interactions between Fe atoms located within the unit cell in four non-equivalent crystallographic positions. The anisotropy of magnetoelastic phenomena [3] and a role of the critical values of ***c***-parameter and/or the distance between the Fe layers in the evolution of interlayer exchange interactions will be discussed from point of view of an instability of the magnetic structures in the R_2Fe_{17} intermetallics.

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Behaviour of resistivity and thermopower of some organic compounds under ultrahigh pressure

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In the present work for the first time a behaviour of some organic compounds (single crystals: $C_{10}H_{10}Fe$, $C_{10}H_{10}Co$ and misfit $(C_{10}H_{10}Co)TiSe_2$) were studied under ultrahigh quasihydrostatic pressure conditions up to 20 GPa. The electrical and thermoelectric (only of misfit $(C_{10}H_{10}Co)TiSe_2$) properties were measured. All the organic compounds possessed by a high insulator-like electrical resistance R which decreased with pressure P. For $C_{10}H_{10}Fe$ and $C_{10}H_{10}Co$ the change of resistivity was inside of 1-2 orders, whereas for misfit $(C_{10}H_{10}Co)TiSe_2$ a pressure-induced metallization was observed (R continuously decreased by 8-10 orders with P). For $C_{10}H_{10}Fe$ and $C_{10}H_{10}Co$ at $P \approx 15$-18 GPa a similar sign inversion of dR/dP was observed, supposedly related to some transformation. Misfit $(C_{10}H_{10}Co)TiSe_2$ exhibited an electron type of conductivity (initial thermopower value was $S \approx -(25\text{-}30)$ μV/K at $P \approx 4$-5 GPa where the thermopower measurements started). Under pressure near 10 GPa an inversion of thermopower happened. The thermopower value achieved a maximum positive value $S \approx +(10\text{-}20)$ μV/K, then droped and near $P \approx 18$-19 GPa S became negative again. The reasons of such behaviour of electrical and thermoelectric properties of ogranic materials are discussed in the paper. The work was supported by the Russian Foundation for Basic Research (Gr. No. 04-02-16178) and by the INTAS (Nr. 03-55-629).

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Magnetic ordering in UCu_2Si_2 under applied pressure

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ALL of the U compounds that display a quantum critical point (QCP) as a function of pressure do so in a manner consistent with itinerant magnetism.[1] It would be of great interest to find a U compound that goes to the QCP in a manner consistent with localized 5f electrons; one candidate is UCu_2Si_2 which is isostructural to the first discovered heavy fermion superconductor $CeCu_2Si_2$.[2] We have performed resistivity measurements as a function of applied pressure to 2.5 GPa on UCu_2Si_2. We find that ambient pressure magnetic ordering temperature of 100 K decreases gradually in a manner consistent with itinerant magnetism. The results will be compared to previous measurements on UCu_2Ge_2.

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Evolution of magnetic ground state of U(Ni,Pd)$_2$Si$_2$ compounds modified by applying pressure

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Majority of UT$_2$Si$_2$ compounds (T = transition metal) possess antiferromagnetic ground state of the AF-I type. This magnetic structure consists of basal-plane layers of ferromagnetically coupled U magnetic moments aligned along the c-axis. The coupling between these layers along the c-axis is simple + - antiferromagnetic (AF-I). UNi$_2$Si$_2$ is the only exception because it exhibits at lower temperatures the uncompensated antiferromagnetic (UAF) structure characterized by the + + - coupling. Small substitution of Pd in UNi$_2$Si$_2$ turns the UAF ground state to the AF-I phase. Application of hydrostatic pressure, on the other hand, promotes the UAF structure. We will report on results of our magnetization, resistivity and neutron-scattering studies of the evolution of magnetic ground state of U(Ni$_{1-x}$Pd$_x$)$_2$Si$_2$ compounds at ambient and high hydrostatic pressure. The overall magnetic phase diagrams involving Ni-Pd concentration, pressure and magnetic field will be presented and discussed in the light of theoretical predictions derived within Ising model.

High-Pressure High-Temperature electrical conductivity study of iron with a laser heated diamond anvil cell

Weijun Huang, Qiliang Cui, Zhi He, Qiang Zhou, Guangtian Zou

The electrical conductivity of iron under high pressure and high temperature conditions was of great use to help people understand not only the basic physical character of electron, but also the interior structure of the earth.

In this paper, we measured the electrical conductivity of iron with a purity of 99.999% under high pressure and high temperature conditions by laser heated diamond anvil cell method. Some interesting result was discussed.

Effects of deuterium insertion and pressure on magnetic properties of $Ce_2Fe_{16}Mn_1D_y$ compounds (y = 0, 1, 2.3).

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Substitution Mn for Fe in Ce_2Fe_{17} compound suppresses the ferromagnetic ground state completely when Mn content reaches $x = 0.5$ [1]. $Ce_2Fe_{16}Mn_1$ orders antiferromagnetically up to $T_N = 198$ K. The magnetic structure can be presented as an incommensurate helix wounding along c-axis of the rhombohedral structure. Application of the pressure leads to the distortion of the helix so that uncompensated ferromagnetic component appears in the basal plane giving the ferromagnetic response of the bulk magnetization [2-3].

In this contribution we present effects of deuterium, D, insertion (negative pressure - lattice expansion) on the magnetic properties of $Ce_2Fe_{16}Mn_1$ together with the high pressure (up to 10 kbar) studies of the magnetic properties of $Ce_2Fe_{16}Mn_1D_y$ compounds (y = 1, 2.3). A ferromagnetic component is created by insertion of D in the antiferromagnetic $Ce_2Fe_{16}Mn_1$. Its Curie temperature T_C increases with increasing D-content reaching $T_C \approx 260$ K for y = 2.3 and remarkably decreases with pressure $dT_C/dp = -3.6$ K/kbar. Temperature behavior of the magnetization of $Ce_2Fe_{16}Mn_1D_1$ compound under pressure becomes complex. Such behavior can be correlated with the changes in electronic structure that are induced by the insertion of deuterium contrary to the pressure effect, where the only interatomic distances are affected.

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Inelastic X-Ray Scattering on Plasmons in Alkali Metals under Pressure

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Recent progress in synchrotron inelastic x-ray scattering (IXS) has made possible the measurement of plasmon dispersions throughout the Brillouin zone from small samples pressurized in a diamond anvil cell. Here, we report results of high-pressure IXS experiments on plasmons in sodium, the prototype of a nearly-free-electron metal. The conduction electron density is the fundamental parameter in the collective-electron physics of metals, and it can be tuned by the application of high pressure. In the case of Na, the electron density can be nearly tripled in the pressure range up to 45 GPa that was investigated here. In addition, pressure affects also electron correlations as well as the electronic band structure. Thus, high-pressure IXS studies are thought to provide valuable input to recent theoretical advances in describing the excitations of interacting electrons in metals. The main observations of the plasmon IXS experiments on Na are firstly that the difference between the free-electron behaviour and the observed plasmon energies increases dramatically with increasing density. Secondly, the plasmon line width increases too, signalling a reduction in the plasmon lifetime under pressure. The results will be discussed in the context of electronic band structure calculations and in comparison with similar experiments on K and Rb.

Conductivity of C_{60} fullerene crystals under multi-step dynamic compression up to 300 kbar

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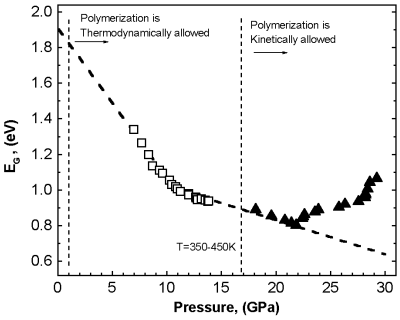
The purpose of this research was measurement of C_{60} fullerene crystals conductivity at high pressures, whether to find out C_{60} metallization. In our experiments we used the mode of multi-step quasi-isentropic dynamic compression of fullerene crystals made by series of consecutive shock waves which makes us possible to reach very much high pressures without considerable warming-up typical for compression by an unitary shock wave.

The most essential received fact in the present work is that under increasing pressure above 20 GPa conductivity instead of the further increase on the contrary starts to fall, that formally corresponds to expansion of effective value of bandgap E_G (Pic.1). This fact can be connected with phase transformations occurring in system according to the data of X-ray research.



Pic.1

Experimental data obtained can be explained with the assumption that energy barrier of C_{60} polymerization becomes lower with pressure increase about equally the bandgap.

Work is executed at financial support of the Russian foundation for basic research, the grant N 03-02-16322, the grant of the President of Russia № NS 1938.2003.2, and program of basic researches of the Russian Academy of Science "Thermophysics and mechanics of intensive energy influences ".

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Alkaline metals electrical conductivity at multi-step dynamic compression

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The purpose of work was studying the phase and structural transitions occurring in metals of the first group of a periodic table of elements (lithium, sodium, potassium), and so in calcium at dynamic compression. Registration of these transitions was carried out by a method of measurement electrical conductivity with simultaneous registration of pressure profile. Experiments have been implemented at a room and liquid nitrogen temperature. As a result of experiments series complex resistivity-pressure dependences have been received. For sodium almost tenfold increase of electric resistance is observed at initial room temperature of experiment and the maximal pressure 100GPa. In experiments with lithium the range of pressure has been expanded up to 210GPa, due to use of special explosive devices of bilateral compression. Results of experiments with lithium testify that up to pressure ~160GPa resistance of samples monotonously increases simultaneously with growth of pressure. The further increase in pressure conducts to a break of a curve and conductivity of a sample sharply increases. The structure of pressure-resistivity dependence for potassium qualitatively coincides with earlier fixed for sodium and lithium and equal 70 times. Using this technique was been measured calcium samples conductivity in a solid phase at shock compression up to 650kbar too. In result for calcium nonmonotonic conductivity-pressure dependence changing was fixed. Let's note, that in unloading electroresistance of all samples came back to a initial value that testifies to convertibility of occurring processes.

Work is executed at financial support of the Russian foundation for basic research, the grant N 03-02-16322, the grant of the President of Russia № NS 1938.2003.2, and program of basic researches of the Russian Academy of Science "Thermophysics and mechanics of intensive energy influences "

THE ELECTRON TRANSPORT OF MONOCRYSTAL ZnO AT NORMAL AND HIGH PRESSURES

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Recently a progress in growth of crystals and their unique physical characteristics (high coefficient value of the electromechanical bond, large width of forbidden band, luminescent properties, radiating stability, etc.) make topical the researches of electron spectrum and transport of this compound. In the temperature integral 77-400 K and hydrostatic pressures up to 9 GPa at 300 K there have been measured electric conductivity, Hall coefficient, and thermal electric power of volume monocrystals n-ZnO with electron concentration $10^{15}\div10^{17}$ cm^{-3} at 300 K. A character of temperature and baric dependences of kinetic coefficients is determined shallow hydrogen like donor, with energy level is located under the bottom of conduction band from a distance E_d (P=0) ≈50 meV at a normal pressure. When pressure increases this level remove from the bottom of conduction band: $E_d=E_d(P=0)+\beta P$, where $\beta=4.7$ meV/GPa. According to experimental data a dependence of static dielectric permeability χ upon pressure is calculated: $\chi=\chi_o(1-4\cdot10^{-2}P)^{-1}$ (P-GPa).

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Synthesis and magnetic properties of $UCoAlH_4$

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The hydrogen absorption characteristics of UCoAl compound under high hydrogen pressures have been investigated. Exposition of UCoAl at 0.5 GPa of hydrogen pressure and 100°C resulted in formation of $UCoAlH_4$ hydride. The crystal structure of this new hydride was refined in the hexagonal type structure ($P6_3/mmc$ space group, a=4.177233Å and c=8.254685Å). Magnetic properties of the UCoAl hydride, studied in the temperature range 2–300 K and fields up to 6 T, exhibit the Curie-Weiss susceptibility with effective moment 2.0 μ_B/U and paramagnetic Curie temperature - 6 K. A weak ferromagnetic component (0.03 μ_B) gradually developing below 30 K, can be tentatively attributed to structure defects.

Quantum Crystallization in Electron-Hole Plasma of Semiconductors under Pressure

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When electrons in a solid are excited to a higher energy band they leave behind a vacancy (hole) in the original band. Such holes behave like positively charged particles. From our direct path integral Monte Carlo modeling we predict that holes can spontaneously order into a regular lattice in semiconductors with sufficiently flat valence bands [1]. The critical hole to electron effective mass ratio required for this phase transition is found to be of the order of 80 in three dimensions and 30 in two dimensions. These hole crystals are intimately related to ion Coulomb crystals in white dwarf and neutron stars as well as to ion crystals produced in the laboratory in ion traps. In particular, we investigated the excitonic phase diagram of Tm[Te,Se] [2] and found the regions of existence of excitons, bi-excitons, many-particle clusters, electron-hole liquid and crystal. From the analysis of pair distribution functions we investigated the fraction of electron-hole and hole-hole bound states at different temperatures and pressures.

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Electrical Behavior of SOI-Like Structures Formed under High Pressure in Nitrogen or Oxygen Implanted Silicon

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Separation of silicon layer from substrate by oxygen or nitrogen implantation is one of the main ways in the development of silicon-on-insulator (SOI) materials. Implantation of oxygen is now well-established and widely used technology of the SOI wafer creation. Due to some unsolved problems (e.g. crystallization of the nitride layer, large leakage current and non-uniform Si/Si_3N_4 interface) the nitrogen implantation does not found wide application in modern electronics. To benefit both from the advantages of silicon nitride (a diffusion inhibition and impurity gettering) and of silicon dioxide (a low leakage current and a planar interface top Si layer / buried oxide) and for the development of the radiation hard materials, co-implantation of oxygen and nitrogen is developing for the fabrication of SOI material with combined insulator. Completed removal of the radiation-induced defects is the main problem of all implantation based technologies, which is enhanced in these cases due to the high fluences used. An application of the high pressure during high temperature post-implantation annealing is a promising way to manage the problem by the transformation of the radiation defects. Electrical and structural properties of multilayer structures formed in silicon implanted with high fluence of either nitrogen or oxygen ions and treated under enhanced hydrostatic pressure of argon ambient up to 1.4 GPa at temperatures ranged 800 – 1300°C has been studied in the present work. Based on current-voltage, capacitance-voltage, cross-sectional transmission electron microscopy, and secondary ion mass spectroscopy measurements, it has been found that the application of HP during post-implantation anneals, allows one to change the defect distribution between the insulator layer and the silicon, and to achieve a degree of control on the charges at interfaces and the carrier concentration in the top silicon layer.

Pressure Dependence of the $^1D_2 \rightarrow ^3H_4$ Emission in Pr^{3+}:YAG

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Photoluminescence related to $^1D_2 \rightarrow ^3H_4$ transitions of Pr^{3+} in YAG is measured in the pressure range from ambient to 160 kbar. The $^3H_4$ ground state is split into $^3T_2$, $^3A_1$, $^3T_1$ and ^3E components due to the cubic field and additionally into non-degenerate states labeled by the irreducible representations of the D_2 symmetry point group: Γ_1, Γ_2, Γ_3 and Γ_4. The excited $^1D_2$ state splits into ^1E and $^1T_2$ states by the cubic field and than the field of the D_2 symmetry removes all the remaining degeneracies. Of interest here is the $^3T_2$ ($^3H_4$) ground state that is split into Γ_3, Γ_1 and Γ_4 components and the ^1E ($^1D_2$) excited state that is split into Γ_1 and Γ_2 states. Since the splitting of ^1E ($^1D_2$) is quite small, one considers that at room temperature the sharp line structure in the luminescence consists of ^1E ($^1D_2$)$\rightarrow \Gamma_3$ and ^1E ($^1D_2$)$\rightarrow \Gamma_4$ emission lines. The emission related to ^1E ($^1D_2$)$\rightarrow \Gamma_1$ is not observed. The transition energies corresponding to ^1E ($^1D_2$)$\rightarrow \Gamma_3$ and ^1E ($^1D_2$)$\rightarrow \Gamma_4$ show different dependencies on pressure. The respective pressure shifts are –0.99 and – 0.52 cm^{-1}/kbar. Since ^1E (^1D)$\rightarrow \Gamma_3$ corresponds to the shorter wavelength, the two emission lines cross-over at a pressure of 110 kbar. To reproduce the energetic structure of the Pr^{3+} :YAG system and the peculiarities of the dependencies of the emission on pressure we have performed calculations in the framework of the crystal field model . The free ion and crystal field parameters, as well as their pressure dependencies, have been determined. We have considered contributions from the cubic field described by $B_q^k(cub)$ and the low symmetry field described by ΔB_q^k separately. Using the superposition model we have simulated the shifts of the individual ligands and related them to the changes in the quantities of crystal field parameters $B_q^k(cub)$ and ΔB_q^k. The main conclusion of our investigation is that, contrary to expectation, the effect of the hydrostatic pressure is not isotropic; it changes the local symmetry of the ion-ligands system.

Electronic properties of NiH_x under pressures: A spin-polarized calculation

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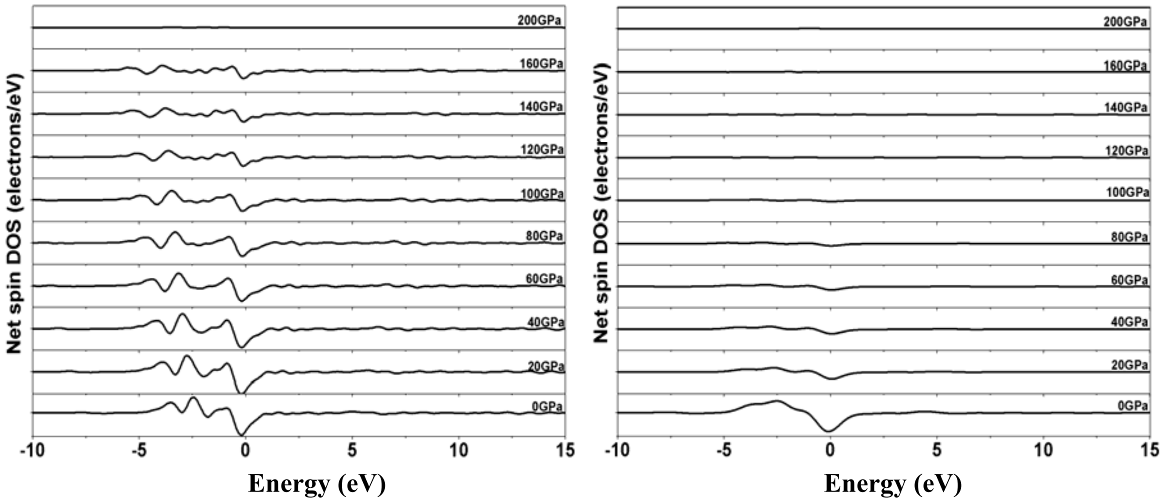
The metal-hydrogen systems have received wide attention due to their technical applications and for testing several theoretical models. In this paper, pressure effects on the electronic structure, and the magnetism in NiH_X systems (x=0,0.25,0.5,0.75,1) are researched based on density functional theory. Geometry optimizations at 0K and high pressures show compression to ca. 200GPa there are no structural phase transition. But we have observed signals of pressure-induced magnetic phase transitions in some NiH_X systems.



(a) $NiH_{0.5}$ (b) $NiH_{0.75}$

FIG.1. Density of state (DOS) difference between contributions from spin up and spin down eigenstates for (a)$NiH_{0.5}$ and (b)$NiH_{0.75}$

At 0GPa, except NiH is paramagnetic, other systems are ferromagnetic. When pressure is increased from 0GPa to 200GPa, paramagnetic NiH holds stably，ferromagnetism in Ni and $NiH_{0.25}$ are getting weaker, and a transition from ferromagnetic to paramagnetic phase happens in $NiH_{0.5}$ and $NiH_{0.75}$ at about 200GPa and 120GPa respectively, as shown in Figure 1. It is found that the magnetic phase transition is sensitive to the hydrogen concentration. With the increasing of hydrogen concentration, transition pressure will decrease in the NiH_X systems.

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$ZnAs_2$ electrical resistance at pressures 20 - 50 GPa

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$ZnAs_2$ is known as a material with anisotropy of properties, according presence both the bonds Zn-As and As-As. Any transformations weren't known in $ZnAs_2$ at quasi-hydrostatic pressures up to 9 GPa. We studied electrical resistance of $ZnAs_2$ at pressures 15-50. The resistance of $ZnAs_2$ decreases by 2-3 magnitudes drastically at pressure ~25 GPa at first cycle of applying pressure, and pressure dependence of resistance have a maximum at the pressure near 35 GPa. The resistance drastically increases by 3-4 magnitudes at pressure ~35 GPa during decreasing pressure. These peculiarities are not observed in consequent pressure loading cycles. We think that irreversible structural conversion take the place in $ZnAs_2$ at pressures ~35 GPa. Resistance temperature dependences have an activation character in the temperature range 77 - 400 K (Fig.1).

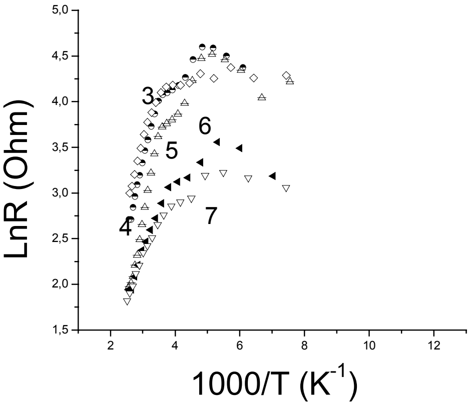

Fig.1. Temperature dependences of pressure (3 – 31,5 GPa, 4 – 35 GPa, 5 – 40 GPa, 6 – 44 GPa, 7 – 45,5 GPa)

Pressure dependence of activation energy has a peculiarity at pressure close to 35 GPa (for a "*fresh*" sample). This work was supported in part by grant BRHE EK-005-X1 (Ural research educational center "Advanced materials").

Acoustic wave propagation at a cobalt/helium interface.

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We have used impulsive stimulated light scattering (ISLS) to measure the velocity of an acoustic wave propagating at the interface formed by a single crystal of cobalt in contact with liquid helium. Dispersion curves of velocity versus in-plane propagation direction to 10 GPa were obtained. In the particular case of propagation in the *xz* plane the acoustic velocity is determined mainly by the cobalt elastic moduli c_{44}, c_{12}, and c_{33}. We have assumed the value of c_{33} and its pressure derivative determined by inelastic x-ray scattering [1] in order to infer the corresponding values for c_{12} and c_{44} that best match our data. These results are compared with IXS and low-pressure ultrasonics data. We find that in the present case the techniques of IXS and ISLS are complementary in terms of the uncertainties associated with the estimation of the various elastic tensor elements.

We also show how ISLS data may be used to infer the bulk modulus and mass density of helium (or other fluids) from interfacial velocities. We suggest combining the technique with laser heating to determine such quantities at simultaneous high temperature and pressure. Since the interfacial wave is localized to within two or three microns of the heated surface uncertainties due to thermal gradients may be expected to be minimized.

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Magneto-optical Kerr effect under pressure

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Diffracted magneto-optical Kerr[1] effect was utilized for the first time to determine the pressure dependence of the magnetization of Fe, Co and Permalloy (Py) up to 10 GPa in a diamond anvil cell. The samples were regular arrays of submicrometer polycrystalline, elliptically shaped particles, evaporated on a 20 µm thick Si substrate. From the measured hysteresis loops, we deduced the shape anisotropy, which depends linearly on the magnetization (M).

The pressure dependence of the magnetization was therefore deduced from the anisotropy variations. Our results show that M increases with pressure in Fe and Py, and decreases in Co. Moreover, the measured changes of M in Fe and Co are much larger than those predicted theoretically. These results provide new data to test the accuracy of future theoretical modesl.

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Electronic Structure and Pressure Induced Magnetic Collapse in $GaCMn_3$

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$GaCMn_3$ exhibits novel magnetic transitions and Kamishima et al[1] recently discovered the giant magneto resistance (GMR) in it and also found a striking change in the Hall coefficient at the transition. They suggested that this change in carrier concentration causes the GMR in this material. It is very important to know the electronic structure for each magnetic state to understand these novel properties and also the origin of the carrier concentration difference between the antiferromagnetic and ferromagnetic phases. Also it is interesting to study the effect of pressure on the electronic structure and magnetic properties of this compound.

We have performed *ab initio* electronic structure calculations of $GaCMn_3$ in the ferromagnetic and paramagnetic phase using Plane Wave Self-Consistent Field (PWSCF) programs (pseudo-potential framework). We have used ultrasoft pseudo-potential with 50 Ry plane wave energy cut-off and taken 240 **k**-point in the irreducible wedge for the Brillouin zone integration and adopted generalized gradient approximation for the Exchange-correlation terms.

Our calculated equilibrium properties are in good agreement with experiment and from our spin polarized electronic structure calculations for the ferromagnetic phase we found that there is a sharp decrease of the ferromagnetic moment near 5 GPa pressure. We also found a large change in the minority spin density of states at the Fermi level (E_F). Interestingly we also find an electronic topological transition near this pressure. To better understand the mechanism of collapse of the moment we have carried out fixed spin moment calculations for equilibrium lattice and found an energy minimum and a shoulder for this system with a small energy difference. Under pressure if the shoulder becomes a minimum having same energy as the other local minimum then a first order magnetic transition may occur.

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STUDY OF SPALL STRENGTH OF NATURAL URANIUM BY LASER INTERFEROMETER METHOD

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It is considered that spall strength is objective enough characteristic for dynamic strength of the material under stretching at microsecond range of loading duration. Spall destruction is multistage, evolutive in time process with formation of destruction region inside inner layers of the material. Most informative way to determine destruction tensions at spall is based on measuring free surface velocity measuring of the sample under investigation. In this case laser interferometer methods not influencing on investigated process are preferred.

In this paper we present the new results of the series of experiments for study of spall strength of the samples of natural uranium with thickness 3,8…10 mm by laser interferometer method Fabry-Perot. Under the values of loading amplitude ≈17 GPa and the rate of deformation $3*10^5$ sec^{-1} in the range of release wave interaction the average value of the spall strength was found to be 3,52±0,37 GPa.

We compared the obtained experimental results with data of other authors. Our results are in agreement with data of other authors for samples with thickness 2…10 mm. Experimental points on the dependence $\sigma_s(W)$ are satisfactorily described by one curve, which relatively quickly rises up to value $\sigma_s \approx 3{,}2$ GPa (W≈370 m/sec, this corresponds to loading amplitude ≈10 GPa), and then in the range W=370…660 m/sec the value σ_s weakly growths up to 3,52 GPa. It can be supposed, that the value σ_s becomes constant and practically doesn’t depend on loading amplitude.

Raman spectroscopy and structural transformations in hydrides under pressure

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Interest in hydrogen as an environmentally safe energy carrier for the future increases steadily and research on new safe and efficient methods to produce, transport and store hydrogen is a very active area. Hydrogen storage in the form of solid hydrides is an attractive alternative for safety reasons, especially since the hydrogen volume density can compete with that in liquid H_2. Light metal hydrides such as $LiBH_4$, $LiAlH_4$ and $NaAlH_4$ also provide high hydrogen densities (5 - 15%) per unit weight, and some materials allow reversible hydrogen absorption-desorption cycling by changing H_2 pressure and temperature.

Little is known about the high pressure behaviour of the light metal hydrides, but such knowledge may be important for applications. For example, $LiAlH_4$ has recently been predicted [1] to transform into a 17% more dense phase at a "low" pressure of 2.6 GPa. We have therefore carried out room temperature Raman studies on some light metal hydrides to investigate their structural properties under pressures up to 6 GPa. These studies have revealed several reversible structural transformations, including a transformation in $LiAlH_4$ close to the transformation pressure predicted in Ref. [1]. While some of these transformations involve significant changes in structural symmetry leading to changes in the number and intensities of Raman lines, we also observe minor anomalies which we identify as the high pressure counterparts of known low-temperature order-disorder transformations. In some cases, additional theoretical calculations have been used as a guide to identify the structures of the new phases.

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Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

High-pressure Raman Study of Ba_8Si_{46}-type Silicon Clathrates

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Silicon (Si) clathrates are covalent bonded cage-like crystals composed of face-sharing Si_{20}, Si_{24}, and Si_{28} polyhedra. The type-I structure is, for example, formed by a simple cubic arrangement of two small Si_{20} and six large Si_{24} per unit cell. The resulting formula is M_8Si_{46} if host Si cages are fully occupied by guest atoms (M=Na, K, Sr, Ba, and I). These compounds continue to attract much attention as new super-conductors, wide band-gap semiconductors, and a new class of thermo-electric materials. These characteristic properties can be understood by the electron-phonon and phonon-phonon coupling mechanisms between the encaged atoms and the framework Si. These couplings are explored in part by the study of high-pressure Raman scattering through their vibrational properties of both guest atoms inside the cages and the host Si framework. Most recently, we have found vibrational modes of guest atoms (Ba, K, and I) in Ba_8Si_{46}, K_8Si_{46}, and $I_8Si_{44}I_2$ compounds by Raman spectroscopy, and observed some phase transitions at pressures up to 30 GPa [1].

In this report, we present high-pressure Raman study of Ba_8Si_{46}-type alloyed silicon clathrates: $Ba_8Au_xSi_{46-x}$ (x=1, 3, 4, 5, 6), $Ba_8Ag_xSi_{46-x}$ (x=0.5, 1, 3, 6), $Ba_8Ge_3Si_{43}$, and $Ba_8Ge_{12}Si_{34}$. The purpose of this research is to study the effect of Au, Ag, and Ge substitutions in the Si framework on the vibrational properties, and to investigate the guest-host interactions by considering their superconducting properties.

For $Ba_8Au_xSi_{46-x}$ (x=1- 6) we observed the Au dependence of Raman spectra at 1 bar and high pressures. Raman peaks related to Ba atoms are found at lower frequencies of 40-100 cm^{-1}, and Si framework vibrations are observed around 110-450 cm^{-1}. The Au substitution created a new Raman band at 70 cm^{-1}, and its intensity increased with x. This strong band can be theoretically reproduced by the dominant contributions of Au atoms [2]. The Si framework band at 435 cm^{-1} shows significant decrease in frequency with Au content. High-pressure effects are also reported.

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High Pressure FT-IR Spectroscopic Study on the Secondary Structural Changes in Insulin Amyloid Fibril and Aggregate

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A number of human diseases, known as amyloidosis, originate from the deposition of stable protein aggregates with highly ordered structures. Recent studies suggest, moreover, the assembly into amyloid fibrils is an intrinsic property for peptides and proteins [1]. However, the intra- and intermolecular interactions which promote amyloid formation and stabilize its organized structures are not understood in detail. In this study, we have examined the pressure-induced changes in secondary structure for the two kinds of insulin aggregate, amyloid fibril and reduction-induced aggregate, by using FT-IR spectroscopy. The parallel β-sheet for amyloid fibril is not unfolded, but dramatically distorted at 1.0 GPa. This structural rearrangement is very elastic, and does not cause the exposure of the backbone amide protons involved in parallel β-sheet to aqueous medium. The dissociation of amyloid fibril into its monomer or oligomer is not likely to be promoted by application of high pressure. On the other hand, the antiparallel β-sheet for reduction-induced aggregate remains distinct at 1.3 GPa. The whole construction is quite rigid compared with that of the amyloid fibril in spite of originating from the same protein. The structural elasticity for amyloid fibril implies the increase in size or number of cavity in the interior. The tertiary interactions between side chains for the amyloid fibril might be less effective than those for the reduction-induced aggregate and native insulin.

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Raman and UV absorption studies on supercritical fluid of oxygen

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Molecular oxygen, O_2, with its characteristic magnetism, exhibits unique behavior under high-pressure. Many high-pressure phases with fascinating physical properties occur in its P-T phase diagram. One of its notable features is an abnormally high freezing pressure, 5.9 GPa, at 300 K. In the supercritical fluid, formation of $(O_2)_2$ molecular units has also been argued up to now and an importance of intermolecular interactions has bee pointed out in the properties of this fluid. Raman spectroscopy is available to probe the intermolecular interaction in question, which depends on the local environment, and to investigate the dynamics of molecular fluids.

In this paper, the vibrational spectra of high-density fluid O_2 are investigated by high-pressure Raman scattering experiments, and the pressure evolutions of the frequency (shown in Fig.1) and the linewidth are discussed from the viewpoint of molecular interactions. UV absorption spectra of molecular oxygen were also measured at pressure up to 1.5 GPa and temperature between 17 and 297 K. In the supercritical phase, an absorption band was observed in a UV region between 4.5 and 7 eV and showed an appreciable enhancement in the intensity with pressure (shown in Fig.2). The observed UV absorption band of high-density oxygen was attributed to the two-molecule process by an antiferromagnetic O_2 pair.

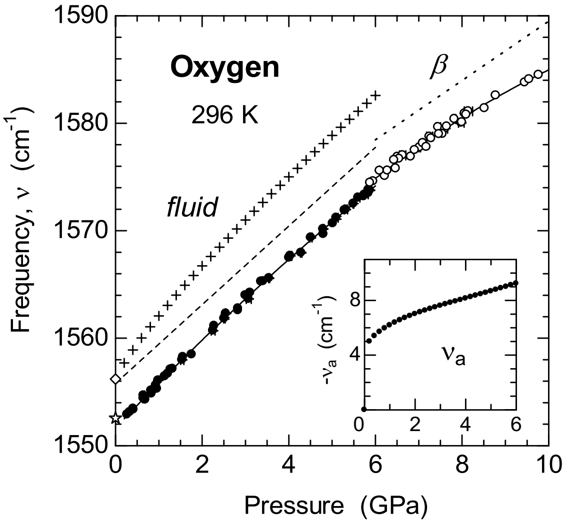

Fig.1 Raman frequency of O_2.

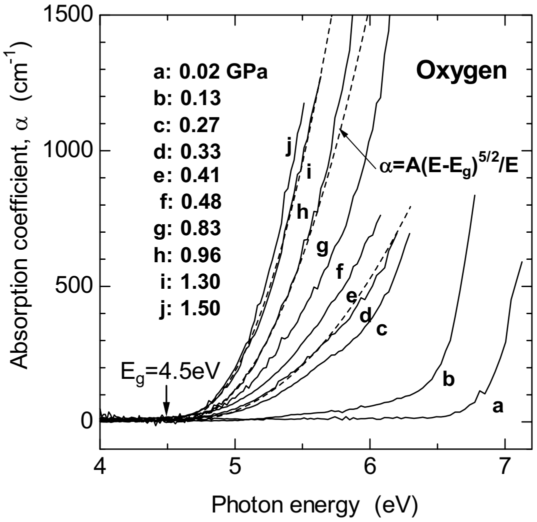

Fig.2 UV absorption spectra of O_2.

Lattice-dynamics of hcp- and ω- titanium by Raman scattering at high-pressure

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Lattice-dynamical studies, performed on Ti metal by Raman spectroscopy for pressures up to 46 GPa, show no softening of the E_{2g} mode of the hcp phase on approaching the transition to the ω-phase, which contrasts the behaviour of its heavier homologue Zr [1]. However, it exhibits an anomalously low mode Grűneisen parameter. Unusual behaviour is also reflected in the pressure response of elastic modulus $C_{44.}$ For the hcp phase it is shown that the temperature shift at room temperature of this mode is dominated by the explicit contribution, which is one order of magnitude higher than the im-plicit shift due to thermal expansion, for both Ti and Zr. Such a behaviour has been observed also in other transition metals, but not in „simple“ metals like Zn, where the implicit term determines the temperature shift [2]. The frequency of the E_{2g} mode of the ω-phase increases in the investigated pressure range, with an ambient pressure mode Grüneisen parameter $\gamma \approx 2$, slightly higher than that of Zr, and becoming smaller under compression. At present, theoretical lattice dynamical studies for Ti are only available for normal pressure. A recent theoretical study of hcp- and ω-Ti [3], according to our best knowledge the only one at present for the ω-phase, being in quite good agreement with the experimental data for the hcp phase, however, predicts the frequency for the E_{2g} mode of the ω-phase 37 cm^{-1} (17%) lower than obtained in the present study. In this context we would like to emphasize that an analysis of the anomaly of the hcp-E_{2g} mode in terms of electronic structure is still missing. These results indicate that the present knowledge of the lattice-dynamics of the Ti-group elements is incomplete and far from being understood.

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Joint 20th AIRAPT – 43th EHPRG, June 27 – July 1, Karlsruhe/Germany 2005

Pressure-induced high-spin to low-spin transition in ferropericlase ($(Mg_{0.8}Fe_{0.2})O$) observed by high-pressure high-temperature Mössbauer spectroscopy.

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$(Mg_xFe_{1-x})O$ ferropericlase with x ~ 0.8 is believed to be the second most abundant phase in the Earth's lower mantle after $(Mg,Fe)SiO_3$ perovskite, and therefore its properties and stability field are important for geophysical and geochemical models of the Earth's deep interior. We performed an in situ investigation of the behavior of $(Mg_{0.8}Fe_{0.2})O$ at elevated pressures (up to 105 GPa) and temperatures (up to 600 K) in a diamond anvil cell (DAC) equipped with internal resistive heater using ^{57}Fe Mössbauer spectroscopy. Below 55 GPa the Mössbauer spectra can be deconvoluted with two Lorentzian quadrupole doublets, one for Fe^{2+} and one for Fe^{3+} sites according to previous models [1]. At pressures higher than 55 GPa we observed a change in the structure of Mössbauer spectra, suggested to be a high-spin to low-spin transition of Fe^{2+} ions. A new subspectral component (Lorentzian singlet) with lower isomer shift appears, and its relative abundance increases linearly with pressure. The pressure range where both spin states coexist is unusually broad (from 55 to 105 GPa), and the crossover point was determined to be 80 GPa. We collected several spectra at different pressures and temperatures up to 600 K, and found that the amount of low-spin atoms is independent of temperature within experimental error. The isomer shift of the high-spin Fe^{2+} doublet depends linearly on pressure with a slope of about -0.003 mm/s per GPa. The low-spin Fe^{2+} singlet has the same pressure slope, but is shifted to lower energies by ca. 0.14 mm/s. Our results in general agree with previous inelastic X-ray scattering measurements of $(Mg_{0.83}Fe_{0.17})O$ [2], where a high-spin to low-spin transition was observed between 49 and 75 GPa.

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Vibrational properties of the $CuGaO_2$ and $CuAlO_2$delafossites at ambient and at high pressure

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Transparent conducting oxides (TCOs) are technological important materials as they are simultaneously transparent and conductive almost like a metal. The full development of their potential optoelectronic applications demands the development of p-type TCOs. The CuMO2 delafossite family, where M=Al, Ga or In, is attracting attention because they present p-type conductivity or, in the case of CuInO2, bipolar conductivity. The delafossite structure (S.G. $R\bar{3}m$) is constituted by hexagonal layers stacked in a O-Cu-O-M sequence. Group theory shows that the delafossite structure has only two active Raman modes, Ag and Eg.

We have carried out Raman measurements and ab initio calculations in ambient conditions and under high pressure in order to identify the modes and also to characterize their pressure evolution. We present in Table I the main results obtained:

		ω_{Eg}(cm-1)	ω_{Ag}(cm-1)	$d\omega_{Eg}/dP$($cm^{-1}GPa^{-1}$)	$d\omega_{Ag}/dP$($cm^{-1}GPa^{-1}$)
$CuGaO_2$	Experimental	368	729	2.78	4.11
	Calculation	366	718	2.4	4.9
$CuAlO_2$	Experimental	418	767	2.9	5.2
	Calculation	421	769		

Table I. Experimental and theoretical Raman active Γ-point phonon frequencies and their pressure dependence.

In both compounds a high pressure phase transition is observed in the experimental spectra (at 26±1 and 36±2 GPa in the case of $CuGaO_2$ or $CuAlO_2$, respectively) . Ab initio calculations suggest the existence of a dynamical instability at about the same pressure.

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Pressure induced structural modifications of As_2S_3 glass

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Amorphous chalcogenide semiconductors present optical properties that render them ideal materials for a number of applications such as optical fibres as well as optical data storage. Structural information for this class of materials as a function of glass composition, temperature and pressure is of great importance as it contributes both to the basic knowledge concerning medium and short range order of the amorphous state and to technological applications by enabling correlations between requested performance and compositional characteristics. This work refers to the pressure induced structural rearrangements of a model chalcogenide glass, As_2S_3. High pressure Raman experiments performed on a thermally annealed sample gave evidence of modifications in the short and medium range order. In order to avoid photo-induced structural rearrangements, off-resonance Raman spectra were recorded up to ~100kbar. The local structure of As_2S_3 resembles that of the corresponding crystal i.e. it is a 2D network consisting of strong intralayer bonds and weak interlayer van der Waals forces. In the Raman spectrum of glass, apart from the vibrational bands attributed to AsS_3 pyramids, vibrational bands of cage-like As_4S_4 species can be resolved as well. Their pressure dependence along with the corresponding dependence of the boson peak is being discussed. Interrelations of the obtained results with the optical properties of the corresponding crystal (orpiment) as a function of pressure are addressed. Finally, differences observed between the Raman spectra recorded upon pressure increase and the corresponding spectra recorded upon pressure release indicate that permanent structural modifications take place.

High-pressure low-temperature spectroscopy of pyrene molecules in commensurate and incommensurate phases of biphenyl

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As a continuation of our recent research into the optical properties of organic crystals exhibiting structurally incommensurate phases [1-3], we have studied the photoluminescence of crystalline biphenyl doped with pyrene molecules in the temperature (T) range 4.7 – 40 K at various pressures (P) between 0.17 and 2.5 kbar.

Depending on P–T values biphenyl exists in three different phases [2]: the normal, commensurate phase (C I) and two incommensurate phases (IC II and IC III). We have studied, at various fixed P values, the T dependence of the zero-phonon line in the phosphorescence spectrum of the sample at 597 nm, which in C I phase appears as a clear-cut singlet but splits to a doublet and even quartet in IC II and IC III phases, respectively [3]. We refined the phase boundary between C I and IC II phases by varying T at several fixed P values and determining the phase transition temperature, T_{pt}, as a T value at which the doublet in IC II phase converges to the singlet in C I phase.

Interestingly, the singlet in C I phase and the centre of the doublet in IC II phase both show the same red pressure shift, –22.4 $\mathrm{cm^{-1}}$/kbar, in the whole T range 4.7 – 40 K studied. But especially interesting are results for lower T values where the phase transition pressure, P_{pt}, is virtually independent of T ($P_{pt} \approx 1.8$ kbar; $T < 10$ K). In this T range the singlet line exhibits anomalous behaviour – by lowering T between ~10 K and 4.7 K the line becomes broader and not narrower. On the contrary, at higher T (10 – 40 K) it behaves normally – becomes broader with increasing T.

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Raman Scattering Studies on n-Heptane under High Pressure

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The phase behavior and conformational equillibria of simple saturated hydrocarbons have attracted considerable attention and have been investigated extensively. The properties of alkyl chains are fundamentally important for understanding a variety of phenomena in biology and polymer science. Vibrational spectroscopy is a powerful tool for investigating conformational and dynamics of molecules in the condensed phase. Application of hydrostatic pressure to molecular systems, held together by van-der-waals interactions, modifies the balance of intra- and intermolecular forces as a result of changes in the distances between molecules. Infrared absorption studies on n-heptane suggested a solid-solid phase transition near 30 Kbar[1]. Recent atomistic molecular dynamics simulations suggested no signatures for a solid-solid transition up to 70 Kbar [2]. In fact some interesting changes take place in the environment around methyl end-groups and its dynamics, namely, there are hindrance to their free rotation with increasing pressures up to 70 Kbar. In the present study, high-pressure studies have been carried out up to 160 Kbar mainly to verify the theoretical prediction and its implications at higher pressures. The study reveals, along with the liquid-solid transition ~ 14 Kbar, a transition around 80 Kbar as seen from Raman spectra in the region of 100 – 1700 cm^{-1}. The Fig. 1 is a typical example of the same. The present study is consistent with the theoretical prediction of hindrance to the end-group rotation and it goes on to suggest a total freezing of the methyl rotation, suggested by disappearance of torsional modes (Fig. 1) and changes in other modes ~ 80 Kbar. This leads to an order-disorder transition ~ 80 Kbar .

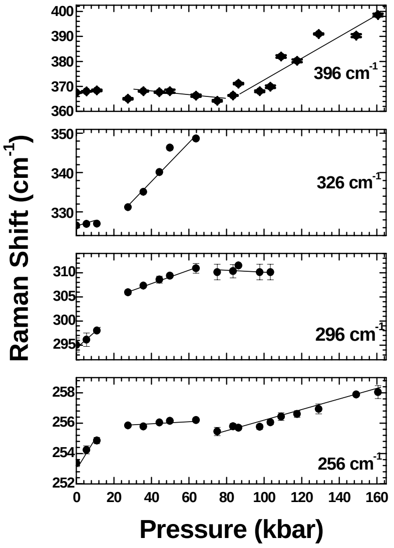

Fig 1. shows the end-group torsional phonon modes of n-heptane as a function of Pressure

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Structural properties of the $CuAlO_2$delafossite at high pressure

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Transparent conducting oxides (TCOs) are technological important materials as they are simultaneously transparent and conductive almost like a metal [1]. In spite of the large interest aroused by the p-type transparent conductor CuAlO2 since its discovery, the nature and value of its band-gap remains controversial [2]. Knowing the evolution of the crystal structure under pressure is necessary in order to undertake further experiments that can contribute to elucidation of the actual electronic structure, such as optical measurements under pressure.

In this communication we will report on the structural behavior of the $CuAlO_2$ delafossite under high pressure. We have performed energy-dispersive and angle-dispersive x-ray diffraction (XRD), and x-ray absorption measurements (XAS) up to 50 GPa in order to establish the $CuAlO_2$ equation of state and determine the evolution of the internal parameter. The sample was in powder or monocrystalline forms. In addition, total energy and band structure calculations were done by ab initio pseudopotential DFT-LDA methods.

From the XRD experiments we establish a considerable anisotropic compression of the unit cell, as happened in the related compound $CuGaO_2$[2]. Preliminary data analysis yields an equation of state given by V_0=39.46 Å^3, B_0=184 GPa and B'=3.87. A high-pressure phase transition is observed at 37±3 GPa. XAS experiments at the Cu K-edge on monocrystalline samples, including polarization, reveal the anisotropic environment of the Cu atom in the high pressure phase.

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Modification of polymer structure by new method of accumulation of high plastic deformation

Lately, new methods of severe plastic deformation based on simple shear, such as equal-channel multiple angle extrusion (ECMAE) and screw extrusion (SE), have been practicized on a large scale. They are widely used for the formation of nanostructural states in metals. In the case of ECMAE, a cylindrical billet is pressed through a unit consisting of several pairs of channels of one and the same diameter, which cross each other at preset angles. During the SE a prismatic billet is forced through a die having screw channel. Its geometry is such that shape and size of the deformed billet do not change. This paper studies possibilities of implementation of the mentioned methods of high plastic deformation accumulation for solid-phase modification of semicrystalline polymers.

The investigated were high-density polyethylene, low-density polyethylene and nylon-6. It has been determined that deformation according to ECMAE scheme results in the extreme dependence of microhardness H_μ on value of the accumulated strain e. The height of H_μ maximum was specified by polymer type and extrusion conditions. Distribution of H_μ over extrudate cross-section is not uniform, it varies with e. At the beginning, the highest values of H_μ correspond to peripheral sections, while the lowest ones – to the center. At high accumulated strain the distribution of H_μ becomes inverted: the maximum values are in the center. The SE provides the growth of H_μ. Moreover, its distribution over the cross-section is not uniform. It is shown that changes in structure taking place in polymers during ECMAE and SE are reflected in spectra of large-angle X-ray scattering and result in redistribution of spectral intensities of diffraction maxima. For deformed polymers, on the DSC curves there are additional peaks in the region of melting temperatures. The optical microscopy data show that under ECMAE and SE there occur the oriented supermolecular formations. They are best of all seen near the surface in regions where H_μ is changed the most.

The obtained results are explained with the attraction of representations on mechanisms of plastic deformation in semicrystalline polymers.

Direct Synthesis and Raman Study of $NO^+NO_3^-$ Ionic Solid and Novel N-O Molecular Crystal at High Pressures and Temperatures

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Nitrosonium-nitrate $NO^+NO_3^-$ was synthesized by a laser heating of a condensed mixture of oxygen and nitrogen compressed to different pressures, up to 40 GPa, in a diamond anvil cell (DAC). Investigation of Raman spectra of the $NO^+NO_3^-$ phase at different pressures and room temperature evidenced the pressure induced transformation of $NO^+NO_3^-$ ionic solid to N_2O_4 molecular crystal in the pressure range from 1 to 3 GPa. Raman data provide strong indications on a decreasing charge transfer between NO and NO_3 ion groups at low pressures. Obtained experimental results support the hypothesis of a rotational disorder of NO and NO_3 complexes and a high symmetry structure of nitrosonium-nitrate at low pressures.

Laser heating of N_2-O_2 mixture at pressures below 25 GPa results in formation of $NO^+NO_3^-$ phase together with a new N-O molecular phase. High-pressure / high-temperature Raman spectra collected from synthesized samples revealed a new crystalline phase of N-O molecular solid with stoichiometry NO_3. The new phase exhibits a considerable P-T domain of stability. Extrapolations of the melting curve of new N-O phase to temperatures below ambient show that this molecular crystal can be recovered at ambient pressure analogously to $NO^+NO_3^-$ phase. Comparative analysis of the Raman spectra of $NO^+NO_3^-$ and of new N-O phase showed discrepancies which can not be reconciled assuming the ionic nature of N-O compound. On the other hand, a resemblance of the fundamental vibrations of NO_3 ionic groups and new N-O solid allowed to identify a probable molecular stoichiometry and a possible molecular symmetry of NO_3 molecules. Unlike to Raman spectra of $NO^+NO_3^-$ compound, Raman spectra of a new N-O phase have smaller number of lattice modes, one of which exhibits a soft behavior, as well as characteristic features of disordered phases of ionic nitrates.

Oxygen Pressure Effects on superconducting (YBaCuO) thin films

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High oxygen pressures have been developed during these last fifty years in Materials chemistry mainly for stabilizing unusual oxidation states of transition metals or for controlling the oxygen stoichiometry in functional materials [1].

Some of us have recently shown [2] that amorphous $YBaCuO_{7+x}$ thin film deposited by sputtering at temperature T≤450°C have unusual oxidation state (x≥1) in opposite to the films $YBaCuO_7$ deposited at T~ 800°C on the single crystalline substrates (MgO or LaAlO3) which are crystalline and super conducting.

The aim of this study was to improve the oxygen distribution in YBaCuO thin film using an annealing treatment (T≤500°C) under oxygen pressures (P≤200MPa) of a composite system formed by cathodic sputtering at T~ 800° followed by deposition at T≤450°C . At first step a crystalline thin film of $YBaCuO_7$ on LaAlO3 substrate was formed followed by deposition on the top of amorphous $YBaCuO_{7+x}$ thin film.

Different physico-chemical characterizations have been developed after this high oxygen pressure treatment either for evaluating the oxygen depth distribution (RBS, Nuclear Reaction Analysis,…) or for following the physical properties (magnetic and electric measurements) of the YbaCuO super conducting thin film.

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SYNTHESIS OF AL$_X$GA$_{1-X}$N AND INN CRYSTALS UNDER HIGH PRESSURES

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We have performed synthesis studies of various III-V nitrides crystals, key materials for optoelectronic and high-power/frequency devices, using a cubic-anvil-type large volume high-pressure apparatus combined with *in situ* x-ray diffraction. Polly-crystallines of Al$_x$Ga$_{1-x}$N alloys covering a composition range of $0 \le x \le 1$ were synthesized by a solid-phase reaction under high pressure. *In situ* x-ray diffraction profiles were measured to observe the alloying process, which started at around 800ºC under 6.0 GPa. Single crystal of Al$_{0.1}$Ga$_{0.9}$N was also successfully obtained by slow cooling of its melt from 2400ºC at 6.5 GPa. For InN, its phase diagram was determined under high P-T conditions up to 20GPa and 2000ºC based on the *in situ* observations, which demonstrates that 19GPa and 1900ºC are needed for its congruent melting.

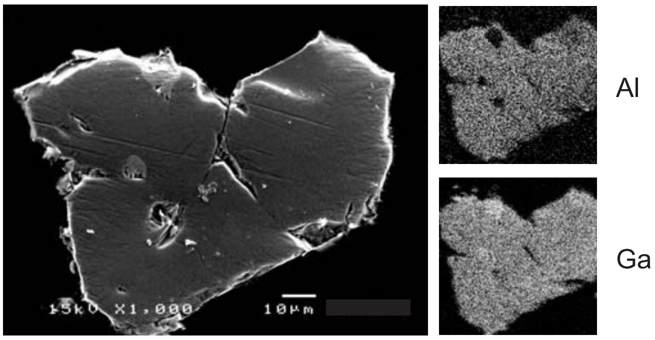

Figure 1 Al$_{0.1}$Ga$_{0.9}$N crystal synthesized from its melt at 6.5GPa and 2500°C

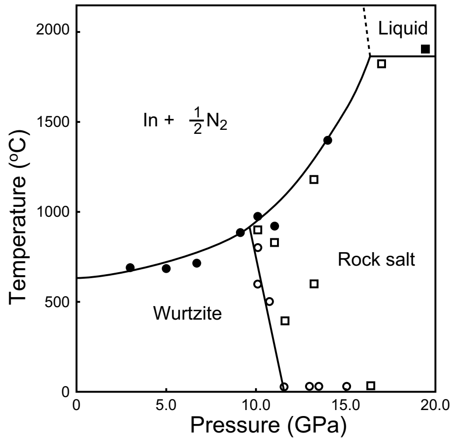

Figure 2 Phase diagram of InN at high P-T determined by *in situ* x-ray diffraction

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High Pressure Synthesis of Single Crystal of Lanthanum Manganese Oxide $LaMnO_3$

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Manganese oxides with perovskite structures have been widely used in solid oxide fuel cells (SOFCs), oxygen sensors and catalysts. Lanthanum Manganese Oxide, $LaMnO_3$, an important one of them, has been reported as a charge transfer type insulator [1] and an A-type antiferromagnetic (AFM) material. The doped $LaMnO_3$, which has been fueled by the colossal magneto resistance (CMR), exhibits a metal-insulator (MI) transition at the Curie temperature (Tc). Here we report the synthesis of single crystal of $LaMnO_3$ at high pressure and high temperature.

$LaMnO_3$ was prepared from La_2O_3 (Aldrich, 99.9%) and MnO_2 (Aldrich, 99.9%), which were mixed in stoichiometric proportion. The starting mixture with the presence of 4wt% distilled water was encapsulated in a sealed platinum tube with a diameter of 5 mm and a height of 12 mm, which was separated by MgO powder from a graphite tube. The experiment was run at 2GPa, 1200 ℃ for 12 hours in a piston-cylinder apparatus. Pressure was calibrated from melting of dry NaCl at 1050 ℃ [2] and the transformation of quartz to coesite at 500 ℃ [3]. Temperature was measured by inserting a Pt-Pt90%Rh10% thermocouple into the high-pressure cell. The sample was quenched before the pressure was released. And the product was characterized by, single-crystal and powder X-ray diffraction (XRD), scanning electron microscope (SEM) and superconducting quantum interference device (SQUID).

Comparison with the traditional synthesis method, big single crystal of $LaMnO_3$ has been obtained by means of high-pressure method.

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$GdHoSi_2O_7$: First Double Rare Earth Elements Disilicate Synthesized Under High Pressure and Temperature

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The single rare earth element (REE) disilicate are of increasing technological interest because of their electrical, optical properties and their application to optimize the properties of ceramic [1,2]. REE disilicate has a complex structural chemistry at room pressure due largely to the monotonic decrease in sizes of the REE^{3+} cation through the lanthanide series. Twelve distinct structure types already have been reported (A, B, C, D, E, F, G, H, I, J, K, and X). It is well known that 14 rare earth elements have the nearly-identical chemical character, with only little increase of covalency from La to Lu. Therefore, it is possible to make up the double REEs disilicates under the conditions of high pressure and high temperature. Herein, we report the synthesis of double-REE disilicate of $GdHoSi_2O_7$.

Single crystal $GdHoSi_2O_7$ was prepared by direct reaction of stoichiometric amounts of $REEO_3$ (Gd_2O_3, Aldrich, 99.9%; Ho_2O_3, Aldrich, 99.9%) in the presence of 3~4 wt% distilled water and amorphous SiO_2 (Alfa Aesar, 99.999%) at 2.5GPa, 1450°C for 12 hours in a piston-cylinder apparatus. Pressure was calibrated from melting of dry NaCl at 1050°C and the transformation of quartz to coesite at 500°C. The experimental temperature was monitored by inserting a Pt-Pt90%Rh10% thermocouple into the high-pressure cell. The starting mixture was encapsulated in a sealed platinum tube with a diameter of 5 mm and a height of 12 mm, which was separated by MgO powder from a graphite tube. The experiment was quenched before the pressure was released. The product was characterized by optical polarizing microscopy (Olympus BX-51), single-crystal and powder X-ray diffraction (XRD) and superconducting quantum interference device (SQUID).

Under high pressure and high temperature, the first double REEs disilicate $GdHoSi_2O_7$ has been successfully synthesized and the measurement of its physical properties is still in progress.

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Stability of micro- and meso-porous materials under high pressure

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Micro- and meso-porous materials with three-dimensional open framework structures, are of great importance in many fields of applied chemistry, such as catalysis, adsorption, separation and host-guest chemistry [1]. But, because of their low thermal and hydrothermal stability, many of their applications have been undoubtedly limited. Mokaya [2] reported that the stability of mesoporous materials can be greatly improved by enhancing the local ordering of the walls. Wu et al. [3] investigated the properties of some mesoporous materials. We studied the properties of mesoporous materials under the conditions of high pressure and high temperature.

Micro- and meso-porous materials NaY zeolite and MCM-41 are used as starting materials, respectively, which were synthesized by hydrothermal reaction in Teflon-line autoclave. High pressure and high temperature experiment was carried on by means of piston-cylinder apparatus. Pressure was calibrated from melting of dry NaCl at 1050°C and the transformation of quartz to coesite at 500°C. Inserting a Pt-Pt90%Rh10% thermocouple into the high-pressure cell monitored the experimental temperature. The starting material was put into h-BN capsule with a diameter of 5.3 mm and a height of 8 mm. The experiment was quenched before the pressure was released. The product was characterized by powder X-ray diffraction (XRD) and thermogravimetric-differential thermal analysis (TG-DTA).

With changes of pressure and temperature, NaY zeolite transformed into another zeolite or inorganic salt and peak position of XRD of MCM-41 shift to high-angle region, indicating a slight shrinkage in pore size and a slight increase in the thickness of the pore walls.

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Uniaxial stress influence on transport properties of 2D holes at p-GaAs/$Al_{0.5}Ga_{0.5}As$ heterointerface under the condition of low temperature photoconductivity

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Negative photoconductivity (NPC) arises in p-GaAs/$Al_{0.5}Ga_{0.5}As$ heterostructures under illumination by a red light emitting diode (LED) below 6K and reveals strongly thermoactivated character [1]. The thermoactivated NPC effect can be described in a model with deep donor-like traps (DDLT) situated near a heterointerface just below the Fermi level (FL) if an energy barrier E_B between the ground and excited by light DDLT states is introduced [1]. We have used uniaxial stress as an external perturbation for additional checking of the model from Ref. 1.

Resistivity and the Hall effect have been measured in 2D hole system at (100) p-GaAs/$Al_{0.5}Ga_{0.5}As$ heterointerface under a combined influence of illumination by a red LED with photon energy 1.9 eV and uniaxial compression up to P=3.4 kbar along [110] direction. 2D hole density p and mobility μ were determined under these conditions in a temperature interval 1.7-20 K.

At 1.7 K carrier density decreases under compression with almost the same average rate $dp/dP = (0.23 \pm 0.03) \times 10^{11}$ cm^{-2}/kbar both in illuminated and dark states. It permits to suppose that at a fixed temperature pressure dependence of this quantity reflects the band structure change near a heterointerface and is not affected by the NPC effect. Just along with this assumption, the value of the barrier $E_B = (3\pm1)$ meV calculated from the temperature dependence of carrier density at the thermoactivated NPC condition remains unchanged under pressure up to 3.4 kbar.

2D hole mobility μ, the other transport property that determines the thermoactivated NPC effect, decreases with temperature below the NPC transition point T = 6 K, and this decrease starts to be much stronger under uniaxial compression: at 1.7 K and P = 3.4 kbar the mobility is 3.5 times less than its value at P = 0. Numerical calculations, performed with all scattering mechanisms at low temperature taken into account [2], indicate that at any pressure the decrease of mobility in the thermoactivated NPC effect is governed by DDLT that are ionized under illumination. According to the calculations, these traps are located at distances 10-50 nm from a heterointerface and their contribution to the scattering processes and mobility decrease becomes more significant under uniaxial stress.

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high-pressure synthesis of the $PbZr_{0.52}Ti_{0.48}O_3$

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Abstract

A lot of attention was given recently both on the electrical and magnetic properties and the preparation method of the perovskite oxides, as the properties depend very much on the synthesis. The pressure, which is similar to temperature and composition, would also influence the structure and properties of solid materials to a certain extent. Therefore, searching materials having excellent properties and the optimal preparation conditions by the high-pressure synthesis method is desirable. In this work, the high-pressure synthesis of the Lead zirconate titanate ($PbZr_{1-x}Ti_xO_3$ or PZT) ceramics has been investigated.

Two kinds of precursors were prepared as follow: (1) a mixture of PbO (99.95%) and ZrO_2 (99.95%) and TiO_2 (99.95%). The molar ratio of PbO, ZrO2 and TiO_2 in the precursor was 1:0.52:0.48. (2) A mixture of PbO and $Zr_{0.52}Ti_{0.48}O_2$ in molar ratio of 1:1. Here $Zr_{0.52}Ti_{0.48}O_2$ was prepared by heat-treated at 1300℃ for 10h after a (0.52:0.48) mixture of ZrO_2 and TiO_2 was ball-milled for 4h. The above precursors were presses by a belt-type press under different pressure and at different temperature for 30min, respectively. The XRD results showed that using a mixture of PbO and ZrO_2 and TiO_2 as precursor, the mixtures of $PbTiO_3$ and ZrO_2 and Pb were obtained in the prepared products under 1.5Gpa and 3.6 GPa at above 880℃. The $PbZr_{1-x}Ti_xO_3$ solid solution has not been formed. Using a mixture of PbO and $Zr_{0.52}Ti_{0.48}O_2$ as precursor, under the condition of 1.5GPa the $PbZr_{0.52}Ti_{0.48}O_3$ perovskite oxide can be obtained only at 710-812℃.

The Raman spectra were measured at room temperature and the relation between the structure of final materials and synthesis conditions has been studies. Three bands could be observed in the samples synthesized under 1.5GPa and 710-812℃. The results indicated that the samples were the single-phase $PbZr_{0.52}Ti_{0.48}O_3$ perovskite structure. The thermal expansion of the single-phase sample has also been investigated from 100℃ to 500℃.

high-pressure synthesis and properties of the perovskite oxide $SmCoO_3$

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Abstract

In electrochemical devices, such as direct methanol fuel cells (DMFCs) or proton exchange membrane fuel cells (PEMFCs) or solid oxide fuel cells (SOFCs), use of ceramic compounds as electrodes might be an important technology innovation. The transition metal perovskite oxide $SmCoO_3$ has been selected as candidate material for this application. Rare earth perovskite preparation technique (synthesis method and subsequent calcining procedures) has a significant influence on its electrical property and catalytic activity. In this work, the high pressure synthesis method was used to synthesize the perovskite oxide $SmCoO_3$.

Using Co_2O_3(99.99%) and Sm_2O_3(99.99%) as precursor, the mixtures were presses by a belt-type press under the pressure of 1.5-4.2 GPa at 1060℃ and under 3.9GPa at the temperature of 710-1230℃, respectively. The XRD results showed that the mixtures of Co_2O_3 and Sm_2O_3 can form the perovskite oxide $SmCoO_3$ above 2.75GPa and 1060℃, but the product is in mixture state. The single-phase perovskite oxide $SmCoO_3$ can be obtained only under the condition of 3.9GPa at 1060℃. Three bands could be observed in the room temperature Raman spectra of the sample synthesized under 3.9GPa and 1060℃. The clearly observed band and the most intense was at 170 cm^{-1}. Two very weak bands were at about 470 cm^{-1} and 680 cm^{-1}, respectively. The result indicated that the sample has the orthorhombic *Pnma* structure.

The electrical conductivity and thermal expansion of the single-phase $SmCoO_3$ synthesized under high pressure have also been investigated in the temperature range of 100-800℃. The conductivity increases with temperature increasing, and a semiconductor to metal transition occurs. But the conductivity of the $SmCoO_3$ synthesized under high pressure was lower than the sample prepared by calcinations, and the reason has been discussed.

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High Pressure Effects on the Structure and Electronic Property of $CaCrO_3$

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Chromium oxides have been widely used as a kind of functional materials since decades years ago. But chromium (IV) oxides with ABO_3 perovskite structure are rare at ambient pressure due to the unusual electronic distribution of Cr^{4+}, and these compounds only can be synthesized under high pressure high temperature (HPHT). Goodenough et al firstly synthesized $CaCrO_3$ under HPHT in 1960s. Since then investigation on this compound is very rare. We also synthesized $CaCrO_3$ recently using similar method and studied the high pressure effects on structure and electronic properties of $CaCrO_3$. *In-situ* high pressure energy dispersive x-ray diffraction measurements with the diamond-anvil cell (DAC) using synchrotron radiation showed the basic crystal structure of $CaCrO_3$ was stable under pressure up to 31GPa. From the P-V/V_0 relationship we found an isostructure phase transition at about 6GPa. According to the Birch-Murnaghan equation of state, we obtained the bulk modulus to be 113GPa in lower pressure region and 152GPa in higher pressure. The electrical and magnetic properties of the sample were further investigated.

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HIGH PRESSURE STUDIES OF MULTIFERROIC FERROELECTROMAGNET BIMNO$_3$

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It is noteworthy that a novel interplay between magnetic and electric property in 3d transition metal oxides has emerged over the past several years, termed as multiferroic. By definition, multiferroic is a group of materials possessing two or more of ferroelectric, ferromagnetic and ferroelastic ordering simultaneously. Although the investigation history of multiferroic can be traced back to the 1950's, its perspective of potential applications including next-generation spintronic devices and high density data storage were corroborated till recently by the discovery of so-called colossal magnetodielectric effect in manganites[1]. The goal of our work is to exploit the multiferroic nature of Bismuth Manganite(BiMnO$_3$). Samples were synthesized under high pressure conditions. We have revealed the ferromagnetic nature of BiMnO$_3$ by magnetization measurement. The ferroelectric nature is partially disclosed through structural phase transition and polarization measurement.

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20th AIRAPT and 43th EHPRG Meeting

Synthesis of Boron Doped Diamond with Diamond Anvil Cell

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Recently the superconductivity was found in the boron-doped diamond synthesized at high pressure high temperature (HPHT) with toroid type high-pressure apparatus at 8–9 GPa, 2,500–2,800 K.[1] This initiates the new round of research fever on boron doped diamond. In this report, boron-doped diamond has been synthesized from graphite mixed with different ratio of B_4C at HPHT using laser heating diamond anvil cell. The starting composition was transformed to diamond compound at pressure ~9GPa, 2200K-2600K as indicated by the in-situ x-ray diffraction pattern with synchrotron radiation source. Raman spectrum of the recovered specimen from HPHT state confirmed that boron has been doped into diamond lattice.

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X-ray topographic and photoluminescence studies of HT-HP treated nitrogen doped silicon crystals

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One of the recent ideas in silicon technology concerns the nitrogen doping moderating the precipitation of oxygen in Czochralski silicon (Cz-Si) during high temperature technological processes. The studies of Cz-Si:N after the high pressure–high temperature treatment have been proven to be useful for understanding the interaction of N and O impurities [1-2].

The 2 mm thick samples with nitrogen concentration, $c_N \leq 5 \times 10^{14}$ cm^{-3}, and oxygen concentration, $c_O \approx 9 \times 10^{17}$ cm^{-3}, cut out from [111] grown crystal, were treated for 5 h at temperatures from 1070 to 1400 K under hydrostatic pressure of argon up to 1.4 GPa. The methods of characterization included synchrotron monochromatic beam topography and rocking curve measurements in 333 reflection of 0.1117 nm radiation. The samples were also studied by photoluminescence methods at 10 K.

The HT-HP treatment did not cause the formation of oxygen related inclusions, usually formed at 1270 K in nitrogen free Cz-Si. The oxygen precipitates producing distinct black-white contrast were observed after the treatment at 1400 K under 1.4 GPa. They produced increased X-Ray diffuse scattering on the tails of RCs while the full widths at the half maximum did not increase. An explanation of the effects induced by the HT – HP treatment in Cz-Si:N has been proposed.

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Crystal structure of $LaAlO_3$ perovskite synthesized under high pressure

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Structural investigations of $LaMO_3$ perovskites (M = Al, Ga, Mn, Fe, Co, Ni, *etc.*) have been carried out intensively in connection with their interesting physical properties. It is known, especially, that $LaAlO_3$ perovskite has rhombohedral symmetry (space group $R\overline{3}c$) under 1 atom and room temperature. However, the details of crystal structure of this perovskite under high pressure have not been reported. In the present study, we report on high-pressure synthesis of $LaAlO_3$ perovskite and its crystallographic characterizations.

$LaAlO_3$ perovskite were synthesized at 4.5 GPa using a 700-ton cubic anvil type of high-pressure apparatus. A 12.5 mm cube of pyrophyllite was used as a pressure medium. Special grade reagents (99.99%) of La_2O_3 and Al_2O_3 were used as starting materials, and mixed well together with NaCl + KCl flux in the molar ratio $La_2O_3 : Al_2O_3 : NaCl : KCl = 1 : 1 : 2.5 : 2.5$. Pressure was increased slowly up to 4.5 GPa, and then temperature was elevated slowly up to 1400 °C. After being kept under this condition for 15 minutes, the sample was cooled slowly down to 1000 °C at the ratio of 0.8 °C/min and then quenched by shutting off the electric power supply. The pressure was released slowly and the sample was recovered to the ambient condition.

A synthesized crystal of $LaAlO_3$ perovskite was characterized using a four circle diffractometer. The result showed that the crystal has orthorhombic symmetry with lattice parameters of $a = 5.1087(3)$ Å, $b = 5.8744(3)$ Å, $c = 8.2581(5)$ Å, $V = 247.83(2)$ Å^3. These lattice parameters suggest that it is isostructural with $GdFeO_3$-type perovskite (the space group *Pbnm*). We will discuss the detailed structure of the synthesized crystal. Moreover, we will report on the results of *in-situ* high pressure experiments of $LaAlO_3$ perovskite.

Synthesis of cBN by Direct Current Arc Discharge Method

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Cubic boron nitride (cBN) has a unique combination of a number of highly desirable mechanical, chemical, thermal, electrical and optical properties [1,2]. In particular, it is superior to diamond in that it does not react with ferrous metals readily. Further more, because cBN is a wide bandgap (E_g≈6eV) semiconductor with a good thermal conductivity, it has the potential usage in high temperature and high power electronic applications. Thus the deposition of cBN thin films as well as the synthesis of bulk cBN materials has attracted extensive worldwide efforts.

In this paper, we will report the synthesis of cBN nanocrystals by the direct current arc discharge method with hBN and NH_3 as the starting material and the working gas, respectively. By this method, we have fabricated nano-scaled cBN crystals under high temperature (3000K) and low pressure (10 kPa) conditions. We suggest that the growth of cBN undertakes a sublimation–re-hybridization–crystallization route. The sublimation of $(BN)_x$ segments is caused by the high temperature and the bombardment of high energy particles. Then the segments transform from sp^2-hybridized to sp^3-hybridized bonding on adsorptions of H, NH, NH_2 or NH_3 radicles. At last, during the fast refrigeration process the crystallization of cBN occurs. The kinetic barrier hindrance is thus overcome by the cooperation of extremely high temperature and bombardment of high-energy particles.

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Atomic structure of Ultra Fine Grained Metals after Intensive External Influences at Study under High Pressures

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Nowadays, the problem of producing ultra fine grained metals with 10-200 nm grain size is among actively developing scientific problems. It is already known that such metals possess unique physical and mechanical characteristics.

In this respect, the reviewed paper aimed at the influence of severe plastic deformation and radiation on atomic structure of ultra fine grained metals is urgent.

The investigation objects were polycrystalline Iridium, Tungsten, Nickel and Copper metals (initial grain size ≈ 20-50 μm).

It has been revealed that in ultra fine grained Iridium influenced be severe plastic deformation a grained structure is formed (the grain size of 20-30 nm), but in the bodies of grains there are practically no defects of structure, however, after irradiation a sub-grain structure, (sub-grain size of 3-5 nm) is formed, and in the bodies of sub-grains there are defects.

The sub-grain structure in the surface and near surface volumes of Iridium was for the first time found as the resulting from the implantation of argon ions at distances, which are the order of magnitude larger than the projective path of argon ions from the irradiated surface.

The sub-grain structure was also revealed in ultra fine grained Nickel and Copper after severe plastic deformation effect (sub-grain size of 3-15 nm), but in the latter case the observed boundary region is broader and the ultra dispersive sub-grain are highly disoriented.

HIGH PRESSURE STUDIES OF EuO

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Abstract

The rare-earth monochalcognides under pressure have been investigated experimentally in the last decades because of their interesting optical, magnetic and electrical properties. Out of these systems, studies of europium monochalogenides EuX [X = O, S, Se, Te] have received a renewed attention because of their technological importance [1-4]. These EuX compounds are semiconducting if the rare–earth ion is in the divalent state and metallic if that is in the trivalent state [4]. Since recently, we have carried out similar calculations on the pure Se, Te and EuS, EuSe, EuTe [4-5], it is tempting to take up the whole series purely from theoretical point of view. In this EuX series, this paper reports ab-initio calculations which have been carried out to study the pressure–induced structural transitions and structural stability of the EuO compound. This paper also reports lattice parameters and bulk modulus values at different pressures for both phases. The first principal tight-binding linear muffin-tin orbital method (TB-LMTO) within local density approximation (LDA) has been used to study the band structure. The phase transition from NaCl (B1) type to CsCl (B2) type structure have been studied and compared with that of experimentally observed value. The bulk modulus values are found to be in agreement with earlier experimental results.

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Effect of Pressure on Superconducting and Stripe Phases in $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ Single Crystals

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Single crystals of $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ were grown by the traveling-solvent floating–zone method. Sr- content was checked by electron-probe microstructure analysis, and the ab- and ac-planes were identified by Laue X-ray diffraction technique. Resistivity was measured by the standard dc four-probe method with gold paste attached as electrodes, which were annealed under flowing oxygen atmosphere at 900°C for a few hours in order to reduce contact resistance. A piston-cylinder teflon-pressure cell was used for hydrostatic pressure with fluorinate liquid No.#70 as a pressure medium. Hydrostatic pressure effect on superconducting transition temperature and the structural transition temperatures were measured upto 1.0 GPa in the $La_{1.25}Nd_{0.6}Sr_{0.15}CuO_4$ single crystals. We found that the low temperature tetragonal phase was suppressed with drastic increase of T_c at a low pressure of ~ 0.1GPa. By comparing the pressure effect on $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ single crystals, we confirm that pressure is an effective two-way control parameter for controlling stripes and superconductivity in La-Nd-Sr-Cu-O single crystals.

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About the synthesis and stability of graphitic carbon nitrides

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Light element-based materials, belonging to the boron-carbon-nitrogen system, exhibit strongly covalent bondings wich implies exceptional properties, particularly on a mechanical point of vue. Taking into account the theoretical calculations of Liu and Cohen who claim a tridimensional C_3N_4 material harder than diamond, we have focused our attention on such a material [1,2]. Many attempts have been made by other groups to synthetize this hypothetical material by means of a variety of techniques such as physical vapor deposition (PVD), chemical vapor deposition (CVD)… Concerning our group, instead of trying the direct synthesis of tridimensional bulk carbon nitride, we have first performed the synthesis of the C_3N_4 graphitic form and then studied its structural behaviour under very high pressure.
This synthesis was successful with a high pressure (2,5 GPa) - high temperature (800°C) treatment of melamine in presence of hydrazine [3]. We present here a new way of preparation for graphitic C_3N_4 at moderate pressure and temperature. Samples have been characterized by XRD, XPS, thermal analysis, IR spectroscopy, Scanning Electron Microscopy. The influence of chemical composition on the stability of the graphitic phase will be discussed.

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20th AIRAPT and 43th EHPRG Meeting

A new high pressure synthesized Cl -0201 superconductor induced by apical oxygen doping

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The crystal structure of high T_c superconductors (HTS) is built of the charge reservoir block and $[CuO_2]$ conducting layer, while the connection between the charge reservoir and $[CuO_2]$ conducting layer is the apical oxygen. Intensive efforts have been made in studying the apical oxygen of HTS.[1, 2] The novel superconducting homologous series Cl-02(n-1)n provide an ideal system to study “apical oxygen” topic. Since the divalence oxygen is heterovalence with the monovalence chlorine, it is possible to induce hole carriers in the compounds simply through substituting O^{2-} for Cl^{1-}, namely by “apical oxygen doping” to induce high Tc superconductivity. The process becomes thermodynamically accessible under high pressure high temperature. This was first realized in the double $[CuO_2]$ layered copper-oxychloride compound $(Sr,Ca)_3Cu_2O_{4+d}Cl_{2-y}$.[3] Using the apical oxygen doping mechanism, for the first time we have been able to synthesize a new single $[CuO_2]$ layered copper oxychloride superconductor $Sr_2CuO_{2+\delta}Cl_{2-y}$ under high pressure high temperature. The magnetic susceptibility as well as resistance measurements indicated that the bulk superconducting transition temperature (T_c) of the sample is 30K.

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High Pressure Synthesis, structure, and superconductivity of $Sr_2CuO_{3+\delta}$

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Sr-Cu-O system has been extensively viewed as a simple composition to build up high Tc superconductors. At ambient pressure, Sr_2CuO_3 forms an orthorhombic structure with CuO chains along the *a*-axis. Studies on Sr_2CuO_3 have revealed that extra O atoms can be incorporated between chains, and in some cases result in the superconducting properties [1]. Therefore $Sr_2CuO_{3+\delta}$ is a useful material to investigate the additional oxygen, their ordering and the tuning effects on superconductivity. Here we report the synthesis, structure evolution and superconductivity with additional oxygen content of the tetragonal $Sr_2CuO_{3+\delta}$. A series of polycrystalline samples with the nominal δ up to 0.9 were prepared under 6.0 GP at 1100°C. A single-phase $Sr_2CuO_{3+\delta}$ superconductor was synthesized using a high-pressure technique. A systematic variation of T_c has been observed as a function of oxygen content. The onset T_c at 75 K of the as-prepared high pressure synthesized sample could be enhanced up to 95 K by post anneal treatment. This ranks one of the highest Tc in a cuprate superconductor that contains only one [CuO2] plane.

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A Designed New Ferromagnetic Ferroelectric Bi_2NiMnO_6

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Recently magnetic ferroelectrics attract much attention because of the possible applications for the data storage and sensor devices. Fascinating coupling between magnetism and dielectric properties is also expected. Unfortunately, magnetic ferroelectrics are rare in the nature and most of these are antiferromagnet with small response to the external field. A classical way to obtain a magnetic ferroelectric is to locate Bi^{3+} ion and a magnetic transition metal ion on A and B sites of a perovskite structure so that the $6s^2$ lone pair of Bi ion and the strong covalent character of Bi-O bond stabilize a noncentrosymmetric distorted structure. According to Kanamori-Goodenough rule, a ferromagnetic insulator can be obtained by distributing 2 kinds of transition metal ions with and without e_g electrons in a NaCl type configuration. We have succeeded in preparing such designed ferromagnetic ferroelectric double perovskite (a perovskite where the B site is occupied by 2 kinds of elements) Bi_2NiMnO_6 by means of high-pressure synthesis at 6 GPa. Structure analysis by synchrotron X-ray powder diffraction confirmed the noncentrosymmetric monoclinic (space group *C*2) structure and the NaCl type configuration of Ni^{2+} and Mn^{4+} ions. This compound showed ferroelectric and ferromagnetic transitions at 440 and 140 K, respectively.

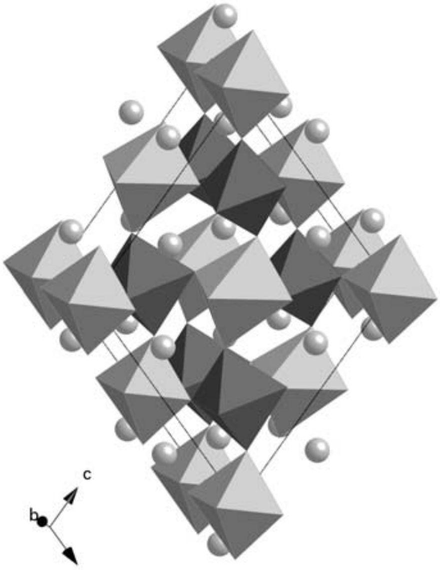

Figure: Crystal structure of Bi_2NiMnO_6. Dark and bright octahedra correspond to $Mn^{4+}O_6$ and $Ni^{2+}O_6$, respectively.

Investigation of Fe and C_{60} interaction under high pressure and shear deformation

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Discovery of fullerenes and rapid development of the synthesis techniques for various forms of nanocarbons (such as nanotubes) stimulates development of a new family of so called nanostructured materials. High-pressure-high-temperature is probably one of the most powerful techniques that allow producing a large variety of bulk, 100% dense materials with nanostructure.

We report on results of investigation of a Fe-C nanocomposite material created by means of high-energy (ball milling) pre-treatment of iron and fullerene C_{60} followed by high-pressure-temperature treatment. The high-pressure-temperature treatment was of two types: 1) quasi-hydrostatic pressure of 7.7 GPa and different temperatures; 2) different pressures plus shear deformation at ambient temperature.

Ultrasonic pulse (microacoustic) technique at frequency 25 MHz was applied to study elastic properties of the samples. Optical microscopy, electron microscopy, scanning probe microscopy and microhardness investigations were carried out to study the structure and properties of the obtained samples.

Dependencies of the mechanical and structural properties on the chemical composition and pressure treatment were investigated. It was found that the properties might be as high as: 210 GPa for bulk modulus; 100 GPa for shear modulus; 260 GPa for Young’s modulus; 16 GPa for microhardness.

Novel Hydrides of RMn_2 Laves Phases Synthesized under Hydrogen Pressure

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Recently a novel hydride YMn_2H_6 has been synthesized from C15 Laves YMn_2 [1,2] under the hydrogen pressure. According to X-ray and neutron powder diffraction experiments YMn_2H_6 crystallizes in the Fm-3m space group with a=6.709(1) Å at 300 K. Thus the initial C15 structure is strongly rearranged to form the structure in which the Y and half of the Mn atoms occupy statistically the 8c site whereas the other Mn atoms, located in 4a site are surrounded by 6 H atoms (24 e). According to our knowledge such kind of hydride has never been observed in hydrides derived from Laves intermetallics. The systematic investigations of RMn_2 Laves (where R is rare earth) was started; first we wanted to prove whether the structure Fm-3m analogous to that of YMn_2H_6 can be obtained when parent metal has C14 type symmetry. We confirmed such possibility for $ErFe_2$ finding novel hydride $ErFe_2H_6$ with Fm-3m structure – the same as YMn_2H_6.

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Characteristics of Bi-Pb-Sr-Ca-Cu-O(BPSCCO) particles prepared by shock-compacted technique

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Shock compaction for high-T_c Bi-Pb-Sr-Ca-Cu-O (BPSCCO) particles have been investigated to obtain higher critical current density (J_c) by shock-compaction technique in order to overcome the weak-link problem around the grain boundaries for higher J_c. As one of the research for electronic devices, BPSCCO oxide superconductors are very attractive material as a highly sensitive magnetic sensor.

In the present research, calcined BPSCCO particles with the average particle size of 2.8 μm was used. After the process of the shock compaction under about 4 GPa and annealed at 850°C for 48 hours, the ΔM (difference of susceptibility obtained from the temperature dependency of field cooling and zero field cooling at 20 Oe) which is proportional to J_c is measured by SQUID magnetometer. As a result, it is found from the susceptibility measurements as a function of temperatures that ΔM clearly increases to 0.0437 emu/g at 5 K and 0.0329 emu/g at 77.4 K for shocked BPSCCO particles after annealed at 850°C for 48 hours, which seems to indicate the new pinning centers around the grain boundaries caused probably by the new defects of vacancies.

Adiabatic Expansion of Shock-Compressed Zinc and Chromium. Equations of State of Metals at High Pressures and Temperatures

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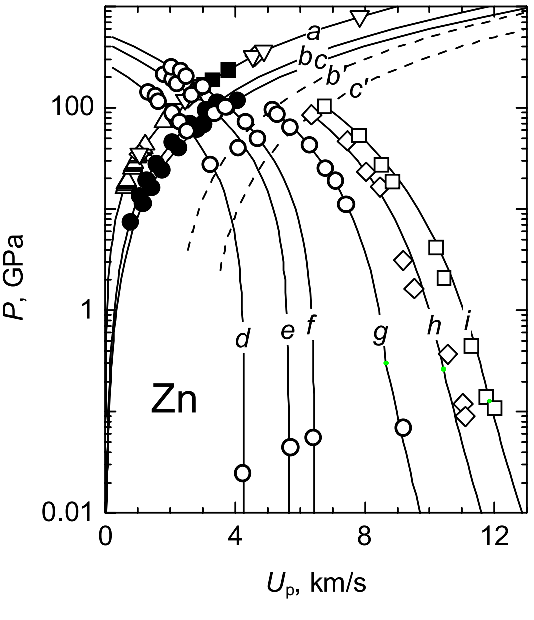
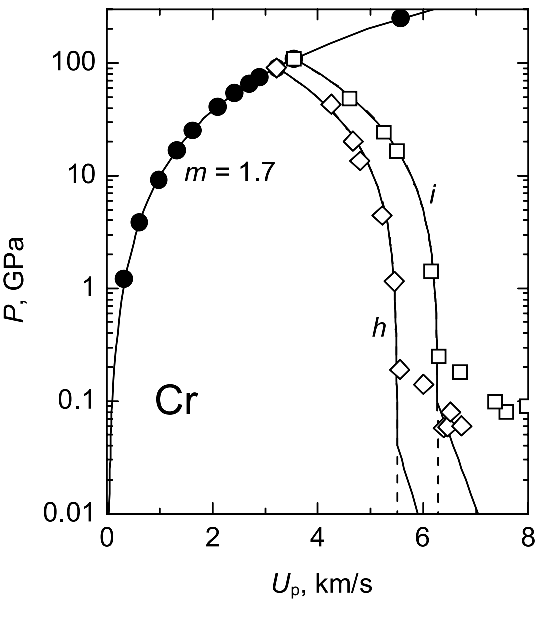
In this work experimentally investigated is expansion of shock-compressed Zn and Cr in adiabatic release waves. Dense liquid states with densities of $\rho \approx 1.2\rho_0$ (where ρ_0 is normal density of metals) and temperatures of $T \sim 14$ kK are generated by shock compression of porous samples up to pressures of 110 GPa. We have measured parameters of both metals on two release isentropes (curves *h* and *i* in figures, new data are denoted by open squares and diamonds) in density range down to $\sim 0.01\rho_0$. The onset of evaporation of Cr is experimentally fixed as additional increase of the expansion rate within the two-phase liquid–vapor region on the phase diagram.





We propose new semiempirical equations of state for Zn and Cr with taking into account the melting, evaporation and ionisation effects. The critical analysis of calculated results in comparison with the newly acquired and available at high pressures and temperatures experimental data is made.

Raman study of olivine under high pressure and high temperature

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Since olivine is believed to be an important phase in the Earth's upper mantle, the characterization of olivine at high pressures and temperatures is an essential part of the earth sciences. The compressional behavior of olivine has been widely studied, but *in-situ* high pressure and high temperature Raman behavior of olivine is less investigated.

In this paper, Raman spectra of olivine have been studied at temperature from 293k to 773k and at pressure to16 GPa in an externally heated diamond anvil cell. We have obtained pressure and temperature dependence of Raman shift. The evidence for the occurrence of phase transition is not presented within the range of conditions investigated.

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Viscosity of liquid Fe-S up to 16 GPa

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Viscosity of liquid Fe-alloy is closely related to convection behaviour of Earth's liquid outer core and also time scale of planetary core formation. In this study, we have measured viscosity of liquid Fe-S up to 16 GPa using in situ X-ray radiography falling sphere method.

Falling sphere viscometry was performed under high pressure and temperature using high speed CCD camera combined with 1500 ton MA-8 Kawai-type multi-anvil device at BL04B1, SPring-8 in Japan. We used WC anvil cubes with truncated edge length of 5 mm. Anvil gap was ~ 2 mm before compression and ~ 0.8 mm at 16 GPa. Starting material was powdered $Fe_{69}S_{31}$ which corresponded to the estimated Martian core composition [1]. Viscosity marker sphere, which was made of Rhenium with a diameter of approximately 140 μm, was put in the upper part of the sample. BN capsule and $LaCrO_3$ furnace were used. Experimental pressure was determined from lattice parameters of MgO pressure marker which was located outside the furnace.

Falling of the spheres were observed at 14 GPa, ~ 1427 K and 16 GPa, ~ 1527 K. Measured viscosity at 200-400 K above the melting point of the sample shows similar viscosity as previously measured for liquid Fe-S up to 7 GPa ($\sim 10^{-2}$ Pa-s) [2]. Therefore, activation volume of the viscous flow is estimated to be quite small as previously suggested (~ 1.5 cm^3/mol) [2]. However, it is necessary to examine the activation energy precisely at the same pressure range to correct the effect of temperature.

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Liquid immiscibility of Fe-FeO and Fe-FeO-FeS system at high pressure and implication for the terrestrial planets

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Melting experiments of Fe-FeO-FeS system has been conducted in Kawai-type multi-anvil apparatus at 15 and 18GPa, and up to 2300°C. At 15 GPa and up to 2200°C, we observed the quenching texture of immiscible two liquids using starting composition of Fe-11.9wt.%O and Fe-10.4wt.%O-2.6wt.%S, whereas one liquid using Fe-8.7wt.%O-7.5wt.%S. At 18 GPa and up to 2300°C, we observed immiscible two liquids using Fe-11.9wt.%O, whereas one liquid using Fe-10.4wt.%O-2.6wt.%S. At 15GPa, our experimental results show that liquid miscibility gap is narrower than previous study [1]. At I atm, Fe-FeO-FeS system has a large miscibility gap [2], but our experimental results indicate that it narrows at high pressure. Both oxygen and sulfur can be in the Earth’s core because the Earth has experienced a moderately high-pressure differentiation., In contrast, oxygen is not likely to incorporated in the Fe-S rich core like Mars and Ganymede because they may have experienced the low-pressure differentiated processes.

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Solubility of silicon and oxygen in liquid iron coexisting $(Mg,Fe)SiO_3$-perovskite and implications for core formation

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Solubility of silicon and oxygen in liquid iron coexisting $(Mg,Fe)SiO_3$-perovskite was investigated at 27 GPa and 2320-3040 K to discuss the core formation process and light elements in the earth's core. These light elements were dissolved into liquid iron to form the core during core formation process. Deep magma ocean is supposed to have extended to a depth of lower mantle in the core formation stage (e.g., Ohtani et al., 1997[1]). Reaction between the liquid iron and $(Mg,Fe)SiO_3$-perovskite, which is the most dominant mineral in lower mantle, must have occurred at base of the magma ocean and could have provided silicon and oxygen as the light elements into the liquid iron. Knittle and Jeanloz (1991)[2] and Hillgren and Boehler (2000)[3] have studied this reaction with a laser-heated diamond anvil cell. However their results are controversial perhaps because of a large temperature gradient in the sample and possible difference in the fO_2 conditions. In this study, high-pressure and temperature experiments have been conducted with a Kawai-type multi-anvil apparatus in order to obtain more reliable results on this reaction and solubility of Si and O in the liquid iron. A reaction between liquid iron and $(Mg,Fe)SiO_3$-perovskite to form magnesiowustite and the liquid iron containing silicon and oxygen was clearly observed at relatively reducing conditions at 2640 and 3040 K at 27 GPa. The silicon solubility in the liquid iron increases with decreasing the solubility of oxygen at a constant temperature. A combination of the solubility of silicon and oxygen significantly increases with increasing temperature at a constant pressure of 27 GPa. This implies a possibility that silicon and oxygen are plausible candidates for the light elements in the Earth's core.

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New high-pressure phase of Al_2O_3 and implications for Earth's D" layer.

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Alumina (Al_2O_3) is an important ceramic material and a major component of the Earth's mantle. According to theoretical [e.g., 1] and experimental [e.g., 2] studies, above 80 GPa corundum transforms into the Rh_2O_3(II)-type structure, and it was expected [1] that above 200 GPa a perovskite-type phase becomes stable.

Using *ab initio* simulations (we have calculated the full *P-T* phase diagram) and high-pressure experiments, we show that a $CaIrO_3$-type phase, isostructural with the post-perovskite phase of $MgSiO_3$ [3,4] becomes stable above 130 GPa. This necessitates a re-interpretation of previous shock-wave experiments [4], and has important implications for the use of alumina in high-pressure experiments. High electrical conductivity of the $CaIrO_3$-type phase of Al_2O_3 suggests an explanation for the high electrical conductivity of the D'' layer of the Earth, dominated by the $CaIrO_3$-structured phase of magnesium silicate. We show that incorporation of Al into $MgSiO_3$ shifts the perovskite/post-perovskite equilibrium to higher pressures, but this is more than compensated by the opposite effect of Fe^{2+} and Fe^{3+} (Ref. 6) at mantle compositions.

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Evaluation of Films for Packaging in High Pressure Food Processing*

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Food treatments implying high pressures use pre-packaging, consequently it appears necessary to validate different packaging films able to be developed in such processes.

Two different packaging films from AMCOR have been evaluated:

- **VIROFLEXAL**: BOLSA 80 MICRAS, coextrusion PA/PE (20/60 µm)
- **RILTHENE**: L SEMI 20/60 MICRAS 870 MM, laminate PA/PE (20/60µm)

Three different physico-chemical characterisations have been used for the evaluation after HHP treatment: (i) mechanical properties (tensile strength and sealing strength) (ii) oxygen permeability, (iii) migration (water, acetic acid 3%, ethyl alcohol 10%, iso-octane).

Two different pressure values have been tested, with a duration of 15 min:

T = +20°C: 400 MPa and 500 MPa

The selection of such values can be justified by the following industrial requirements: a temperature of +20°C and a pressure between 400 and 500 MPa being considered as the experimental conditions able to inactivate bacteria and different others micro-organisms.

** This study has been supported by the « Conseil Régional d'AQUITAINE » in the scope of the AQUITAINE-EUSKADI Scientific cooperation.*

t1High Pressure Behaviour of Packaging Films for Freezing P3 rocesses*

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The development of high pressure freezing processes implies the selection of packaging films able to be used in such condition.

In this study three different packaging films from SOPLARIL have been selected: **RSD100** (100 µm): 20 µm PA/10 µm Glue/70 µm PE medium density – Tubular co-extrusion, **RSE100** (100 µm): 30 µm PA/10 µm Glue/60 m PE free radical, linear – Cast co-extrusion, **RC302** (110 µm): 40 µm PA/15 µm Glue/55 m PE surlyn, ionomer Zn – Cast co-extrusion.

Three different physico-chemical characterisations have been investigated for evaluating their high pressure behaviour:

- mechanical properties: → tensile strength and sealing strength
- oxygen permeability,
- water permeability,
- migration (water, acetic acid 3%, ethyl alcohol 10%, iso-octane).

The experimental conditions used are: pressure = 200 MPa, duration = 15 min, temperature = -20°C. The selection of such values can be justified by the industrial requirements: -20°C, 200 MPa conditions correspond, in the phase diagram of water, to the limit where water remains in the liquid state (application for HP freezing or HP defreezing).

* *This study was supported by ACTIA (project RA 01.10)*

Protective effect of mono- and disaccharides on *Escherichia coli* cells against high pressure and sub-zero temperature

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The objective of the investigations was to determine the viability of one of the pressure sensitive strains of *Escherichia coli* exposed to pressure of 193 MPa and –20 °C in the presence of glucose, saccharose, and lactose. This high pressure was generated during 40 min at sub-zero temperature in a sealed vessel filled with water. The saccharides protected the cells of *E. coli* against high pressure depending on the kind of sugar and the growth phase of bacteria. After pressurization the numbers of viable cells of *E. coli* in the stationary phase, resuspended in phosphate-buffered saline (pH 7), was decreased by about 5 log cycles, while in 0.027 M solution of glucose only by about 0.5 log cycle. In case of saccharose this effect was achieved at a concentration of 0.275 M. The least effective was lactose – in 0.275 M solution the number of *E. coli* after pressurization decreased by about 3 log cycles. During prolonged pressure treatment, up to 24 h, the protective effect of saccharides decreased and the inactivation level of *E. coli* was similar regardless of the kind of sugar. The protective effect of saccharides was lesser in case of cells in the exponential phase of growth than in the stationary phase and did not depend on the concentration of saccharides in the studied concentrations range 0.027–0.275 M. *E. coli* cells in the exponential phase were inactivated by about 7 log cycles in buffer solution and by about 6 log cycles in all investigated saccharide solutions. It may be concluded that although the pressure generated in the sealed vessel at –20 °C was effective in reducing the viable number of tested microorganism in the buffer, the saccharide components of food can protect the pressure sensitive microrganisms, especially cells in the stationary phase of growth. However, this level of high pressure, in combination with other factors limiting bacterial growth, could be sufficient to ensure the microbial safety of food.

Possibilities of shelf-life prolongation of commercial fresh squeezed carrot juice by HPP pasteurisation

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In the recent years, fresh squeezed non-pasteurized carrot juice with declared one day shelf-life when stored in the refrigerator at the temperature lower than 6°C, has appeared on the Polish market.

In spite of such a short shelf-life period, in case of incidental contamination with pathogenic bacteria, able to multiply also in refrigerator conditions, risk of food born diseases becomes probable. Another cause of food born disease might be improper storage of juice by consumers.

There are reports in the literature documenting mass food poisoning following consumption of fresh non-pasteurized apple and citrus fruit juices in different countries. Therefore, fresh squeezed juices carry health risk for consumers, as well as waste risk for the producer, related to the necessity to return unsold in one day juice products.

Fresh squeezed carrot juice in original commercial containers was taken from the market following directly delivery from the manufacturer. The total bacterial count (according to method EN ISO 4833:2004) estimated at baseline averaged 10^5 cfu. One part of the juice containers was then subjected to HPP at the following conditions: 500 MPa, 5 min., temp. 2°C.

Significant reduction of bacterial count (by 4 $\log_{10}$ cycles), proper quality of juice, and preserved sensory quality of the fresh product were observed in the high pressure treated samples up to 5 days of storage at refrigerator conditions. However, in the juice samples not subjected to HPP, after 48h increase in bacterial count by 2 $\log_{10}$ cycles (10^7 cfu) and presence of moulds in average concentration of 50/ml.

HPP technology seems therefore a first-line option for pasteurization of fresh fruit and vegetable juices. Transfer of this method to small and medium enterprises (SME's) could be a milestone on the way to widespread implementation of this novel preservation method, assuring safety of minimally-processed food products.

ANTIBACTERIAL ACTIVITY OF MICROFLORA IN THE PRESSURIZED YOGHURTS

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Many strains of lactic acid bacteria and bifidobacteria, as used in the manufacture of fermented milk products, reveal antagonistic activity in relation to Gram-positive and Gram-negative bacteria, including pathogens. The substances which cause the so-called non-specific inhibition include mainly lactic acid and acetic acid, hydrogen peroxide and bacteriocins. The highest quantities of H_2O_2 are produced by lactic acid bacteria, including L. delbrueckii ssp. bulgaricus which constitute, together with Str. thermophilus, the microflora of yoghurt.

In the experiment, the antibacterial properties of yoghurts, preserved by the method of high pressures, were examined. Yoghurts, as obtained from MEY 92 and MYE 95 cultures, produced by Danisco Biolacta Food (Olsztyn, Poland) were subjected to pressurization under 200 – 400 MPa/15 min., in the intervals of 50 MPa. The yoghurts were stored at temperature of 4^oC for four weeks. During the storage, the antibacterial activity of the yoghurts' microflora in relation to nine test strains (Enterobacter A1, Enterobacter A1/17, E. coli 3, E. coli 323, E. coli 366, Klebsiella 449, Klebsiella 499, Proteus 16 and Proteus J), was examined.

The non-pressurized yoghurts demonstrated antibacterial properties in relation to all test strains. The pressure of 200 MPa weakened insignificantly the antibacterial properties of yoghurts' microflora. The application of the pressures of 250 – 400 MPa inhibited the antibacterial activity of the microflora of yoghurts in relation to most of the test strains. After the application of the pressures of 300 – 400 MPa, yogurt with MYE 95 lost completely the antibacterial activity whereas yoghurt with MYE 92 revealed the inhibiting activity only in relation to Enterobacter A1. During the storage, microflora of yoghurt with MYE 92 showed stronger antibacterial activity.

EFFECT OF PRESSURIZATION ON ENZYMATIC ACTIVITY OF COMMERCIAL COAGULATING PREPARATIONS

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The studies were conducted with the aim to determine the effect of pressurization in the range of 20 – 100 MPa /15 minutes on coagulating activity and proteolytic activity of the commercial coagulating preparations: of natural Hala rennet and preparations obtained with the use of genetically modified microorganisms - Chymax, Chymogen and Maxiren.

The effect of pressurization on enzymatic activity of the examined commercial coagulating preparations was determined from the results of the changes in coagulation activity of milk proteins and in proteolytic activity according to modified Anson method. The activity of the studied preparations was determined directly after pressurization and after 24 hours of storage at temperature of 5°C.

The analysis of the obtained results shows that the pressurization in the tested range of the pressures affects the enzymatic activity of the studied preparation in a differentiated way, depending on the level of the employed pressure, type of coagulating preparation and the conditions of determination.

An insignificant lowering of coagulating activity of the examined preparations as a result of pressurization under 20 MPa and a small increase as a result of pressurization in the range of 40 – 100 MPa was found.

The decrease of proteolytic activity was stated for Chymogen preparation as a result of pressurization under 20 – 100 MPa, irrespectively of the conditions of determination.

The storage (24 h/5°C) of the pressurized coagulating preparations caused lowering or insignificant increase of coagulating activity and proteolytic activity, depending on the type of the preparation, level of the employed pressure and the conditions of determination.

Formation of new casein structures by high pressure - *in situ* viscosity measurements and structure analysis after treatment

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Casein particles or gels are aggregates of casein submicelles and casein monomers which are stabilised by non-covalent bonds. During pressure increase, casein micelles dissociate to submicelles by weakening these bonds; during pressure release, the binding forces take effect again. Instead of the original casein micelle new hyper-structures are built up. It was shown that the pressure release rate significantly influences the structure formation of pressure-induced casein gels with 15% casein [1]. The higher the pressure release rate, the firmer the structures after high pressure treatment.

In this project the high pressure-induced viscosity of a 5% casein solution was measured *in situ* with a rolling ball viscometer [2] and observed during pressure release phase. Water binding, particle size and viscosity of the samples were analysed after pressure treatment.

During pressure increase to 600 MPa the viscosity of the casein solution increased and remained nearly unchanged during the holding phase of 30 min. After a pressure release rate of 600 MPa/min the viscosity of the solution was higher than the one of the untreated solution and large casein particles were detected. A slow pressure release rate of 20 MPa/min resulted in the lowest viscosity and smaller casein particles.

Finally, a better understanding of pressure-induced structure formation of casein micelles in ultra-high pressure treatment may offer opportunities for the creation of novel dairy products.

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Melting of copper and nickel; the role of *d*-electrons

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The present study was undertaken in order to establish the role played by *d*-electrons in filled and partially filled bands in determining melting curves by focusing on the neighboring fcc metals Cu($d^{10}s^1$) and Ni(d^9s^1). Melting curves were measured in a laser-heated diamond-anvil cell[1,2] for Cu to 97 GPa (3800 K) and for Ni to 84 GPa (2970 K). The melting slope (dT/dP) for Ni is found to be about half that of Cu. It appears that the "withdrawal" of a single electron from the filled Cu *d*-shell, to "create" Ni, is sufficient to cause a large decrease in the melting temperature. This confirms the important role played by partially filled *d*-bands[3] in determining melting curves and is consistent with previous measurements for fcc transition metals with partially filled *d*-bands [1,2].

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In-situ Combined X-ray Diffraction and Conductivity Measurements of Pr Metal: Evidence of the Isostructural Phase Transition

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A methodology of simultaneous X-ray diffraction and conductivity measurements of materials in a diamond anvil cell has been developed. Synchrotron powder diffraction and resistance measurements of Pr as a function of pressure and temperature were carried out simultaneously in order to confirm or discard a hypothesis of an isostructural phase transition and of a critical end point in the vicinity of dhcp-fcc structural phase transition in the phase diagram of this metal. Resistance of Pr metal showed a complicated behavior which was consistent with previous high-pressure experiments. The conductivity measurements on decompression revealed an anomalous increase of resistance starting from about 10 GPa at 350 K. The onset of this anomaly was observed within the stability domain of the fcc phase in the phase diagram. The Bragg reflections from dhcp phase were not present in diffraction images even at lower pressures. The temperature affects differently the pressure of structural fcc-to-dhcp phase transition and the pressure of the conductivity anomaly onset. While the negative slope of dhcp-fcc phase transition line in P-T phase diagram of Pr is confirmed, the onset of anomaly in conductivity is shifted towards higher pressures.

Obtained results confirm the hypothesis that the anomaly in conductivity is associated with an isostructural phase transition in the cubic Pr, whereas the structural fcc-dhcp transformation follows and partially overlaps the electronic transformation. The developed methodic of simultaneous conductivity and diffraction measurements demonstrated reliability and ability to reproduce the relative changes of the resistance on decompression.

High-pressure phases of cadmium phosphide, Cd_3P_2

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At ambient conditions, Cd_3P_2 is a semiconductor like Zn_3P_2. Both compounds have a tetragonal unit cell with eight formula units. The space group is $P4_2/nmc$ (137). The Cd atoms are situated in three of four deformed tetrahedral sites, and the P atoms are in octahedral sites. Pistorius et al. [1] have redetermined the crystal structure at ambient conditions, and also studied the melting curve of Cd_3P_2 in the pressure range 0 – 4 GPa. However, so far little is known about possible pressure-induced solid-solid transformations. In the present work we have used energy-dispersive x-ray diffraction and synchrotron radiation in conjunction with the diamond-anvil cell to study the crystal structure of Cd_3P_2 in the pressure range 0 – 30 GPa. The equation of state and the zero-pressure bulk modulus have been determined for tetragonal Cd_3P_2. These results are compared with theoretical *ab initio* calculations using the full-potential linear muffin-tin orbital (LMTO) method together with the atomic-sphere approximation (ASA). A phase transformation is found to occur at about 6 GPa. It is likely that the high-pressure phase is related to the Cd_3As_2 and Zn_3As_2 V phases, which are both orthorhombic with space group *Pmmm* [2]. An amorphous component is found to develop at pressures above about 20 GPa.

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Liquid gallium under high temperature and high pressure conditions

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The combination of experimental techniques such as x-ray absorption spectroscopy (XAS), x-ray absorption temperature scan (SEXAD) and energy-scanning x-ray diffraction (ES-XRD), have shown to give information of unprecedented accuracy about phase transitions (melting, freezing), existence of metastable phases and local structure in the liquid state.

Gallium is a low-melting point metal which is known to be polymorphic showing several phase transitions and metastable modifications as a function of pressure and temperature. Moreover, liquid Ga shows some anomalies in the macroscopic properties at high pressure and temperature and a possible existence of polymorphism in the liquid state could be suggested, but no detailed and systematic studies were performed using the advanced techniques used in this work.

By the combined use of the XAS, SEXAD and ES-XRD [1], we investigated the local structure of liquid Ga under high pressure and high temperature conditions and the possible existence of liquid-liquid transitions at high pressure.

We found that the pair distribution function g(r) reconstructed for liquid gallium is in good agreement with previous experimental results.

In addition, x-ray diffraction data show that solidification is observed above 2.9 GPa at room temperature, well beyond the liquid-solid coexistence line (1.9 GPa at 300 K) allowing us to observe the liquid phase in overpressure conditions.

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Pressure dependence of the phase-diagram of the ruthenocuprates

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We study the dependence on filling and pressure of the superconducting and ferromagnetic critical temperatures of the ruthenocuprates [1, 2], within the two-band model [3]. At zero pressure, we find separate regions of coexistence of superconductivity and ferromagnetism as a function of filling, with contiguous regions merging together as pressure increases. As a function of pressure, a stronger enhancement of the magnetic phase results in a reduced pressure effect on the superconducting critical temperature. Comparison with recent experiments on the determination of the critical temperatures as a function of the pressure is also discussed [4, 5].

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Soft phonon in the incommensurate phases of bromine and iodine studied by Raman scattering

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Molecular dissociation and metallization in simple molecular solids have been an attractive subject for long time. Up to now, various diatomic-molecular solids such as hydrogen, oxygen, nitrogen, and halogen (chlorine, bromine, iodine) have been investigated under high pressure. According to a recent study for iodine, a new solid phase (phase V) was discovered just before the molecular dissociation [1]. The intermediate phase V existing in between the molecular phase I and monatomic phase II, takes a structure formed by modulating incommensurately the phase-II structure.

In this work, we have investigated the phase V of solid bromine as well as iodine by using high pressure Raman spectroscopy. For both bromine and iodine, a new Raman band was observed in the phase V (see Fig. 1) and found to shift to low frequency side with pressure. This Raman band can be assigned with an amplitude mode which is peculiar to the incommensurate structure. Considering that the displacive phase transition often indicates the soft phonons and incommensurate phase, the present observation allows us to understand the molecular dissociation as a displacive phase transition.

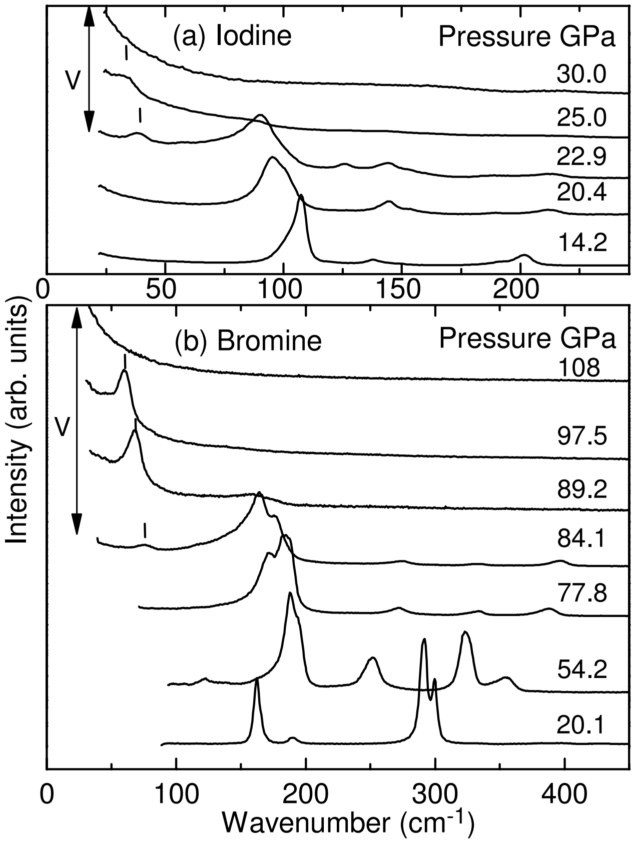

Fig. 1. Raman spectra obtained for iodine and bromine under high pressures.

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Phase relations and structures of CuI phases at high pressures and temperatures

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Copper iodide (CuI) is a much studied material because of the fast-ionic behavior of Cu ions in a high temperature phase (CuI-I) with fcc anion sublattice which appears above 682 K at room pressure. On increasing pressure at ambient temperature the compound transforms from a zincblende structured phase (CuI-III) to a rhombohedral phase (CuI-IV) at p=1.7 GPa, to a tetragonal phase (CuI-V) at p=4.5 GPa and to an orthorhombic distorted rocksalt structure in phase (CuI-VIII) at p=17 GPa [1]. The p-T phase diagram determined by DTA measurements [2] is remarkably complex and limited to 4 GPa.

Using a multi-anvil high-pressure device and synchrotron radiation, we have performed X-ray *in situ* observations of CuI under high pressure and high temperature up to 22 GPa and 1800 K to investigate the phase relations and crystal structures of high-pressure phases. The stability fields of CuI-IV, V, I and VII have been determined whereas CuI-VI was not observed and a rocksalt structured phase appears above 10 GPa and 700 K instead. We have also attempted electric conductivity measurements under pressure. The newly obtained p-T phase diagram and the structure and electric property of appeared phases will be discussed.

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X-ray diffraction study of ZnO beyond 200 GPa

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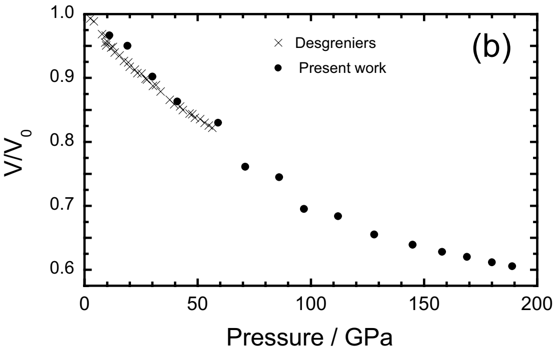
The crystal structure of ZnO at ambient pressure is the fourfold-coordinated wurzite structure (B4). A theoretical report described that the B4 phase transforms to the sixfold-coordinated NaCl structure (B1) at 9.32 GPa and the B1 phase transforms to the eightfold-coordinated CsCl structure (B2) at 256 GPa [1]. The B4 phase transformed to the B1 phase at 9.1 GPa and the bulk modulus of the B1 phase was reported to be 142.6 GPa [2]. Our reported work has probed the B1 phase of ZnO up to 202 GPa by using synchrotron X-ray diffraction [3] and up to 225 GPa by this present report. We will extend the pressure range up to 300 GPa in the coming experiment at SPring-8.

The pressure-volume data of the B1 phase up to 190 GPa are accumulated as shown in Figure with the previous report. This may allow us to evaluate the bulk modulus of the B1 phase precisely by reducing the error in the evaluation of B0', however the volume at ambient pressure for the B1 phase is assumed. The bulk modulus was calculated by Birch's equation to be 193.6 GPa. This value is substantially large compared to the previous theoretical and experimental reports [1,2].



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Pressure-Induced Amorphization of Zintl phase $BaSi_2$

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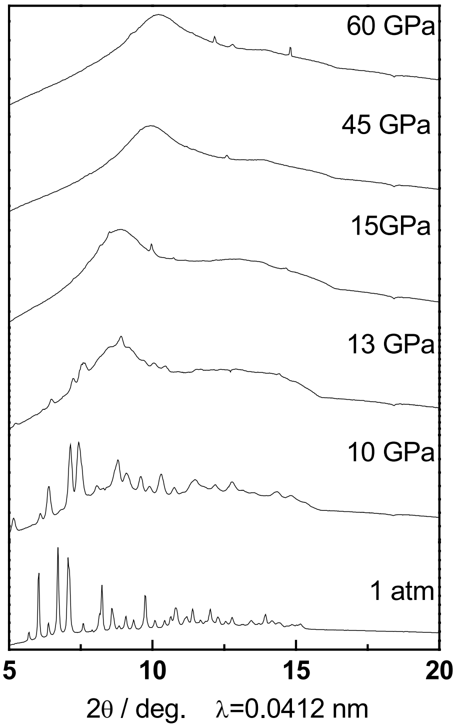
A Zintl phase $BaSi_2$ is semiconducting and has the characteristic crystal structure with the Si coordination number 3. Imai et al. investigated the phase transition of $BaSi_2$ at high pressure and temperature (HPHT) up to 10 GPa and 1300 K [1]. It is found that the HPHT trigonal $BaSi_2$ with the puckered graphitic Si layer shows superconducting with Tc=6.8 K. If the puckered layer becomes flattened the crystal structure is isostructural with MgB_2.



In this paper we report the result of the high-pressure x-ray diffraction up to 60 GPa at ambient temperature. The experiment was carried out at BL10XU beam line at SPring-8 and at BL18C beam line at Photon Factory in Japan. Pressure was generated by a diamond anvil cell with the top surface of 0.3 mmϕ in diameter and was determined by the Ruby fluorescence method. A 1:1 mixture of pentane and isopentane was used as a pressure-transmitting medium. Figure shows the x-ray diffraction profiles under various pressures. The bulk modulus of $BaSi_2$ was calculated by Birch-Murnaghan's equation to be 36.7 GPa fairly larger than the previous estimation [1]. The pressure-induced amorphization occurred around 10 GPa. The amorphous phase is quenchable after the upstroke to 60 GPa.

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High pressure infrared spectroscopy of yttrium hydride

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Yttrium, a trivalent rare-earth metal, forms hydride (YH_x) for hydrogen concentration x ranging from 0 to 3. Dihydride (YH_2) is a metal having a fcc structure with hydrogen atoms occupying the interstitial tetrahedral sites (T-sites) of the metal lattice. When the hydrogen concentration exceeds x~2.86, a metal-insulator transition takes place with a structural change into a hcp metal lattice [1]. Hydrogen atoms occupy the interstitial octahedral sites (O-sites) to open the band gap as a result of the *s*(H)-*d*(Y) hybridization or the charge transfer from metal to hydrogen.

We synthesized yttrium hydrides by pressurising the raw metal in fluid hydrogen in a DAC. A few-μm-thick foil became transparent at pressures below 1 GPa and x-ray diffraction measurements revealed formation of the hcp structure of YH_3.

The IR absorption spectra were measured up to 25 GPa. Three intense peaks were observed at 700, 900 and 1300 cm^{-1}, which were assigned as one proton vibrational mode of O-site and two of T-site [2], showing shifts to high frequency with pressure (Fig.1). The spectral change was observed at 12 GPa in agreement with x-ray diffraction results showing a hcp-fcc structural transition [3]. The T-site peak shifted to low frequency and the O-site peak increased in intensity with the structural transition. The observed frequency shifts were related to the nature of hydrogen-metal bonding.

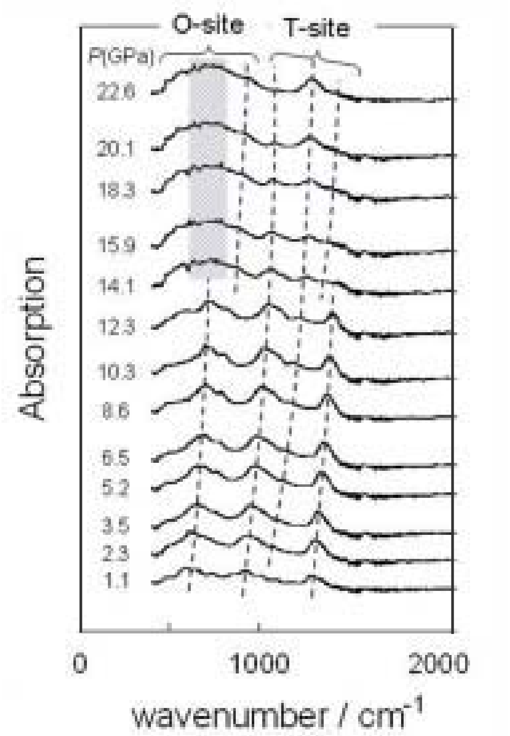

Figure 1 Infrared spectra of yrrtium hydride measured up to 22.6 GPa.

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Pressure-induced structural phase transition of alkali-earth dihydrides

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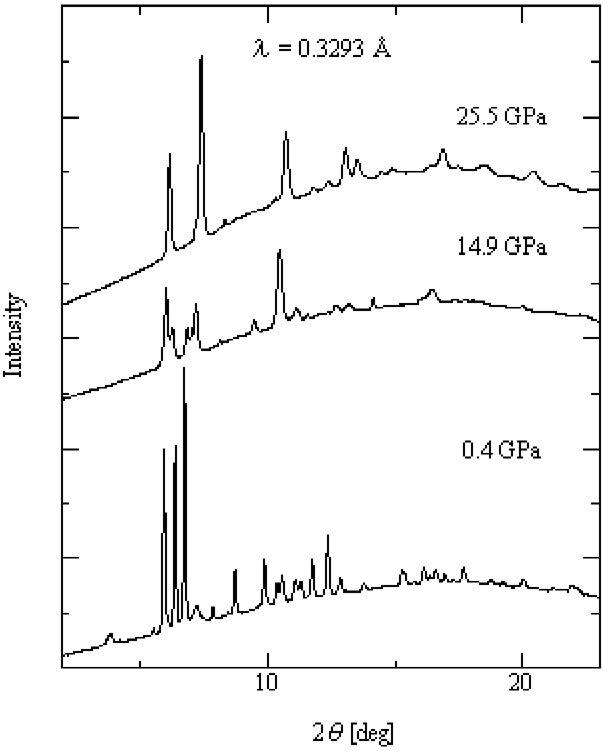
At ambient conditions, alkali-earth dihydrides crystallize into the cotunnite-type structure ($PbCl_2$-type; Pnma). The coordination number of a cation in the cotunnite-type structure is 9, which is the highest number among the AX_2 ionic compounds at normal conditions. A large number of dioxides and difluorides transform to this cotunnite-type structure under high pressure. Up to now, two types of structure, a hexagonal Ni_2In-type and monoclinic $P2_1/a$ structures, are reported as the post-cotunnite structure.

We present the results of powder X-ray diffraction measurements on CaH_2 and SrH_2 at high pressures and room temperature. The sample was loaded with a ruby chip into a hole of a metal gasket of a DAC in a dry box. X-ray diffraction measurements were performed using synchrotron radiation sources at Spring-8. Powder patterns were obtained by an angle dispersive method with an image plate detector. The figure shows the typical diffraction profiles of CaH_2 at selected pressures. The structural transformation took place at pressure around 15 GPa. The high -pressure phase is assigned to a hexagonal lattice with cell constants of a = 3.512 and c = 4.593Å(25.5 GPa), the c/a ratio of which is close to that of a Ni_2In-type structure.



Formation of tungsten hydride at high pressure and room temperature

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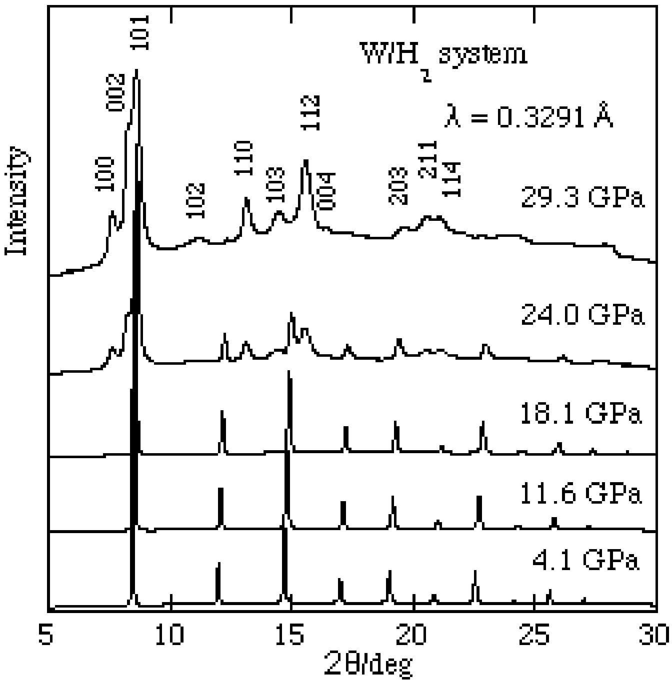
Most of transition metals form metal hydrides under high pressure, incorporating hydrogen in interstices of a pristine crystal lattice. Tungsten hydride, however, has not been known because the enthalpy of hydrogen dissolving in tungsten is very large. Thus tungsten is frequently used as a metal gasket to seal hydrogen at high pressure. Powdered W of a stated purity of 99.95 % (Nilaco Co. Ltd.) was loaded together with hydrogen at a gas pressure of 180 MPa in a diamond anvil cell by the use of a gas-loading system at room temperature. High-pressure powder X-ray experiments were carried out with synchrotron radiation sources on the beam line BL10XU and BL04B2 stations at SPring-8. Powder patterns were obtained by an angle dispersive method with an image plate (IP) detector. The figure□shows the typical diffraction profiles of W/H_2 -system at selected pressures. The structural transformation took place at pressure around 24 GPa. The high -pressure phase is assigned to a hexagonal lattice with cell constants of a = 2.870 and c = 4.593Å (c/a = 1.600) at 29.3 GPa, which indicates that tungsten forms a metal hydride above 24 GPa and transforms into the anti-NiAs-type structure.



Volume compression of Mg and Al to multimegabar pressure

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The high-pressure behavior of the third-period metals, Mg and Al, has been extensively studied because of their simple electronic structures. Especially, Al with comparably large compressibility is expected to be a candidate for a precise pressure marker under multi-megabar pressure range. Previously predicted structure phase transitions by first-principles total-energy calculations [1] are also of a great interest since these transitions are controlled by the *s-d* electron transition.

In this study, the volume compression curves of Mg and Al were measured at pressure up to 158 and 222 GPa, respectively, by powder x-ray diffraction experiments. Fig. 1 shows the present P-V relation of Mg. While a hcp-bcc transition of Mg was observed at 50 GPa, corresponding to the previous report [2], the K_0 and K_0' of the EOS of bcc-Mg were determined to be 68.7(7) GPa and 3.47(4), respectively. For Al, the theoretically predicted fcc-hcp transition was not observed at pressure up to 222 GPa. The result is consistent with the previous report [3].

These results will be discussed in comparison with other *sp* simple metals (Si, P, and S) as well as the results of theoretical calculations reported previously.

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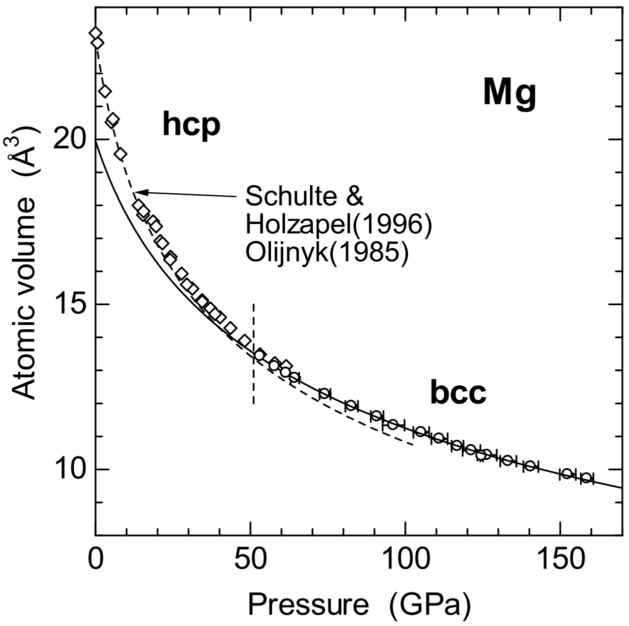

Fig. 1 Compression curves of Mg at 297 K.

Pressure-induced transformations of sodium alanate

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Recently, low-Z hydrides have been focused as hydrogen storage materials with high gravimetric hydrogen capacities. Especially sodium alanate $NaAlH_4$, whose relative weight of stored hydrogen is 7.5 wt%, attracted interest because it exhibited reversible absorption/desorption of hydrogen by doped with titanium. [1] Using *ab initio* simulation, Vajeeston et al. [2] reported that $NaAlH_4$ transformed to a denser form with $SrMgH_4$-type structure at 6.43 GPa, indicating that hydrogen might be stored more efficiently. In the present study, we explored the high-pressure transformation of $NaAlH_4$ experimentally by means of *in situ* Raman scattering spectroscopy and x-ray diffraction measurement.

$NaAlH_4$ was compressed in a helium medium up to 50 GPa using a diamond-anvil-cell. A drastic change in Raman spectrum was observed at about 10 GPa, suggesting a pressure-induced transformation from the ambient-pressure form to high-pressure one. However, x-ray pattern of the high-pressure form did not correspond to $SrMgH_4$-type structure, which Vajeeston et al. have suggested. With further increase in pressure, additional transformations were detected at about 20 and 30 GPa both by Raman and x-ray. These transformations occurred reversibly with small hystereses in pressure.

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High-pressure Raman study of Ga_2O_3

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In-situ high-pressure Raman study and X-ray diffraction of β-Ga_2O_3 has been carried out from 0 to 21 GPa at room temperature with a gasketed diamond anvil cell. It has been found that the pressure-induced phase transition occurred near 13GPa. This result suggests that a new phase of β-Ga_2O_3 should be formed at 13GPa.

Monoclinic gallium oxide (β-Ga_2O_3) is an important wide band gap (*E*g = 4.9 eV) material because of good chemical and thermal stability[1],so much attention has recently been given to the synthesis of single-crystalline β-Ga_2O_3 nanoribbons, nanosheets and nanowires. However, high pressure behavior of β-Ga_2O_3 is less investigated. The transformation from β-Ga_2O_3 to α-Ga_2O_3 (rhombohedral) under high temperature and high pressure conditions was first reported by Remeika [2] [3] in 1966. High pressure Raman behavior of β-Ga_2O_3 is not reported.

In this work we have studied vibrational properties of β-Ga_2O_3 at ambient and high pressure using Raman spectroscopy. Raman experiments have been complemented with X-ray diffraction measurements in a diamond anvil cell. We present evidences for the occurrence of β-Ga_2O_3 to α-Ga_2O_3 phase transition at high pressure.

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Single crystal X-ray diffraction study on high-pressure phase of $KHCO_3$

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Under atmospheric pressure, $KHCO_3$ undergoes an antiferrodistortive phase transition of an order-disorder type between Phase I (High-temperature phase, Space group:$C2/m$) and Phase II (Low-temperature phase, Space group:$P2_1/a$) at T_N=318K [1]. Two HCO_3 groups in the crystal structure are bonded by two H-bonds, and formed $(HCO_3)_2^-$ dimers. A dimer has two stable rotational angles around the *c* axis, these dimers are disordered in phase I and ordered with an antiphase configuration in phase II. Recently, two new phases are discovered. One is phase III, induced by shear stress. Phase III is assigned to a ferrodistortive phase having an in-phase configuration of dimers [2]. The other is unassigned phase discovered at high pressure. The high-pressure phase undergoes the reversible phase transition observed at about 2.8 GPa [3,4].

We have observed X-ray diffraction of $KHCO_3$ single crystal at high-pressure using an X-ray diffractometer with an imaging plate area detector (Rigaku, R-axisIV^{++}) and a four-circle diffractometer at the beam line BL-10A of Photon Factory, KEK, Japan. Phase transition with sample volume change was optically observed. Above the phase transition pressure, some phases were observed by X-ray diffraction. X-ray intensities from one of the observed high-pressure phases were corrected, and the structure will be discussed.

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[4] H. Kagi, T. Nagai, J.S. Loveday, C. Wada, J.B. Parise Am Mineral. 2003, vol. 88, 1446-1451

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Metastable high-pressure GaSb-Mn phases

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Solid solutions of the transition metals from the group of iron (Fe, Ni, Cr, Co, and Mn) with A^3B^5 compounds are potentially semiconductors or semimetal with ferromagnetic properties and, so, may be quite perspective materials for a use as base elements in the spintronic technology. Here we present the study of metastable high-pressure phases in the stochiometric GaSb-Mn system. We have found that upon high-temperature treatment at 6 GPa one can obtain new GaSbMn crystalline phases, first, preliminarily a simple cubic (a=2,946±0,001 Å) at ≈400 ^oC and, second, of the $CuAl_2$-type (a=6.426±0.004 Å, c=5.349±0.004Å, c/a=0.83, and space group *I*4/*mcm*) at T>400 ^oC. At T~300 ^oC we obtained upon quenching an amorphous phase with a small admixture of crystalline manganese, where the structural data for amorphous phase (a GaSb-Mn solid solution) are quite similar to those for tetrahedrally-bonded amorphous GaSb.

The room-pressure properties for all new phases, including density, structural data, resistivity, and preliminary magnetic properties, are also presented. The both synthesized crystalline GaSbMn phases are metastable and during the differential thermal analysis experiments demonstrate complicated two- or three-stage kinetics of decay, where the final state of the samples upon room-pressure annealing includes crystalline zinc-blend GaSb, MnSb of NiAs type, and Ga. Preliminary study have shown ferromagnetic properties with quite high Curie temperatures practically for all synthesized metastable GaSb-Mn alloys. Finally, the presented data show that high pressure can be efficient instrument for creating new magnetic semiconductors among Solid solutions of the transition metals from the group of iron and A^3B^5 compounds.

Phase transitions and amorphization in $HfMo_2O_8$ under pressure

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$HfMo_2O_8$ belongs to the class of framework-structured materials of the type MX_2O_8 (M = Zr, Hf and X = W, Mo), which have drawn considerable interest due to their negative thermal expansion behaviour. At ambient conditions $HfMo_2O_8$ stabilizes in a trigonal lattice (α-phase) [1]. The structure of α-HfMo2O8 consists of HfO_6 octahedra, which share all the corners with the MoO_4 tetrahedra. Three of the MoO_4 tetrahedra apices are linked to HfO_6 octahedra, while the fourth apex points towards the interlayer region. This kind of framework arrangement of the octahedra and tetrahedra makes this structure flexible and comparatively less dense and hence highly amenable to transformation to denser phases on compression.

High pressure structural investigations on α-$ZrMo_2O_8$, which is isostructural to α-$HfMo_2O_8$ has shown two successive phase transformations: α - δ (monoclinic) phase at 1 – 1.1 GPa and δ - ε (triclinic) phase at 2 –2.5 GPa followed by amorphization above 10 GPa [2]. α-$HfMo_2O_8$ has been found to transform to a 20% denser monoclinic (β) phase at 2.15 GPa and 560°C [1]. To our knowledge no other reports on the high pressure studies on $HfMo_2O_8$ are available till date. Therefore we have carried out high pressure powder X-ray diffraction (ADXRD) measurements on both α and β phases of $HfMo_2O_8$ to investigate the high pressure phase transitions in these materials and to look into the pressure induced amorphization (PIA).

High pressure ADXRD measurements were carried out at the ELETTRA Synchrotron source, Trieste at a λ of 0.7 Å up to 35 GPa. α-$HfMo_2O_8$ is found to undergo two successive phase transformations similar to α-$ZrMo_2O_8$ at about 1.2 GPa 2.6 GPa respectively. On further compression above 30 GPa α-$HfMo_2O_8$ undergoes irreversible amorphization. The PIA in α-$HfMo_2O_8$ is attributed to the kinetic hindrance for transformation to the β-phase. β-$HfMo_2O_8$ gradually amorphizes on compression above 35 GPa. However no other high pressure phase transition is observed in this material. When heated at 5 GPa and 800°C, β-$HfMo_2O_8$ decomposes to the parent oxides. Also when annealed above 850°C β-$HfMo_2O_8$ reconverts back to α-$HfMo_2O_8$. Therefore the PIA in β-$HfMo_2O_8$ is attributed to the kinetic hindrance to decomposition.

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Keywords: *High pressure, Phase transition, Negative thermal expansion, Pressure induced amorphization*

Pressure-induced structural phase transitions in tellurium up to 91Gpa

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Pressure-induced structural phase transitions in tellurium were studied by high-pressure energy dispersive X-ray diffraction techniques at room temperature up to 91Gpa. Powders of high purity(99.999wt%) tellurium were studied in the gasketed diamond anvil cell. a T301 steel gasket(250μm thick, with a central hole of 80μm in diam) was used to contain the sample, and the diamond anvils with a 300μm top surface were used to generate high pressure.. A methanol:ethanol:water mixture in a 16:3:1 ratio was used as the pressure-transmitting medium, and the pressure was determined by the well known ruby fluorescence measurement.

Jameison and McWhan(1965) [1]suggested that a simple cubic structure might be stable at intermediate pressure, but this speculation has not been confirmed yet. The purpose of our study is to confirm that whether the simple cubic structure of tellurium exists at a higher pressure. The result suggests that the bcc structure of tellurium is stable up to 91Gpa. Although the simple cubic structure was not found, a little change of the structure has been turned up with pressure increasing, and a phase transition at about 14Gpa was observed besides of the phase transitions at 4Gpa, 6.4Gpa, and 26-32GPa.

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X-ray Diffraction and Equation of State of Solid Silane to 93 GPa at Room Temperature

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Solid silane (SiH_4) has been studied under high pressure at room temperature to 93 GPa in a diamond anvil cell (DAC). The crystal structure and P-V equation of state were determined by energy-dispersive x-ray diffraction with microcollimated synchrotron radiation source. We find that solid SiH4 has a body centered tetragonal (bct) structure with possible space group I4/mmm over the pressure range investigated based on in-situ measurements of x-ray diffraction peaks. The data were fit to a Vinet and Birch equation of state respectively with $K_o = 56.65 \pm 3$ GPa, $K_o' = 7.72 \pm 0.20$ GPa, $V_o = 28.64 \pm 2.4$ cm^3/mole and $B_o = 49.49 \pm 4$ GPa, $B_o' = 8.68 \pm 0.15$ GPa, $V_o = 28.84 \pm 2.5$ cm^3/mole. This is the first experimental report for solid silane at high pressure at room temperature.

Oral

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Structural properties, infrared reflectivity, and Raman modes of SnO under pressure

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Tin monoxide crystallizes at room temperature in the layered litharge structure. The compound has stereochemically active lone-pair electrons and it is semiconducting under normal conditions. We have investigated the high-pressure behavior of SnO using a combination of experimental methods (monochromatic synchrotron x-ray diffraction, Raman spectroscopy, and synchrotron MID-IR reflection). The litharge-type structure is observed up to at least 30 GPa. Changes in interatomic distances are determined via full Rietveld refinements of diffraction patterns. SnO undergoes an insulator to metal (IM) transition at 5(1) GPa; this electronic change is attributed to the closure of an indirect gap. Zone-center Raman mode frequencies are hardly affected by the IM transition. Our results will be discussed in the light of several first-principles calculations, e.g. [1-3], as well as related experimental studies of structural and dynamical properties [4-6].

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Effect of pressure on structural and dynamical properties of $LiCoO_2$ and $NaCoO_2$

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The layered sodium cobaltites Na_xCoO_2 ($x \leq 1$) have attracted attention recently in the framework of correlated-electron physics and superconductivity. On the other hand, the most remarkable property of the structurally related compounds Li_xCoO_2 is allowing reversible removal and reinsertion of the Li ions as utilized in rechargeable Li batteries. We have studied the structural and spectroscopic properties of the fully charged (x = 1) semiconducting compounds $LiCoO_2$ and $NaCoO_2$ at high pressures by synchrotron x-ray diffraction and Raman spectroscopy. Both compounds have a similar layered structure with space group R-3m. At variance with predictions of a layered to cubic transition of $LiCoO_2$ at moderate pressures, the x-ray diffraction data show no sign of a phase change up to 30 GPa, as is also supported by Raman spectroscopy. A similar behavior is found for $NaCoO_2$. Detailed information about the effect of pressure on the metal-oxygen bond lengths, in particular the compressibility differences of Li(Na)-O and Co-O bonds, is obtained via full Rietveld refinements. The pressure coefficients for the observed A_{1g} and E_g Raman modes and thus the mode-Grüneisen parameters were determined for both compounds. The experimental results obtained here serve as a test for published and ongoing first-principle calculations of the static and dynamic properties of cobaltites. Preliminary experimental results will be reported on the structural properties of alkali-deficient metallic cobaltites with $0.5<x<1$.

Pressure-induced phase transitions in $KFe(MoO_4)_2$

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$KFe(MoO_4)_2$ is a layered compound exhibiting temperature-induced ferroelastic and antiferromagnetic phase transitions. In this work, $KFe(MoO_4)_2$ has been studied by Raman scattering up to 4 GPa. We have found significant changes in the Raman spectra at about 1.3 GPa that were interpreted as a structural phase transition from the D_{3d}^3 phase to most likely D_{3d}^4 phase. This transition was shown to be reversible. Upon further increase of pressure the crystal exhibited a phase transition into another phase at about 1.8 GPa. The large increase in the number of observed Raman lines and large frequency changes of the observed modes indicated that this transition leads to a lower-symmetry phase with significant distortion of the unit cell. This phase remains stable upon releasing the pressure. Therefore, we may conclude that the second phase transition is irreversible. The X-ray diffraction studies performed for the high-pressure phase outside the pressure cell revealed that this phase is triclinic and partially amorphous. The amount of amorphous phase is significantly reduced by heating the sample up to 380ºC, but the symmetry of the phase remains unchanged.

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New Structure Transition from simple cubic calcium under High Pressure

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Calcium (Ca) forms a fcc lattice at ambient conditions and transforms to bcc lattice at 20 GPa and to simple cubic structure (sc) at 32 GPa [1]. And it has been reported that this sc structure is stable up to 85 GPa. The electrical property and the crystal structure of some alkaline earth metals at high pressure are governed by the pressure-induced *s-d* electron transfer. The maximum value of the superconducting transition temperature (T_c) is obtained at the state of the completion of the *s-d* electron transfer, where the crystal forms Ba-IV structure. In the case of Ca, its T_c increases with pressure and reaches 15 K at 150 GPa [2]. It could be expected in the possible higher-pressure phase, such as Ba-IV type phase, than the sc phase.

Here we have investigated X-ray diffraction study on Ca up to 130 GPa. The polycrystalline sample was loaded into the diamond-anvil cell without any pressure transmitting medium. Pressures up to 70 GPa were determined on the basis of the ruby pressure scale. The pressure determination above 70 GPa were conducted from the d values on the basis of the equation of state of Pt and Re, the latter of which was used as gasket metal. The diffraction patterns were collected on BL-18C and BL-13A at photon Factory (KEK).

We found that sc phase is stable in the wide region form 32 GPa to 117 GPa. By further compression, a structure change was clearly observed in the diffraction pattern. It indicates the existence of a new high-pressure phase. The sc phase is not stable above 117 GPa. But the structure of the new high-pressure phase remains to be determined.

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High Pressure Mechanochemistry: Conceptual Multiscale Theory and Interpretation of Experiments

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Fifteen mechanochemical phenomena observed under compression and plastic shear of materials in rotational diamond anvil cell (RDAC) are systematized. They are related to strain-induced structural changes (SCs) under high pressure including phase transformations and chemical reactions. The objective of the paper is to develop a simple, three-scale continuum thermodynamic theory and closed form solutions which explain these phenomena. At the nanoscale, a model for strain-induced nucleation at the tip of a dislocation pile-up is suggested and studied. At the microscale, a simple strain-controlled kinetic equation for the strain-induced SCs is thermodynamically derived. A macroscale model for plastic flow and strain-induced SCs in RDAC is developed. These models explain why and how the superposition of plastic shear on high pressure leads to: a) a significant (by a factor of 3-5) reduction of the SC pressure, b) reduction (up to zero) of pressure hysteresis, c) the appearance of new phases, especially strong phases, which were not obtained without shear, d) strain-controlled (rather than time-controlled) kinetics, or e) the acceleration of kinetics without changes in the SC pressure. Also, an explanation was obtained why a nonreacting matrix with a yield stress higher (lower) than that for reagents significantly accelerates (slows down) the reactions. Some methods of characterization and controlling the SCs are suggested and the unique potential of plastic straining to produce high-strength metastable phases is predicted [1-3]. Phase transformations in BN, Si and Ge are considered in detail.

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Structural changes and pressure-induced chemical decomposition of boric acid

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X-ray powder diffraction studies along with complementary Raman and infrared spectroscopy measurements disclosed the pressure-induced chemical decomposition of boric acid, H_3BO_3. The layered triclinic structure of H_3BO_3 suffers a highly anisotropic compression associated to a strong reduction of the interlayer spacing. The starting structure becomes unstable at about 2 GPa and decomposes on a cubic polymorph of the metaboric acid, HBO_2, and ice. Two structural modifications of ice, ice VI and ice VII, are formed in the course of the chemical decomposition of boric acid. X-ray diffraction data suggest a new polymorph of H_3BO_3 as a precursor structure of the decomposition process. The triclinic lattice of the new phase has a translation period corresponding to 3 layers of hydrogen-bonded $B(OH)_3$ molecules in place of the 2 layers period observed in the initial phase. The large volume variation and the important structural changes associated to the decomposition suggest a high free energy of activation. This yields a slow kinetics at room temperature, and a phase composition very dependent of the specific pressure-time path followed by the sample. Based on the obtained results a mechanism for the chemical decomposition of H_3BO_3 is proposed and the possible role of hydrogen bonds in the observed transformations is discussed.

Investigations of phase transformations in red mercuric iodide under high pressure

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Abstract

We have investigated the behavior of red mercuric iodide (α-HgI_2) under high pressures using in situ x-ray diffraction and optical absorption measurements. Our experimental results indicate that the tetragonal to orthorhombic phase transformation, observed at 1.4 GPa, is accompanied by an abrupt increase in the band gap while the nature of the gap does not change. In addition we find that all the Raman active mode frequencies increase with pressure up to 1.3 GPa, beyond which the modes of the tetragonal phase disappear and new modes appear supporting the tetragonal → orthorhombic structural transition around this pressure. At still higher pressures, at ~ 7.2 GPa, HgI_2 undergoes an orthorhombic to hexagonal phase transformation marked by a discontinuous decrease in the band gap as well as its character changes from direct to indirect type. These studies suggest that HgI_2 may metallize at ~ 40 GPa, if not prevented by any other structural change.

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Phase competition and the effective time scale for resolidification

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We investigate the time scale for pressure-induced solidification in a molten metal by simulating the process using molecular dynamics techniques. We find that the time to solidification in the simulation depends on the availability (or lack thereof) of competing solid phases into which the liquid can crystallize. We demonstrate this dependence using both a highly accurate, quantum-based potential (the MGPT potential) and a simple, Morse-like potential that has been modified to alter the relative stability of various solid phases.

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Stability of the langasite structure under pressure

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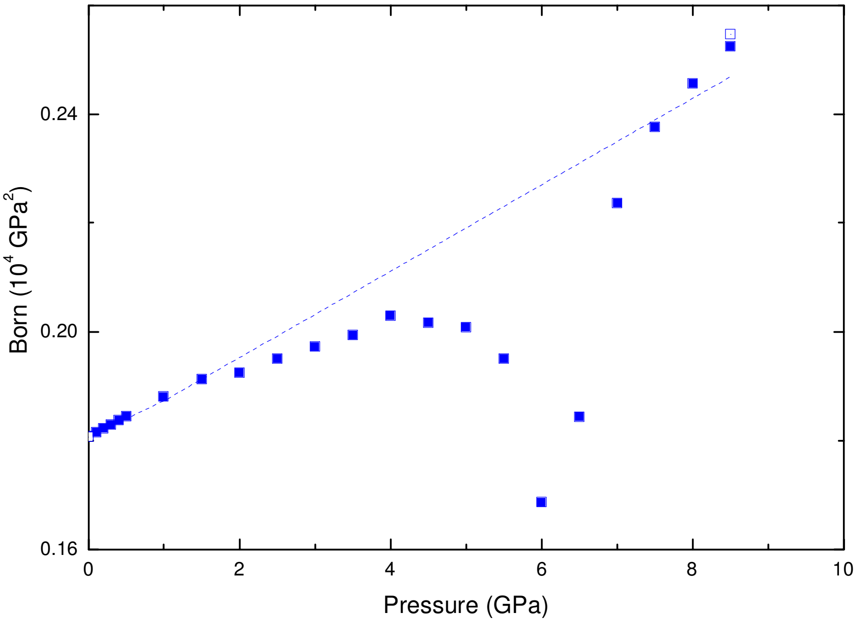
The langatate which belongs to the langasite family, is known to be a promising successor of quartz for high technology resonators. Its structure is closely related to those of quartz and consequently the question of its stability under pressure is of prime interest from both technological development and theoretical point of view.

Up to now, its basic properties, phase diagram, equation of state, elastic constants are controversial or unknown. Results presented here have been obtained by x-ray diffraction and ultrasonic method [1]. The elastic tensor has been entirely determined under pressure and the Born criterium extracted.



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High pressure induced phase transitions dynamics in ammonium halides.

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Phase transitions in polycrystalline ammonium halides NH_4X (X: F, Cl, Br) induced by high pressure were found. The transitions become apparent in jumps in resistivities by orders of magnitude from the value more than 10^8 Ohm down to several kOhm at the threshold pressure P_c of about 40, 27 and 15 GPa for ammonium chloride (NH_4Cl), fluoride (NH_4F), and bromide (NH_4Br), respectively. Similar sharp transitions were observed near P_c in the temperature dependence of resistivity. A hysteresis typical for first-kind phase transitions was observed in the resistance of all three materials in dependence on pressure and temperature. The steady-state values of P_c were reached after sufficiently long exposure of samples under stress. The duration of the pressure treatment is quite different for these three materials. Initial loading of the samples by the pressure of 50 GPa causes the change in the resistance only after the exposure under stress during a month for NH_4F, about 10 days for NH_4Cl and seconds for NH_4Br. The correlation between the times of such a treatment, as well as between P_c values and the density of the materials (the atomic weight of halogens F, Cl and Br) was found. All the ammonium halides show metal-like behavior under high pressures similar to that of alkali halides.

The time dependence of resistivity of the ammonium halides at changing pressure was studied. The relaxation of resistivity obeys the exponential low at the pressures far enough from the critical ones; the relaxation times are tenths seconds or minutes. At the pressures close to P_c, the resistivity relaxation becomes highly non-exponential; the time delay of hours to days appears before the phase transition (resistance jump).

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Possible reaction paths in acetylene derivatives under pressure

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Acetylene and its derivatives can be regarded as model systems for high-pressure chemistry due to the high reactivity of the triple bond. A number of examples of pressure-induced chemical reactions have been recently reviewed. [1,2]

Although most high-pressure reactions occurring in simple molecular systems lead to polymeric materials, geometrical restrictions might lead to intermediate species that can be of interest in new synthetic routes. In order to illustrate this possibility, we discuss here the possible reaction paths of the condensation process occurring in the monoclinic (C2/m) phase II of dimethylacetylene. The reaction process is studied by Raman spectroscopy and analyzed in the light of the density functional theory at the B3LYP/6-311++G(2*d*,2*p*) level. Differences with previous results for acetylene are provided. The possible stabilization of highly reactive intermediate species by pressure is considered, and implications on new synthetic routes are discussed.

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Structural transformations in pre-annealed Czochralski silicon treated under enhanced temperature-pressure

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Processing of Czochralski silicon (Cz-Si, basic semiconductor in microelectronics) at high temperature (HT) leads to clustering of oxygen always present in Cz-Si (oxygen content, c_o, can reach $\geq 1.1\text{x}10^{18}$ cm^{-3}), with a creation of SiO_{2-x} precipitates exhibiting tensile stress on the matrix. Oxygen precipitation, the stress mentioned and so the defect structure of Cz-Si are affected by hydrostatic pressure (HP) exerted by inert medium at HT [1]. The effect of HT – HP treatment (typically for 5 h) at 1230 / 1400 K under HP up to 1.2 GPa on structural transformations in Cz-Si was investigated by microhardness, photoluminescence (PL) and related measurements. To create nucleation centres for precipitation (NC's), Cz-Si was subjected to one step pre-annealing at 720 K (samples A, resulting $c_o = 1\text{x}10^{18}$ cm^{-3}) or to 4 steps pre-annealing at up to 1000 K (samples B, $c_o = 3.6\text{x}10^{17}$ cm^{-3}).

Pre–annealing of Cz-Si at 720 K for up to 20 h affects its microhardness (H) only slightly while the B samples are less hard (H equals to 15.9 and 14.4 GPa, respectively). The HT – HP treatment of A samples results in decreased c_o (after the treatments at 1230 K under 0.01 GPa and 1.2 GPa, c_o equals to $7.3\text{x}10^{17}$ cm^{-3} and $5.8\text{x}10^{17}$ cm^{-3}, respectively). The treatment of B samples at 1230 / 1400 K under HP results in increased H (up to 16.6 GPa) while the density of dislocations (evidenced by the presence of PL lines at 0.81 eV and 0.87 eV) decreases with HP in the case of treatment at 1230 K but increases after the treatments at 1400 K.

Structural transformations in treated Cz-Si are related to the effect of HP on the creation and stability of NC's as well as on diffusivity of oxygen and of Si interstitials.

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Thermodynamic Properties of Organic Molecular Crystals from First Principles

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The objective of this work is to determine thermodynamic properties of a class of organic molecular crystals referred to as energetic materials from first principles quantum mechanical solutions of the many body Schrödinger equation.

Near current state of the art techniques for solving the approximate quantum mechanical equations for systems of nuclei and electrons are incorporated in computer programs such as CRYSTAL and ABINIT. The calculations are computationally intensive, requiring near state of the art computational capability. In addition, we are able to take advantage of new techniques involving embedded clusters in which a relatively small group of atoms may be treated quantum mechanically while embedded in a classical field which reproduces the crystal environment. While this method is less precise than full periodic structure methods, calculation of the 0 K isotherm of 1,1-diamino-2,2-dinitroethylene (FOX-7) with this method compares favorably with full periodic structure calculations.

In recent work, the 0 K isotherms of solid nitromethane, FOX-7, and β HMX were calculated. It was found that Hartree-Fock calculations give the best agreement with experiment and a calculation with complete optimization of the internal molecular coordinates gives excellent agreement with experimental data. For the best results, especially for anisotropic materials, it is necessary to optimize both atomic coordinates and lattice parameters under a fixed volume constraint.

In addition, the full equation of state was constructed for FOX-7 from ab-initio calculations giving results which compare remarkably well with experimental data. The above zero temperature contribution to the free energy was calculated from the phonon frequency spectrum obtained with density functional theory (DFT) in the local density approximation (LDA).

Powder x-ray diffraction study on mercury up to 200 GPa

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Mercury becomes solid at about 1.2 GPa at room temperature. After solidification, it undergoes several structural phase transitions under pressure [1]: alpha (simple rhombohedral), beta (body-centered tetragonal), gamma (orthorhombic) and delta (hcp). The delta phase is reported to be stable to at least 67 GPa [1]. First-principles calculation predicts a wide stability range for the delta phase up to 1 TPa [2]. In order to study the structural stability of the delta phase at ultrahigh pressures, we have carried out powder x-ray diffraction experiments on mercury up to 193 GPa at room temperature. No phase transition was observed in this pressure range. The *c/a* axial ratio decreased from 1.75 to 1.64 at the highest pressure. We have fitted the Birch-Murnaghan equation of state to the present pressure-volume data. For high-pressure phases, it is better to use the bulk modulus and its pressure derivative at a reference pressure as fitting parameters, rather than to use those at atmospheric pressure [3]. This is due to the large uncertainty in volume of the high-pressure phase extrapolated to atmospheric pressure. By using the reference pressure of 50 GPa, we have obtained the bulk modulus and its pressure derivative as 292 GPa and 5.5, respectively. General trends in the variation of the *c/a* axial ratio for hcp metals under pressure will be discussed including the comparison with the same group elements Zn and Cd [4].

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High-pressure phase transformations and EOS of AWO_4 tungstates

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AWO_4 tungstates (A = Ca, Sr, Pb, or Ba) crystallize in the scheelite structure ($I4_1/a$, Z = 4) and have important technological applications as laser-host, luminescence materials, scintillators, photoanodes and oxide ion conductors. The scheelite-type tungstates have been focus of recent studies at high-pressure because of the identification of several phase transitions [1, 2]. We have performed angle-dispersive x-ray diffraction (ADXRD) and x-ray absorption near edge structure (XANES) measurements in $CaWO_4$, $SrWO_4$, $PbWO_4$, and $BaWO_4$ under high pressure up to 20 GPa. ADXRD and XANES experiments were performed in a DAC at the APS (16-IDB beamline) and the ESRF (ID24 beamline), respectively. Similar phase transitions and transition pressures have been observed for the four tungstates using the two techniques. The four materials are found to undergo a scheelite-to-fergusonite phase transition at 10.5 GPa, 9.9 GPa, 9 GPa, and 7.1 GPa, respectively. The fergusonite phase ($C2/c$, Z = 4) remains stable up to the 20 GPa for CaWO4 and SrWO4, but a second phase transition is observed in BaWO4 and PbWO4 above 13 GPa. Our results are compared to those found in the literature and supported by *ab initio* total energy calculations. The systematic study of all the components of the scheelite tungstate family allowed us to obtain a deep understanding of the structural pressure behaviour of these compounds. In particular, we analyzed the origin of cation size effect on the transition pressure and found a linear relationship between the charge density in the scheelite octahedra and the bulk modulus of studied compounds. Finally, based on the observed data an equation of state for the four studied tungstates was obtained.

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Pressure induced structural transition in $AgSbSe_2$

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X-ray diffraction experiments at high pressures up to 65 GPa were performed on $AgSbSe_2$ compound using synchrotron radiation and diamond anvil cell in the angle dispersive geometry at ambient temperature. The compound undergoes B1 to B2 transition through an intermediate orthorhombic structure around 41 GPa. The pressure-induced transition observed in this system is similar to the B1-B2 transition observed in the iso-structural $AgSbTe_2$ alloy [1] and follows the phase transition sequence of II-VI binary analogues. The results will be discussed in detail.

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New phase transitions in gypsum

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Gypsum ($CaSO_4{\bullet}2H_2O$) is one of the most common sulfate minerals, forming in a variety of environments including hydrothermal vents near mid-ocean ridges, diagenetically altered marine sediments, and evaporate deposits. It contains both molecular water and molecular-like sulfate groups ionically bounded to calcium ions. Recent high-pressure Raman and IR studies give different interpretations compared with synchrotron energy dispersive x-ray diffraction (EDXD) studies regarding the phase transition ~5 GPa as well as the pressure-induced evolution above 5 GPa.

In this work, we use different techniques including synchrotron far-IR spectroscopy and Raman scattering at U2A beamline, EDXD and angle dispersive x-ray diffraction (ADXD) at X17C beamline to study the phase transitions. The synchrotron far-IR spectra confirmed the pressure-induced phase transition in gypsum around 5 GPa based on the changes of IR lattice vibrational modes and frequency discontinuities of these modes with increasing pressure. ADXD studies further confirmed this phase transition from monoclinic to orthorhombic symmetry around 5GPa. Both IR and ADXD showed that this high-pressure is fully reversible. It also revealed that the white synchrotron radiation induced dehydration due to the intrinsic features of this high-pressure phase in gypsum during the EDXD measurements. This quenchable high-pressure phase has been studied by IR and Raman as well and is determined as following:

CaSO4•2H2O → high pressure phase (orthorhombic ~5GPa) → CaSO4• 0.8H2O

An intermediate metastable phase of α-quartz and its phase transformation induced by high static pressure

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After considering that the factors of local collision and shear stress have not been reflected in the high static pressure, a laboratory method of combining the high-energy mechanical ball milling and high static pressure has been suggested for modelling synthesis of coesite in the earth' s surface. A mechanical collision– induced intermediate phase of α-quartz has been discovered. Its condition of easily crystallizing into coesite induced by high static pressure is 3.0 GPa, 923 K, and < 1.0 min. The Raman peaks for the coesite synthesized by the present method have covered over the information of those natural and synthesized coesite obtained before. Here we clarify the implications of the coesite synthesized by this method in geo-science, and suggest another possible formation mechanism for coesite in the earth' s surface, which is different from the hypothesis of plate exhumation in the earth that was based on the coesite formation condition of high static pressure in laboratory.

Stability of molecular ionic solids upon compression

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Raman spectroscopic measurements of K_2CrO_4 upon compression in an argon pressure medium reveal a series of structural transitions between ambient conditions and 50 GPa. The solid remains crystalline to the highest pressure measured. This behaviour is consistent with an emerging trend upon compression for the extended class of A_2BX_4 solids which are isostructural to K_2CrO_4. In particular crystals with size ratios of anionic tetrahedral BX_4 groups to interstitial A cations below 1.45 remain crystalline at all pressures examined whereas those having ratios higher than 1.45 become amorphous.

Metastable crystalline and amorphous tetrahedral GaSb-Ge and InSb-Ge solid solutions: The relation between configurational and topological disorder and elasticity

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We present the systematic study of the structure and elastic properties of the metastable crystalline and amorphous ternary $(GaSb)_{1-x}Ge_{2x}$ and $(InSb)_{1-x}Ge_{2x}$ solid solutions with composition varied over all concentrations of components. The basic idea of the high-pressure technology for synthesis of these metastable substances as bulk amorphous samples consist in the complete solution of the components under pressure in the region of stability of the metallic high-pressure phases of Ge, GaSb, and InSb (at P>8 GPa) with subsequent solid-state amorphization to semiconductor phase upon compression. The metastable crystalline $(GaSb)_{1-x}Ge_{2x}$ solid solutions are in turn obtained by room-pressure crystallization of the corresponding amorphous compounds before their decay into an eutectic mixtures. By the way the whole set of the synthesized samples provides a controllable variation of the configurational and topological disorder in tetrahedrally-bonded semiconductors.

For $(GaSb)_{1-x}Ge_{2x}$ solid solutions, it is found that elastic moduli for crystalline phases are systematically higher than those for amorphous counterparts or comparable at all Ge concentrations x. The both amorphous $(GaSb)_{1-x}Ge_{2x}$ and $(InSb)_{1-x}Ge_{2x}$ solutions have elastic moduli considerably below a potential linear interpolation between the corresponding characteristics of crystalline Ge and GaSb or InSb. Particularly, for the $(GaSb)_{1-x}Ge_{2x}$ solid solutions, it is found that the moduli of crystalline phases initially decrease with Ge concentration, falling down to minimum values at 20 to 30 % of Ge. The minimal values of elastic moduli for amorphous samples are observed at 50 to 60 % of Ge.

Using experimental data, we argue that elastic softening of tetrahedrally-bonded solid solutions, both amorphous and crystalline, is related to the degree of geometrical disorder, which in turn includes contributions of configurational (or chemical) and topological disorders.

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High Pressure Study on the structure of several iron-tin intermetalic compounds

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The system iron – tin exhibits several intermetalic compounds like Fe_3Sn [1], Fe_5Sn_3 [2], Fe_3Sn_2 [3], FeSn [4] and $FeSn_2$ [5]. The compounds FeSn and $FeSn_2$ are antiferromagnetic whereas the others are ferromagnetic. According to the Fe-Sn phase diagram [6] only the antiferromagnetic compounds are stable at ambient conditions. By quenching the ferromagnetic compounds these intermetalics can also be investigated at room temperature.

We will present an x-ray diffraction study to pressures above 25 GPa of the described Fe-Sn intermetalic compounds performed at the HPCAT beamline 16IDB at the APS/Argonne.

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Variation of the Jahn-Teller distortion with pressure in perovskite layers A_2CuCl_4. Local and crystal compressibility.

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We investigate how pressure modifies the Jahn-Teller (JT) distortion associated with the axially elongated $CuCl_6$ octahedra in the $[C_3H_7NH_3]A_2CuCl_4$ perovskite layer (A: Rb, CH_3NH_3, $C_2H_5NH_3$, $C_3H_7NH_3$). The aim is to elucidate whether the antiferrodistortive (AFD) structure exhibited by Cu^{2+} in the layers favours disappearance of the JT distortion thus of AFD or whether pressure induces tilts of the $CuCl_6$ octahedra preserving the molecular distortion associated with the JT effect [1,2]. For this purpose, we carried out X-ray absorption (XAS) and X-ray diffraction (XRD) experiments under pressure along the series whose interlayer distances vary from 7.75 to 12.33 Å. The use of both XAS and XRD techniques allows us to perform a complete structural study which is difficult to accomplish from XRD due to preferential orientation and texture. The analysis provides the variation of the Cu-Cl distances of the elongated octahedron as well as the intra- and interlayer Cu-Cu distances with pressure. Interestingly, the different compressibility of the bulk crystal and the $CuCl_6$ octahedron. Apart from the anisotropic variation of the crystal volume, the local $CuCl_6$ bulk modulus is an order of magnitude bigger than the crystal bulk modulus. This huge difference has been related to the stiffness of the Cu-Cl bonds which preserves the JT distortion of the $CuCl_6$ octahedra for pressures up to 20 GPa according to the JT energy (E_{JT}= 0.25 eV/Cu). A salient conclusion is that the application of pressure to these layered perovskites induces octahedron tilting rather than suppression of the JT distortion. A complete analysis of the variation of the JT distortion with pressure along the series will be presented at the Conference.

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Hexagonal perovskite in silicate

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Hexagonal silicate perovskite was confirmed in the $SrSiO_3$ compound by *in-situ* angle dispersive x-ray diffraction at high pressure. The perovskite was crystallized from pressure-induced amorphous $SrSiO_3$ in a diamond anvil cell by laser heating at 35 GPa. The crystal structure was same as the 6H-$BaTiO_3$ perovskite. On releasing the pressure, the perovskite also changed into an amorphous state. It is suggested that the possible structures in ABX_3 perovskites could depend on the ionic radii of the constituent elements. The tolerance factor, $t = (r_A + r_X) / \sqrt{2}(r_B + r_X)$, where r denotes the ionic radii of each element, has been viewed as such an indicator [1]. In case of ideal cubic perovskite, the value should be close to 1.0 as seen in $CaSiO_3$ perovskite. If a smaller tolerance factor is applicable, for example, $MgSiO_3$ (t = 0.90), the orthorhombic perovskite structure is stable. In contrast, for a tolerance factor greater than 1.0, which is caused by a large A^{2+} cation corresponding to $SrSiO_3$ (t = 1.04), the BX_6 octahedron changes its connecting mode from corner sharing to face sharing to keep an acceptable amount of space for the A^{2+} cation. This change repels the B^{4+} ions of the face sharing octahedron. As far as we know, this is the first report suggesting the existence of hexagonal perovskite in silicates.

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High-pressure study of $NaBH_4$ at 300 K.

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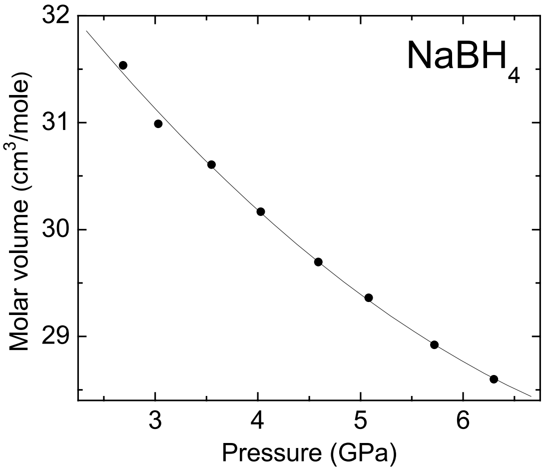
$NaBH_4$ is an ionic compound that is considered as a good material for fuel cells. The search for insulator-to-metal phase transition in compounds with high hydrogen content is a problem of fundamental interest because it is directly related to the problem of H-metal and because the densification of hydrogen is chemically effective through the presence of other constituents [1]. Recently, there is a growing interest for light hydrides because they are materials with high hydrogen-storage capacity [2, 3]. We present a high-pressure study of $NaBH_4$ by Raman and infrared spectroscopy, and by synchrotron x-ray diffraction.



$NaBH_4$ powder was loaded in a membrane diamond-anvil cell at ambient temperature in a dry-air box to prevent any reaction with water. At ambient temperature, we measured Raman and infrared spectra of $NaBH_4$ up to 85 GPa, and we performed synchrotron X-ray diffraction up to 60 GPa. At 2.7 GPa, the unit cell of $NaBH_4$ is cubic (*Fm3m* space group) with four molecules and the cell parameter is a=5.9389(5) Å. We measured the evolution of the molar volume with pressure between 2.7 and 6.3 GPa (see above figure). It undergoes a reversible phase transition at 6.8 GPa and this phase is stable at least up to 85 GPa. With preliminary refinement of the x-ray data, we determined a hexagonal unit cell with eight molecules ($P6_3$ or $P6_3/m$ are possible space groups), and the cell parameters are a=8.2646(5) Å and c=5.5575(5) Å at 12 GPa. From spectroscopic data, $NaBH_4$ remains an ionic compound to 85 GPa, and there is no discontinuity in the frequencies of the molecular modes.

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Structural relationships between $Sr_5Ta_4O_{15}$ and related layered $Sr_2Ta_2O_7$ through Crystallographic Shear.

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The striking similarity between related structures with different composition shed light on possible ways in which solids can accommodate correlated defects associated with nonstoichiometry. This is the case of perovskite-related structures which present an extraordinary compositional flexibility. This flexibility arises from the ability of the perovskite type (ABX_3) (1) to regularly intergrow with layers of different compositions. Well known examples include anionic deficiency, leading to the homologous series $A_nB_nX_{3n-1}$ (2) and cationic deficiency, which originates the well known $A_{n+1}B_nX_{3n+1}$ (3) Ruddlesden-Popper series, whereby perovskite blocks regularly intergrow with ABO_2 and AO NaCl-like layers, respectively. Several approaches to the description of these solids have been proposed in recent years.

The careful study of the Sr-Ta-O system by means of X-ray and electron diffraction and high resolution electron microscopy allowed us to describe two different structures with the $Sr_5Ta_4O_{15}$ and $Sr_2Ta_2O_7$ compositions. Such careful control leads to understand local structural changes as a function of the progressive annealing temperature. The structural relationships which can be established between these related phases is the subject of this paper, where a mechanism based on crystallographic shear is applied.

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Incommensurate structures
in the group VIa elements
above 100 GPa.

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The high-pressure behaviour of sulphur has long been known to be extremely complex, and it is only recently that it has begun to be simplified [1, 2]. The stable crystal structure at ambient conditions, S-I, comprises covalently-bonded S8-rings arranged in an orthorhombic structure [3]. Although S-I has been reported to undergo a gradual transition to an amorphous form on compression at room temperature [4-6], we observe S-I to transform directly to tetragonal S-II [7] at 38 GPa with no evidence of any intermediate amorphous phase. Single-phase diffraction profiles of S-III were observed above 95 GPa, and these revealed that S-III adopts the same incommensurately modulated monoclinic structure as Se-IV and Te-III. Sulfur is thus the first element observed to have an incommensurately modulated structure above 100 GPa. On pressure decrease a previously unreported phase of sulfur can be assigned to the triclinic structure of Se-III and Te-II. In this contribution we describe our most recent results on S-III and Se-II.

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High pressure study and electronic structure of the super-alloy $HfIr_3$

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The high melting temperature, good high temperature strength and good oxidation and corrosion resistance of iridium-base alloys suggests that they are interesting candidates for super-alloys for the aerospace industry [1]. This study presents the room temperature crystallographic, metallurgical, and electronic properties of the face-centered intermetallic compound $HfIr_3$, as a function of pressure. Both X-ray diffraction (XRD) measurements and full potential linearized augmented plane wave (LAPW) calculations were applied. No phase transition was observed in the XRD measurements up to a pressure of 27.6 GPa, and a total volume contraction of $V/V_0 \cong 0.92$, Fig. 1. Holzapfel equation was used to fit the volume-pressure curve to the equation-of-state, Fig. 2. The bulk modulus (B) at ambient pressure calculated in three ways, from the data in Fig. 2, from sound-velocity and density measurements, and from the LAPW calculations are B=279±4 GPa, B=297.9±2.5 GPa, and B=324 GPa, respectively. This material has a remarkably high-density value of $\rho=20.564\ g/cm^3$, and a high hardness value of $605\pm26\ Kg/mm^2$.

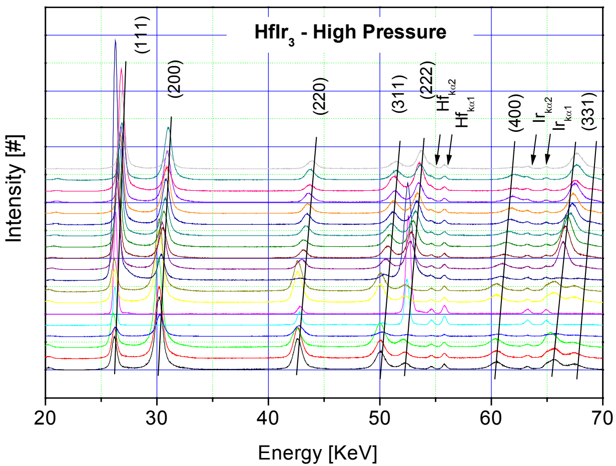

Figure 1: X-ray EDS powder diffraction of $HfIr_3$ as a function of pressure.

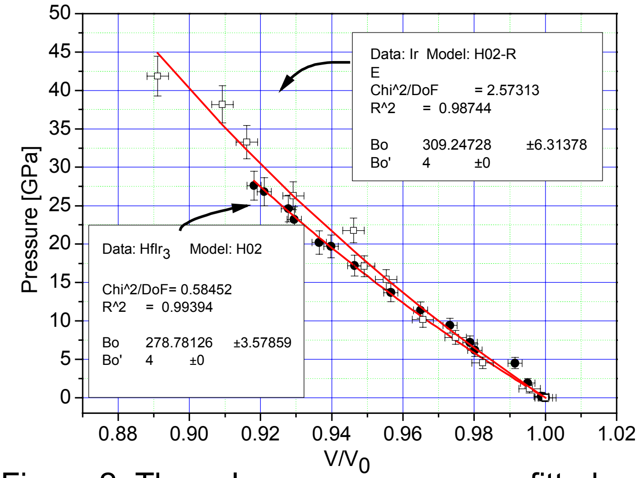

Figure 2. The volume-pressure curve fitted with a modified Holzapfel Equation.

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Orbital ordering behavior of $Nd_{0.5}Sr_{0.5}MnO_3$ under high pressures

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Many findings in the transport, magnetic and structural properties have revealed that orbital degree of freedom, Coulomb repulsive interaction, Jahn-Teller effect and superexchange interaction play very important roles in colossal magnetoresistance effect[1,2]. $Nd_{0.5}Sr_{0.5}MnO_3$ is an orthorhombic phase showing complicated magnetic structures and orbital ordering versus temperature. High pressure, as one of thermodynamic parameters, influences the charge, spin and/or orbital ordering of a sample. The synthesized $Nd_{0.5}Sr_{0.5}MnO_3$ polycrystalline bulk sample shows FM, A-type AF and charge ordering CE-type AF transitions on cooling from room temperature to 78K. We consider that the abundant magnetic structures are caused by phase segregation. We have investigated the orbital ordering behavior under hydrostatic pressures up to 7.5 GPa using the cubic anvil apparatus and found that low pressure favors the A-type AF phase with $d(x^2-y^2)$ orbital ordering and the CE-type AF phase with $d(3x^2-r^2)/d(3y^2-r^2)$ orbital ordering, while suppresses the FM phase with disordered orbital ordering; however, high pressure favors the A-type phase and suppresses the CE-type AF phase. Transport property enhancement and large resistance changes under high pressures are observed.

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Comparative high pressure behaviour of $Sc_2(WO_4)_3$, $Y_2(WO_4)_3$ and $Al_2(WO_4)_3$

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Abstract

Using x-ray diffraction and Raman scattering techniques, high pressure behavior of three tungstates of the family $M_2(WO_4)_3$, all having orthorhombic structure at the ambient conditions, has been investigated,. Of these $Sc_2(WO_4)_3$ transforms reversibly to a monoclinic phase at low pressures and transforms irreversibly to an amorphous phase at beyond 7 GPa. In contrast, in $Y_2(WO_4)_3$ the initial orthorhombic phase transforms smoothly to a disordered phase at 4-6 GPa. In aluminium tungstate [$Al_2(WO_4)_3$], our results confirm the recent observations of two reversible phase transitions below 3 GPa. In addition, we find that this compound undergoes two more phase transitions at ~ 5.3 and ~ 6 GPa before transforming irreversibly to an amorphous phase at ~ 14 GPa. The correlation between the stability range of orthorhombic phase and counter cation size suggests that $Y_2(WO_4)_3$ may have a largest field of negative thermal expansion in this family of compounds.

Atomic structure of pressure-induced amorphous semiconductors

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The paper will briefly review and discuss results of our investigations on the atomic correlations in amorphous Zn-Sb, GaSb, GaSb-Ge and Al-Ge alloys. These semiconductor alloys were prepared by solid state reactions in the course of heating the quenched high-pressure phases [1]. The structure of the final products was studied by neutron diffraction for the Al-Ge, GaSb and GaSb-Ge alloys and by transmission electron microscopy for the Al-Ge and Zn-Sb ones. The samples thus obtained were proved to be homogeneous bulk amorphous materials containing no crystalline inclusions.

Only minor changes in the tetrahedral short-range order were observed for the amorphous GaSb and $Zn_{41}Sb_{59}$ alloys compared to crystalline GaSb and ZnSb phases with similar chemical compositions. Essential distortions of the tetrahedral network were established for the amorphous $Al_{32}Ge_{68}$ and $(GaSb)_{76}Ge_{24}$. The effective coordination numbers, $n_{\mathrm{eff}} = 4.5$ and 4.25, respectively, in those alloys were found to appreciably exceed $n_{\mathrm{eff}} = 4$ characteristic of the ideal tetrahedral structure. The Reverse Monte Carlo (RMC) calculations for the amorphous $Al_{32}Ge_{68}$ have shown that the Ge atoms do not form a tetrahedral arrangement, the corresponding first coordination number being $n_1 = 2.88$. The Al-Ge and Al-Al correlations ($n_1 = 5.53$ in total) increase n_{eff} to the observed value of 4.5, while the Al atoms do not construct a continuous network through the sample ($n_1 = 1.37$).

Fourier transformation of the measured structure factor of amorphous $(GaSb)_{76}Ge_{24}$ clearly showed the existence of two different nearest-neighbour distances. The RMC simulations demonstrated that Ge atoms in this alloy do not form clusters and randomly substitute Ga and Sb atoms. The calculations also showed the occurrence of a large chemical disorder in the amorphous $(GaSb)_{76}Ge_{24}$ and GaSb alloys, where about 30% of the nearest neighbours were atoms of the same kind (Ga-Ga or Sb-Sb pairs).

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High Pressure Studies of Unusual Metals: Eu & Be

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Investigations of the high-pressure properties of metals are important to geophysics, planetary science, technology development and basic science. Experimental studies of metals at high densities serve to validate and extend fundamental understandings of electronically-driven behavior and transitions. Advances in diamond anvil cell capabilities and diagnostics are enabling studies of metals at high pressures that can address long-standing questions and predictions. Two systems of interest are the lowest-Z metal Beryllium, and the “anomalous” lanthanide Europium. Both of these metals exhibit unusual behavior at low pressures. At high temperature and low-pressure the HCP-BCC phase line in Beryllium has a negative pressure derivative [1]. The extension of this phae line remains an open question. Europium is a divalent metal, an exception to the systematics of neighboring trivalent lanthanide metals. A transition through mixed valency and to divalency has been the subject of theoretical and experimental studies [2,3], but remains an open question in need fo further experimetnal study.

We have studied these metals to pressures exceeding 100 Gpa using x-ray diffraction and, in the case of Be, Raman spectroscopy. Our results are generally consistent with previous studies, and suggest the possibility of the onset of novel behavior. In this presentation, our results and progress toward resolving questions regarding the behavior of Europium and Beryllium at high pressures will be discussed.

This work was performed under the auspices of the U.S. DOE by the Univ. of Calif., LLNL under contract No. W-7405-Eng-48. Use of the HPCAT facility was supported by DOE-BES, DOE-NNSA (CDAC), NSF, DOD–TACOM, and the W.M. Keck Foundation. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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On the orthorhombic phase controversy at megabar pressure in Ti

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Recent experimental findings of the orthorhombic phases in Ti [1-2] were unexpected, as earlier theoretical simulations had predicted ω (AlB_2-type)- to β (body centred cubic-BCC) transition. Also, different experiments observed the α–ω transition scattered in the range 2 - 11.9 GPa in Ti. But the more controversial issue has been the occurrence and transition pressures of its γ and δ phases, both of them having orthorhombic structure. Among these inconsistencies are the results of Ref. 3 that no orthorhombic phase occurs at all at high pressures. On the other hand Kutepov and Kutepova [4] obtained much better agreements with the experimental data regarding the structural transitions; but the nature of their total energy curves in the γ phase near 13 Å^3/atom volume and the nature of enthalpy curve in the phase in the 135-145 GPa range appear highly suspect.

Hence, with the aim to resolve the prevailing confusion about the high pressure behavior of Ti, we have carried out extensive accurate first principles electronic structure calculations employing VASP and WIEN2k programs. Our total energy calculations show the existence of only γ phase in very small pressure region and the δ phase is not elastically stable at any volume compressions. The δ phase always relaxed to bcc structure. Various transitions pressures obtained by our calculations will be presented along with the critical comparison with literature.

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Hunting the SC16 and Cmcm phases in ZnS at extreme conditions

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Zinc sulfide is a II-VI semiconducting material with two archetypal crystalline structures at room conditions, namely wurtzite and zincblende. After the first phase transition to NaCl structure, reported in several experimental studies, a further transition to a *Cmcm*-like distorted rocksalt structure above 64 GPa was observed [1,2]. No investigations exist about the high pressure and high tempearature behaviour of ZnS. From a theoretical point of view, for pressures below 65 GPa different calculation methods have found that the SC16 phase is thermodynamically stable in a pressure range below that where the NaCl structure is experimentally observed [3,4]. The fact that the SC16-ZnS has not yet been observed experimentally at room temperature may confirm the argumentation that the formation of the SC16 phase is hindered by kinetic-energy barriers. Therefore, the possibility of observing SC16-ZnS in a way similar to SC16-GaAs [5] is an open question and experimental investigations are invited to explore this prediction.

We have performed X-ray diffraction measurements at high pressure up to 40 GPa and temperature up 1000 K. No evidence of SC16 phase has been observed in the upstroke nor in the downstroke pressure runs between the zincblende and the NaCl phase. A combined X-ray diffraction and X-ray absorption experiment has been carried out up to 85 GPa at room temperature. A post-NaCl phase has been observed both in diffraction and absorption data above 65 GPa. A detailed analysis is under way to verify whether the high pressure phase is *Cmcm* and to give information about its short range chemical ordering.

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Effect of pressure on the crystal structure of hydrous ringwoodite up to 7.9 GPa

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The specimen used in this study was a single crystal of hydrous ringwoodite synthesized by Ohtani and Mizobata (1998) using a multi-anvil apparatus at conditions of 1680˚C and 22 GPa. Electron microprobe analysis showed a chemical composition of 42.83wt% SiO_2, 56.42 wt% MgO, yielding a total wt% of 99.25 (H_2O excluded) with Mg/Si being 1.97. The H_2O content measured by SIMS was 0.200(±0.004) wt %. The unit cell content is calculated to be $Mg_{1.97}SiH_{0.03}O_4$. Sets of X-ray diffraction intensities up to 7.9 GPa to sin / =0.87 Å^{-1} were measured with a single crystal of 35x35x24 μm using synchrotron radiation of wave lengths 0.6998 Å, 0.7017 Å, 0.6958 Å, 0.6961 Å and 0.7019 Å at ambient pressure, 3.2 GPa, 5.0 GPa, 6.2GPa and 7.9 GPa, respectively at the beam line BL-10A, Photon Factory, Tukuba, Japan. The wave lengths were calibrated by the unit cell constants of a ruby standard crystal. The modified Merrill-Bassett type diamond anvil pressure cell was used. The 4:1 fluid mixture of methanol and ethanol was used for pressure medium and SUS301 plate was used for gasket. The pressure was calibrated using the ruby fluorescence method. The unit cell parameters were obtained using 18~36 reflections with 2θ from 16° to 50°. The calculated isothermal bulk modulus using the unit cell volumes at ambient pressure, 3.2 GPa, 5.0 GPa, 6.2GPa and 7.9 GPa with the Birch-Murnaghan equation of state assuming K'=4 was K_0=184(6) GPa. The density calculated with the unit cell content $Mg_{1.97}SiH_{0.03}O_4$ and the unit cell volume at ambient pressure was 3.544 gr/cm^3 which is 0.5% smaller than the 3.563 gr/cm^3 value of anhydrous ringwoodite (Sasaki et al., 1982).

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X-ray Diffraction Studies of Single Crystals at High Pressure using Synchrotron Radiation

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X-ray diffraction from single crystals is the most descriptive method of analysing solid-state structure. Ideal detailed structural analysis of materials at high pressure should include single crystal diffraction studies. Most studies of this nature use in-lab radiation sources. [1] Only a few studies of single crystal diffraction using synchrotron radiation have been done. [2] The restricted cone angles on a DAC severely limit the spots per pattern, especially when Be plates are not used. In addition, materials with small unit cells yield very few spots per pattern in comparison to macromolecules such as proteins.

We have done x-ray diffraction experiments of single-crystals in DACs at high pressure at Cornell University's synchrotron source (CHESS). The beamline used was configured for angle-dispersive diffraction, and image plates were used as detectors. Our samples were small molecular crystals (RDX or 1,3,5-trinitrohexahydro-1,3,5-triazine), loaded in Merrill-Bassett type DACs, mounted on a two-circle Diffractometer. The DAC was oscillated over 4° around an axis perpendicular to the x-ray beam. Data were obtained at 1, 2 and 3.5 GPa. An existing data analysis package (DPS/Mosflm/CCP4, usually used by protein crystallographers) was used indexing and peak integration.

Structure factors were obtained at 1 GPa and structural analysis was performed using MaXus crystallographic software. Compared to the ambient pressure structure, significant bond distortions, angular distortions and ring puckering are evident at 1 GPa. The 2 and 3.5 GPa data indicates the existence of two separate phases, a phase change to a monoclinic structure, or a twinned crystal. It is possible that the phase change previously seen at 4.5 GPa occurs at lower pressure.

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High Pressure Behaviour of Mn_3GaC

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The manganese based intermetallics, Mn_3GaC, with cubic antipervoskite type structure falls in to an intermediate class of materials between the rare earth manganetites and the normal metallic alloys. Mn_3GaC has an Invar like antiferromagnetic (AFM) ground state stable below 160 K. At the transition to a ferromagnetic (FM) phase (163.9 K), the lattice parameter undergoes an isostructural collapse *i.e.*, exhibits negative thermal expansion (NTE). The computed electronic debsity of states (DOS) at E_F of the AFM and FM phases of Mn_3GaC are similar resulting in a ground state with competing order. The present high pressure angle dispersive X-ray diffraction investigations on Mn_3GaC up to 35 GPa are aimed at investigating the signatures of the strong interaction between the magnetic and the structural properties of Mn_3GaC on the compressibility and its structural stability under pressure.

High pressure ADXRD measurements with in-situ Ag pressure calibrant were carried out on powdered Mn_3GaC at the synchrotron radiation source at Elettra [proposal No. 2002308. The ambient cubic phase is retained up to 35.0 GPa . The P-V relation (equation of state {EOS}) fitted to third degree Birch Murnaghan equation of state yields the bulk modulus and its pressure derivative as 140.5 GPa and 3.34 respectively. Though from the low temperature behaviour, an anomaly in equation of state is expected, none is observed in the P-V data. It may be noted that various types of anomalies, a linear pressure variation of the volume (ZrW_2O_8, $ZrMo_2O_8$, $\alpha NbOPO_4$), a small B with very large B'(Pu, $\beta NbOPO_4$), and / or decrease of B with pressure over a limited pressure region ($Al_2W_3O_{12}$, FeNi alloy) are found in several materials that either exhibit or are prone to NTE. A detailed computational investigations of electronic and magnetic structure under pressure and measurements at very close spaced pressure points currently in progress may reveal subtle anomalies in this material.

A High Pressure X-ray Powder Diffraction Study of Elemental Erbium.

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Abstract: As a member of the Lanthanide series, elemental Erbium is part of a fascinating class of Rare Earth metals that possess complex electrical, magnetic, thermal, and other behaviors that are little understood. In this spirit, we have undertaken X-ray powder diffraction studies of elemental Erbium at room temperature in the interest of elucidating the phase structure of the material at high pressures above 40 GPa using the HP-CAT synchrotron X-ray beamline in the Advanced Photon Source at Argonne National Laboratory. In these studies, cyclohexane was used as an excellent nonreactive and quasi-hydrostatic pressurizing medium.

+ Deceased

Optical Studies on Solid Methane at Room Temperature to 301 GPa: Indication of Metallization

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Abstract

Pressures were measured using a submicron thick x-ray diffraction marker on the wall of the sample hole which eliminates the need for a highly collimated x-ray beam. Reflectivity and transmission measurements were used to measure the refractive index to 301 GPa. From 34 GPa to 216 GPa the refractive index varied linearly with pressure but then jumped substantially by 301 GPa. There was no noticeable absorption on the energy range 1.15 – 2.9 eV at pressures to 216 GPa, but substantial absorption was present at 301 GPa. The ratio of the molar reflection divided by the molar volume, R/V should approach one in the long wave length limit if metallization has occurred. There is a large jump in the R/V for methane between 216 GPa and 301 GPa, an indication of metallization. As an alloy with a preponderance of hydrogen it may be a high Tc superconductor.

Oral

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Solvothermal crystal growth of GaN: evaluation using Li_3GaN_2 as nutrient and ammonia as solvent.

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The synthesis of GaN single crystal appears as a challenge to prepare substrates for developing different micro-electronic or opto-electronic devices.

The most investigated crystal growth method involving severe pressure and temperature conditions [1] and solvothermal processes being promising [2], solvothermal crystal growth of GaN has been evaluated.

Ammonia as nitriding solvent has been selected – GaN being not so soluble in such a solvent Li_3GaN_2 was used as nutrient. Solvothermal transport experiments have been carried out both in subcritical and supercritical conditions. GaN deposition on seeds has been evaluated through XPS characterizations.

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Preparation of Homogeneous Mixtures of Nanoparticles/Thermite Mixtures by Rapid Expansion of Supercritical Dispersion (RESD)

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Bulk nanoparticles tend to be available particularly as agglomerates of primary particles. Mixing nanoparticles by co-milling or other mixing techniques result in mixtures of existing often nearly unaffected agglomerates. To solve this problem and to obtain homogeneous mixtures of isolated particles the processing of nanoparticles is often accompanied by a liquid dispersing step in which the agglomerates were broken. Due to surface tension forces and surface potentials the particles tend to reagglomerate during the subsequent evaporation step of the dispersing liquid ("coffee drop effect").

By using a supercritical fluid as the dispersing fluid, the process conditions can be tuned such, that a liquid state can be avoided. By expanding the dispersion through a nozzle to atmospheric conditions the particles were forced to desagglomerate and can be sprayed directly on a substrate. In this work, mixtures of nanoparticles were produced in two different scales: The preparative scale processes nanoparticles in the order of one gram, whereas the analytical scale device directly prepares milligrams of nano particle mixtures into a DSC pan for subsequent thermo analytical examinations.

As an example the result of a Rapid Expansion of a Supercritical Dispersion (RESD) mixing of molybdenum and alumina nano particles analysed by EDX scanning is shown in figure 1.

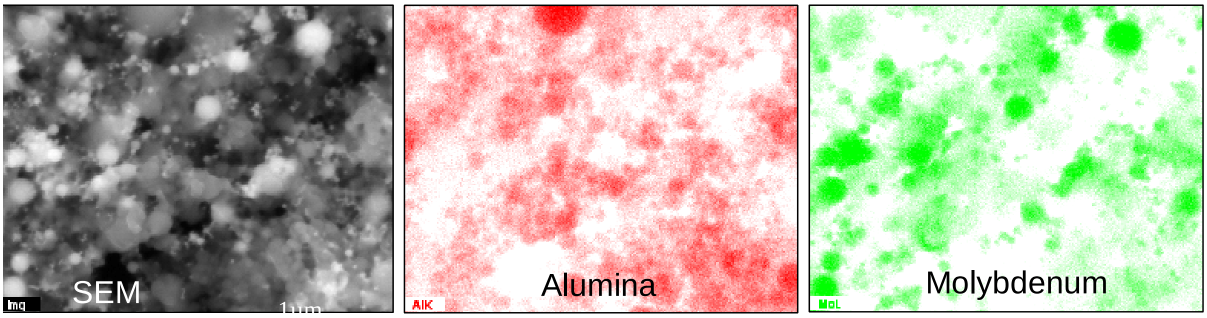

Figure 1: SEM and EDX scan of an Al/Mo mixture after RESD processing

The composition contains an Al/Mo weight ratio of 1/3.8. The particles were stirred at 15 MPa and 323 K for 15 minutes in CO_2. The supercritical dispersion expanded through a nozzle with 60 µm diameter and a length of approx. 500 µm. The particles were collected on a silicon wafer substrate for subsequent analysis.

The elemental analysis shows a high degree of homogeneity of the mixture formed on a silicon wafer substrate. It has been observed, that the existing agglomerates of the used species could have been cleaved.

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Synthesis of Needle Type Rare Earth Oxide by Solvothermal Treatment of Rare Earth Chloride

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Solvothermal reactions have been widely studied for the synthesis of a variety of inorganic materials [1]. However, the use of chlorides as starting materials has been scarcely examined, because hydrochloric acid, generated during the reaction, is corrosive to metals. We found that the reaction of rare earth (RE) chloride hydrates in 1,4-butanediol (1,4-BG) at 300 ºC for 2 h in the presence of small amounts of *n*-hexylamine and 1,6-hexanediamine yielded phase-pure $RE(OH)_2Cl$ for La-Dy, but the product obtained from Ho-Yb and Y was a mixture of $RE_2O_3·xH_2O$ and $RE(OH)_2Cl$ [2]. In this work, the morphology of the products obtained by the solvothermal reaction of RE chloride was investigated.

The reaction of RE chloride hydrate (Y, Er and Yb) in 1,4-BG at 300 ºC for 2 h gave a mixture of $RE(OH)_2Cl$ and $RE_2O_3·xH_2O$, and the product was composed of irregularly-shaped and needle-like particles. When the reaction time was prolonged to 10 h, $RE(OH)_2Cl$ and $RE_2O_3·xH_2O$ were formed for Er or Y but pure-phase $RE_2O_3·xH_2O$ was obtained for Yb. As shown in Fig. 1, the latter product was comprised of needle-shaped crystals with 0.2-0.6 μm width and 5-15 μm length. The reaction in toluene at 300 ºC for 2 h yielded pure-phase $Yb_2O_3·xH_2O$ and SEM image of the product showed the formation of irregularly-shaped particles. By the prolonged reaction time (6 h), the morphology of $Yb_2O_3·xH_2O$ was changed to needle-shaped crystals, which was much smaller than those obtained in 1,4-BG. These $Yb_2O_3·xH_2O$ products decomposed to Yb_2O_3 at around 400 ºC in air, presenting the needle-shaped morphology and it was maintained even after calcination at 800 ºC.

Fig. 1. SEM image of $Yb_2O_3·xH_2O$ obtained in 1,4-BG at 300 ºC for 10 h.

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Recrystallization of Acetaminophen and Sulindac from the Batch and Continuous Supercritical Anti-Solvent Precipitation

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Abstract

The supercritical anti-solvent (SAS) precipitation is an important high pressure process for the recrystallization and micronization of pharmaceuticals. We compare the experimental results from either the batch or continuous SAS process for the recrystallization of acetaminophen (non-steroidal anti-inflammatory drug) and sulindac (antibiotics) using supercritical carbon dioxide as the anti-solvent. The experimental apparatus includes the carbon dioxide supply, recrystallization and depressurization sections. The high pressure vessel in this study has a volume of 75 ml. Solutions of either pharmaceutical dissolved in various solvents were investigated in this study. Upon introducing the supercritical carbon dioxide, volume expansion resulted in the formation of micronized particles. The morphology and crystalline properties of these pharmaceuticals were observed before and after the SAS processes. Taking acetaminophen for example, the particle size was larger than 100 μm before the treatment. It decreased to 60 μm after the batch SAS process, and to less than 10 μm after the continuous SAS process. The morphology also changed from the original irregular and broken shape to short rod crystalline after the continuous SAS process. On the other hand, smaller particles of sulindac were obtained from the batch process, rather than the continuous treatment. Effects of various operation parameters such as temperature and pressure in these SAS processes were analyzed and discussed. The optimal conditions for the micronization of these pharmaceutical particles using the supercritical technology are reported.

Measurement of Dielectric Property of Compressed Gases in the Critical Region.

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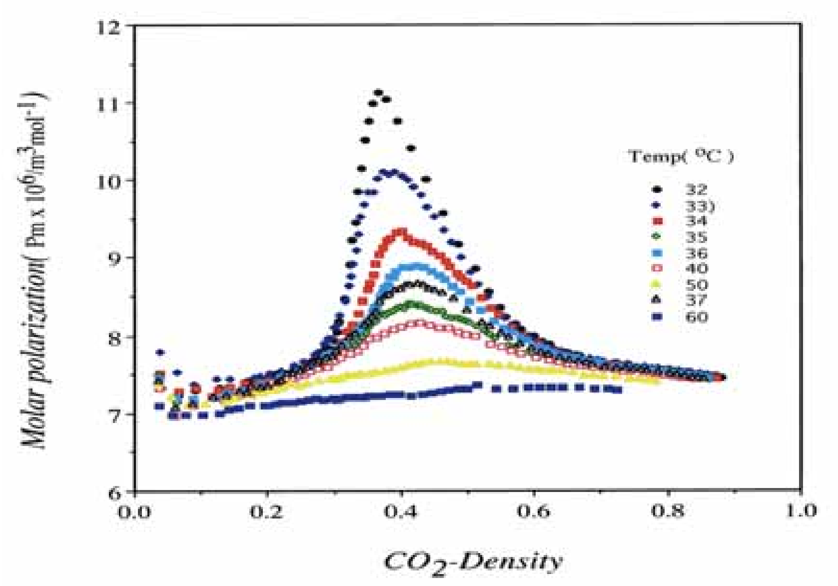
ABSTRACTS

It has long been speculated without clear pysico-chemical evidence that strong molecular association could be induced near the critical point. We have developed a reliable instrumentation for measuring the dielectric property of compressed gasses such as carbon dioxide, ethane, ethylene and nitrous oxide, in the critical region. This method is capable to evaluate physical property, static permittivity and a molar polarization, based on the electric capacitance. A typical example of our capacitance measurement is demonstrated below. The relationship between the molar polarization of carbon dioxide and the density is shown as a function of temperature.



Molar polarization was clearly enhanced near the critical region (ρ_c=0.46), depending upon the temperature.

This paper will present a firm set of experimental data concerning electric capacitance of the several compressed gases, and discuss about the molecular association around in the critical region.

Generation of Discharge Plasmas in Supercritical CO_2 and Its Application to Organic Reaction

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Large-capacity discharge plasmas have great capability of many applications such as sterilization, deodorization, dioxin treatment, and water treatment. We have tried to generate large-capacity discharge plasmas in high-pressure and high-temperature fluids including their supercritical states and recently found that the discharge plasmas could be generated in supercritical carbon dioxide. For this purpose, we designed and manufactured an experimental apparatus, and tried to explore the operating conditions where the plasmas could be generated through the experiments at various conditions (305-333 K and 0.1-20.0 MPa) in supercritical CO_2. As a result, it was found that discharge plasmas could be produced in supercritical CO_2 as well as in gaseous CO_2 and the brightness of the plasmas became higher as the pressure increased at a constant temperature. It was also found that the breakdown voltage depended upon the density of CO_2 at near- and supercritical pressures at above the critical temperature of CO_2. Next, this phenomenon in supercritical CO_2 was applied to reactions of organic compounds for developing a super-rapid molecular conversion method.

Extraction of Astaxanthin from *Haematococcus pluvialis* using Supercritical CO_2 at High Pressure Condition

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Astaxanthin (3,3'-dihydroxy-β,β'-carotene-4,4'-dione) is a ketocarotenoid oxidized from β-carotene. Due to its attractive red colour and higher antioxidant activity than α-carotene, β-carotene, lutein, lycopene, cantaxanthin and vitamin E, astaxanthin can be used as a food colourant and in medicine. *Haematococcus pluvialis* has high concentration of astaxanthin, about 0.5 to 3% astaxanthin on a dry weight basis. In this study, astaxanthin from *Haematococcus pluvialis* has been extracted using supercritical CO_2 and modified ethanol to obtain high concentrated of astaxanthin. The antioxidant activity of extract has also been tested by diphenyl pycril hydroxyl (DPPH) and measured by UV-Vis Spectrophotometer. The effect of pressure, temperature, CO_2 flow rate and the existence of ethanol on total extraction yield, astaxanthin extracted and astaxanthin concentrated in the extract were studied. Extraction was carried out at 200 – 550 bar of pressure, 40 – 80^oC of temperature, 2 – 4 ml/min of CO_2 flow rate, 1.67 – 10 % volume of ethanol:CO_2. The extract was analyzed by a Shimadzu Liquid Chromatograph LC-10AD, equipped with Diode Array Detector SPD-M10A and a 5C18-MS Waters of column. Maximum astaxanthin content in *H. pluvialis* sample was obtained by soxchlet extraction using dichloromethane as solvent. Maximum astaxanthin content was 3.43% weight. Astaxanthin extracted and concentrated increased with increasing pressure at high pressure but decreased with increasing temperature at low pressure (200 bar). Maximum extraction yield, astaxanthin extracted and concentrated were 22% weight of sample, 87% of astaxanthin content in sample, and 12% of total extract, respectively. The antioxidant activity of extract degraded with the existence of ethanol.

Comparison of essential oil composition of *Salvia mirzayanii* obtained by supercritical fluid extraction and hydrodistillation methods

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Supercritical fluid extraction (SFE) has been widely used to the extraction processes in pharmaceutical industries. Besides application of SFE in pharmaceuticals, it has been applied on a wide spectrum of natural products and food industries such as natural pesticides, antioxidants, vegetable oil, flavors, perfumes and etc [1-2].

Salvia is one of the most important genera of the Family Lamiaceae. Several species of salvia are used in folk medicine as antiseptics, astringents and spasmolytics[3].

The effect of different parameters such as temperature, pressure, modifier volume, dynamic and static extraction time on the SFE of the plant were investigated. The orthogonal array experimental design method was chosen to determine experimental plan, L_{25} (5^5). In this design the effect of five parameters and each at five levels were investigated on the extraction efficiency and selectivity [4].

Further more, the essential oils of the plant were isolated by hydrodistillation in Clevenger-type apparatus for 5 hours. The chemical compositions of the SFE extract and hydrodistillation were identified by GC-MS and determined by GC-FID.

The main components of *Salvia mirzayanii* were Linalool, Linalyl acetate, α-Terpinyl acetate, δ-Cadinene, Spathulenol, Cubenol and α-Cadinol. The extraction yield, based on hydrodistillatin was 2.2% (v/w), and based on the SFE varied in the range of 0.65-10.59% (v/w) under different conditions

Key word: *Salvia mirzayanii*; supercritical fluid extraction; hydrodistillation; essential oils.

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SOLUBILITY OF PCP AND HCB IN SUPERCRITICAL CARBON DIOXIDE AT HIGH PRESSURE

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Abstract

A new thermodynamic model was developed for modeling the solubilities of solide solutes in supercirtical carbon dioxide at high pressure .the model combines the cubic Soave equation of state (EOS) with the Wong Sansler (WS) mixing rule (MR) . the model is applied to correlate the solubilities of Penta chloro phenol (PCP) and Hydroxy chloro benzene (HCB) in supercritical carbon dioxide at costant temerature , at high pressure .

The model provides a better vorrelation than the conventoinal models that use Peng Robinson –EOS (PR-EOS) with Quadratic Van Der Walls (VW) or Wong Sandler (WS) mixing rule (MR).

Keywords: solid-fluid equilibria; Equation of state; mixing rule; wong sandler; binary mixture; supercritical carbon dioxide .

Lanthanum Aluminate Formation in Water Vapors under Sub- and Supercritical Conditions

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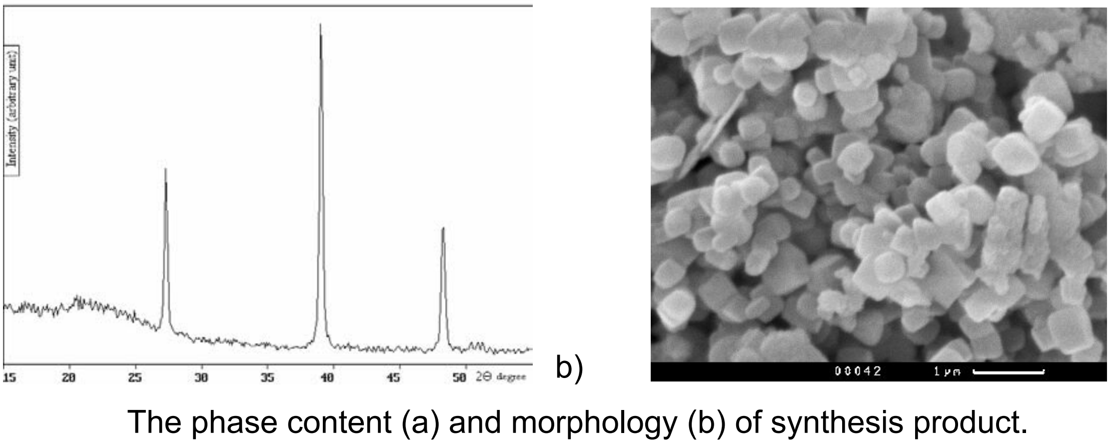
Fine–crystalline lanthanum aluminate powders were prepared by the thermovaporous treatment of mechanical mixtures of lanthanum oxide and aluminum hydroxide. The formation process of $LaAlO_3$ crystals has been investigated by X-ray diffraction and SEM. The properties of synthesized pure and doped lanthanum aluminate have been studied by chemical spectral analysis, electron diffuse reflection spectroscopy and by the luminescent analysis. The particle morphology was observed using SEM.

The lanthanum aluminate synthesis was carried out in two stages in water vapor medium. At first, the precursor mixture was treated by water vapor at 200 °C (P=1.5 MPa) during 20 – 22 hours, and then in water fluid at 400 °C (P=22 MPa) during 18 – 24 hours. The nucleator ($<$ 1%) was added in the reaction mixture. The temperature of the synthesis in water fluid was about 1000 °C below that of the sintering process in air. After the first stage of synthesis the product was the mixture of two phases: lanthanum hydroxide and disordered boehmite. The finish product was comprised of lanthanum aluminate with the crystal sizes 200 – 600 nm. The considered way of the synthesis allows to producing the pure or doped lanthanum aluminate. Therefore, lanthanum aluminate doped by Eu was produced. This material was characterized by an intensive luminescence near 590 and 620 nm.



a) b)

The phase content (a) and morphology (b) of synthesis product.

Removal of carbon dioxide from the gas produced by hydrothermal biomass gasification

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The production of hydrogen and methane by reaction of organic matter using hydrothermal gasification is feasible for feedstock with high moisture content. Wastes from the agricultural sector can be used, e.g. grape residue, rests of plants or sewage sludge. Typical reaction conditions are temperatures of about 600 °C and a pressure of 30 MPa. By cooling, the product gas phase separates from the liquid effluent which will contain the inorganic compounds and a low quantity of residual organic matter.

A high pressure gas washer can be easily integrated in this gasification system resulting in a reduced carbon dioxide content in the product gas and thus a higher hydrogen and methane partial pressure. This theoretical concept was demonstrated in the pilot plant VERENA.

Experimental data which will prove the effectiveness of this concept will be shown. Experiments for the carbon dioxide removal with a model gas mixture and during gasification experiments of real biomass were carried out.

The model gas mixture used consisted of hydrogen (52 volume-%), methane (20 %), carbon dioxide (27 %) and carbon monoxide (1 %). This gas composition is similar to the gas phase achieved in biomass gasification experiments. The gas flow, the water flow and the pressure in the washing column were varied in the experiments.

Up to 98 % of the carbon dioxide could be removed by this technique at optimized conditions. The hydrogen loss in the lean gas amounted to about 6 %, the methane loss to about 8 %. The cleaned model gas contained about 75 % of hydrogen.

Hydrothermal reforming of alcohols, pyroligneous acid and pyrolysis oil

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Hydrothermal reforming is a promising method to generate a product gas rich in hydrogen and methane. Educts with a high water content and thus low calorific value can be used without any pre-drying or upgrading step. At hydrothermal conditions the organic compounds react with water to form a fuel gas. Depending on the educts, conversions at a hydrocarbon/water ratio up to 1:1 (for methanol, corresponding to a solution of 64 w.-%) are possible; the residence times are in the range of a few seconds.

Reforming reactions were studied in tubular flow reactors; the tube length was 1000 mm. The high pressure tubes were made of the nickel base alloy 625 or the stainless steel SS316. Experiments were performed at pressures of 25 up to 45 MPa and temperatures in the range of 400 to 700° C.

Bio-ethanol, pyroligneous acid and the water-soluble pyrolysis oil (often called ‘bio crude oil’) fraction are starting materials from renewable primary products. Bio-ethanol is generated by fermentation, pyroligneous acid and bio crude oil by thermo-chemical treatment of biomass.

Pyroligneous acid is a by-product from the production of charcoal and consists of 75 % water, in which 12 % acetic acid and homologues, 2 % methanol, 1 % acetone and methyl acetate and about 10 % wood tar are dissolved. The production of bio crude oil delivers a water-miscible fraction with a lower calorific value whose use for conventional gasification procedures is not cost-effective, however is well suitable for hydrothermal reforming.

The product gas consists mainly of hydrogen and smaller amounts of methane, carbon dioxide and carbon monoxide. Decomposition, methanation and watergas-shift reaction are strongly influenced by the choice of the material of the inner reactor wall, the surface to volume ratio and addition of catalysts like potassium salts.

Preparation of low-density porous glass ceramics under Hydrothermal Conditions

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On the previous research work, the present authors had been suggested an alternative route for the preparation of porous materials from waste glass through compaction by hydrothermal hot pressing (HHP) conditions. The treatment was conducted at a much lower temperature of 200°C for 1 h with 10 wt% water content under a loading pressure of 20 MPa and particle size <38µm [1]. On the present research work, the effect of expansion of the HHP compacts by varying the type and amount of additives such as dolomite, slag and sodium carbonate was investigated. Low density porous glass ceramics was prepared by mixing the glass powder with inorganic compounds under the hydrothermal hot pressed following the conventional heating of HHP compacts as it was reported [1]. SEM observations showed the presence of the called new phase in presence of all additives, however with the addition of only 5-wt% sodium carbonate on the glass powder, the HHP compact had a greatest new phase, which it is increased by the action of the sodium ions that promoted the reactivity between the glass and water under hydrothermal conditions. Consequently, the maximum expansion of HHP compacts was obtained after conventional heating temperature at 700 ºC for 1h. The expanded product reached low relative density value of 0.3464 g/cm^3.The current value was lower than the density value (0.40g/cm^3) of the expanded glass prepared at similar conditions temperature of 750C in air for 1h

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High selective synthesis of acrolein from glycerol in high pressure and high temperature water

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In a coming biomass society, various conversion processes of biomass materials with high selectivity and high speed must be demanded. Triglyceride such waste vegetable oil is gained much attention because bio-diesel is accepted as the sustainable energy resource. The bio-diesel is synthesized by methanolysis of triglyceride into methylester. The by-product of the methanolysis is glycerol and its effective utilization is also required. Glycerol is a C3 compound as same as propane and propylene. It was reported that acrolein (it is synthesized by partial oxidation of propane and is a precursor of acrylic acid) was produced from glycerol with a high selectivity within 50 % conversion of glycerol in high pressure and high temperature water (HHW) [1], [2]. Nevertheless, the yield of acrolein was still low at the higher conversion of glycerol. In this study, we performed glycerol reaction in HHW by use of a batch and a flow apparatus with and without adding an acid catalyst. As a result, it was confirmed that almost 80 % of acrolein was obtained at 90 % of glycerol conversion with acid catalyst in supercritical condition (673 K). The dehydration of glycerol into acrolein was quite sensitive against pressure in supercritical condition because it was assumed to depend on proton concentration in water. We also developed a simple model of glycerol conversion into acrolein and analyzed the kinetic parameters. The rate constant of acrolein decomposition is always higher than that of acrolein formation in the absence of acid catalyst. On the other hand, it was revealed that the rate constant of acrolein formation overcame that of acrolein decomposition by adding acid in supercritical condition.

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Mechanism of the incorporating of the dopant ions into the structure of oxides in supercritical water fluid.

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In the present report are given the result of study of the mechanism of incorporation of doping ions in structure of fine-crystalline corundum (α-Al_2O_3) and yttrium-aluminium garnet ($Y_3Al_5O_{12}$) formed in water vapor in supercritical conditions [1]. Synthesis of oxides was carried out upon two-stage heating at 200-270°C and then at 400-410°C under water fluid pressures 20 – 26 MPa in autoclaves with special container. As precursors were aluminum hydroxide (hydrargillite) and yttrium oxide. The dopants were added in reaction medium as oxides or water solutions of salts. The chemical compounds of chrome, iron, neodymium and manganese were dopants. The products were studied by physical-chemical methods. A study revealed that the state and allocation of doping ions in a crystal lattice of oxides is determined not only by conditions of synthesis (T °C and P MPa), but also by chemical composition and charging state of a dopant, by its concentration, and by content of impurities in precursor.

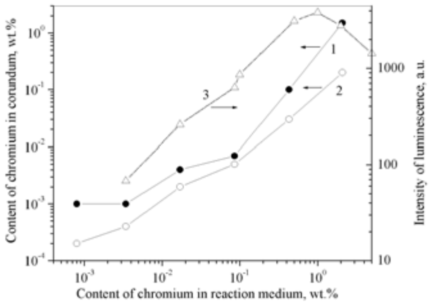

Fig.1. Dependence of the content Cr^{+3} in corundum according to a chemical-spectral analysis (1), to EPR-studies (2) and luminescent emission on the chrome content in reaction medium (3).

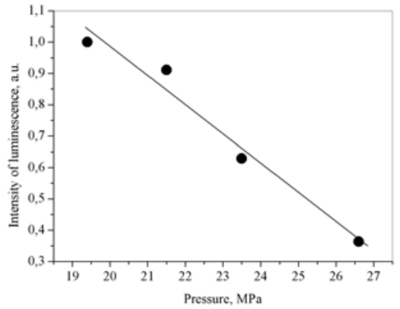

Fig. 2. Change of amount of Mn^{+4} centers of luminescence (678 nm) in corundum lattice with the increase of water vapor during synthesis of corundum at T = 400°C.

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Hydrothermal Preparation of Hydroxyapatite Solid solutions and Their Photocatalytic Property

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Calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, designated as Ca HAp] is a main inorganic constituent of vertebral animal’s hard tissues and has attracted our attention due to their properties as bioceramics, catalyst, adsorbent, and so on. Because of the flexibility of the HAp structure, metal ion sites can be replaced by various divalent cations including Sr, Ba, Pb, Cd, and so on. HAp can be prepared by aqueous or solid state reaction. The aqueous reaction usually gives low crystalline HAp, and the solid state reaction causes the formation of hydroxyl defects in the structure. The hydrothermal reaction, however, provides high crystalline HAp without hydroxyl defects.

In this study, solid solutions in the systems of Ca-Sr, Ca-Cd, Ca-Pb HAp were successfully prepared by hydrothermal reactions at 200°C for 12 hours from aqueous solutions of metal nitrates and ammonium phosphate. The lattice parameters of the Ca-Sr, Ca-Cd HAp solid solutions linearly changed with the compositions, while discontinuous change was observed in Ca-Pb HAp solid solutions. The results of the Rietveld analysis indicated that the metal ions of Pb, Sr, and Cd all preferentially occupied M (2) sites in the HAp structure. All these solid solutions had photocatalytic ability to decompose dimethyl sulfide under UV irradiation. The effect of the composition and particle size of the solid solutions on their photocatalytic properties was investigated.

Preparation of Analcime-c Zeolite From Fly Ash Powder Hydrothermally Treated in Fluorine Solutions

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Large volumes of fly ash are annually produced at CFE power plant Co. (Coahuila, MEXICO), and this solid waste has become an environmental problem because shortage of storage places and environmental pollution. Hitherto, the hydrothermal treatment of fly ash under alkaline conditions has been the subject of many investigations. The major Zeolite A and P type were synthesized under these conditions; however, a preliminary refining step is required in order to eliminate some impurities. In the present work, we have aimed to remove some amount of the amorphous and crystalline silicates (Mullite and Quartz) during the zeolite formation, which we expect to occur on fluorine mineralizer under hydrothermal conditions.

The fly ash consists of spherical particles (particle size of 20 μm) and contains an amorphous silicate phase and two crystalline phases (Mullite and Quartz) as major constituents. Fly ash powder (1 g) was placed at the bottom of a conventional stainless steel microautoclave. The solution used as mineralizer was NaF with a concentration of 0.5 M. The hydrothermal treatments were conducted at three different temperatures (150, 200, 250 °C) for a reaction interval over the range of 4–96 h. The Na-zeolite type, Analcime-c and P, were predominantly formed in the NaF solution (0.5 M). The formation of the Analcime-c zeolite proceeded for a short reaction interval of 8 h at a temperature of 250 °C. The present results indicate that during the hydrothermal treatment in NaF, because the preliminary fly ash powder heat and chemical treatments must be neglected. Leaching of impurities such Ca, and the adjustment of the zeolite chemical composition occur simultaneously during a single hydrothermal treatment. The formation of the Analcime-c zeolite is discussed on termns of the fly ash reactivity in fluorine solutions.

The new high pressure powder diffractometer on the Kurchatov Source of Synchrotron Radiation.

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The characteristic of Synchrotron Radiation (SR) such as high brightness, high energy range were found to be quite adequate for high-pressure experiment.

The new powder diffractometer is plased at the working station "Mediana" at the Kurchatov Source of Synchrotron Radiation (KSSR, Moscow). The diffractometer is consists of the following main systems: monochromators system, device for positioning high pressure cell and detector system. The focusing of photons by means of Laue-geometry diffraction from mosaic crystals has been used [1]. With diamond and SiC anvils high pressure cells [2] it is possible to perform powder diffraction experiments at pressures up to 50 GPa. The sample volume of about 0.005–*0.0*3 mm^3 is used and the typical exposition time is about 4-7 h.

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High-brilliance X-ray system for high-pressure in-house research.

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Synchrotron technique is ideally suited for *in situ* X-ray diffraction studies in DAC in the megabar pressure range. However, there are a number of difficulties in combining the synchrotron operation with the other requirements. Many phase transitions, in particular in complex systems, require chemical transport over distances of several microns (e.g. decomposition reactions). These processes are thermally activated, but rather slow due to the low diffusivities in the high-pressure phases. Reliable results can, therefore, only be achieved by extended run duration (up to 12 hours or more per one PT-step). Furthermore, the study requires intermittent use of other measuring techniques (such as Mössbauer, Raman, IR, electrical conductivity), which are available in-house, but not at synchrotrons.

Newly installed at BGI X-ray system consists of three major components –RIGAKU FR-D high-brilliance source, OSMIC Inc. Confocal Max-Flux optics, and SMART APEX 4K CCD area detector.

FR-D high-brilliance X-ray Mo rotating anode generator operates at load up to 3.3 kW. The initial beam spot has elliptical shape with the FWHM vertical axis of about 200 μm and horizontal axis of about 100 μm. The initial beam is further focused by confocal CMF optics. Utilizing constructive interference as in Bragg diffraction, thin film multilayers reflect X-rays at larger angles than total reflection mirrors, yielding a larger capture angle and thus larger flux. Significant advantage of multilayer mirrors is their capability to act as natural band-pass filter, automatically monochromazing the beam thereby providing more intensity with much lower background. Custom made collimating and focusing 100 mm long mirrors are realized by curving the mirror surfaces into parabolic shapes. A two-dimensional reflection system is realized by using two mirrors in a „side-by-side“ Kirkpatrick-Baez scheme. Each mirror independently reflects X-! rays in one of the two perpendicular directions. With „side-by-side“ scheme both mirrors of Confocal Max-Flux optics are manually positioned in order to optimize the performance parameters including flux, spectrum, and divergence. In order to enhance the system application for DACs, CMF optics is designed for focusing on the sample plane that provides the round beam with the FWHM diameter of about 40 μm. SMART APEX CCD detector with large 62 mm 4K chip provides unit demagnification and sensitivity of ≈170 electrons per photon.

Application of the new in-house X-ray system will be demonstrated on the examples of studies of gold, iron oxides, and sodium silicates at elevated pressures and temperatures. We will provide also a comparison with the results obtained for the same samples at ESRF and APS synchrotron facilities.

A compact new pressure apparatus up to 10GPa

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We have been developing a new pressure cell for the general-purpose experiment in multi-extreme-conditions. To see critical phenomena such as QCP(Quantum Critical Point) behaviours or exotic superconductivities, a high-pressure cell must be compact to cool down to cryogenic temperature. Also, the homogeneity of pressure must be kept because the critical phenomena sometimes disappear due to the randomness caused by inhomogeneity of pressure. And the most important requirement is 'high' pressure. The ordinary piston-cylinder-type cell satisfies compactness and hydrostaticity, though pressure is limited to not more than 4GPa. In other words, the high-pressure region above 4 GPa is STILL the frontier for the solid state physics.

A newly designed pressure cell[1] has been developed by Nakanishi *et al.*. This cell realizes nearly hydrostatic high-pressure(~ 6 GPa) condition and large sample space (~ 1.0 1.0). The load is applied uniaxially to the pressure cell, and the inhomogeneity of pressure in the sample space is moderated by using a liquid medium. We have continued further improvement of this original design in order to generate higher pressure and the maximum pressure has reached 10GPa at room temperature. We can easily perform precise transport measurement such as the 4-terminal electrical resistivity in this cell. Recently we have succeeded in the NQR measurement up to 8GPa in low temperatures. Expanding the sample space to 1.5 is our next challenge.

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The Paris-Edinburgh cell combined with a T-cup module for X-ray diffraction at high pressure and temperature

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The 'Paris-Edinburgh' (PE) cell is currently used for a wide range of measurements such as neutron and X-ray diffraction, EXAFS, Compton scattering, inelastic neutron and X-ray scattering, and ultrasonic studies. This method provides excellent powder statistics, well defined and almost uniform temperature conditions, allows the study of liquids at high (P,T) and enables to recover macroscopic samples.

One of the limitations of the standard design of the PE cell so far is its accessible (P,T) domain, restricted to ~ 10 GPa and 2000 K. However, *in situ* X-ray diffraction studies at conditions beyond these limits are extremely attractive in various domains of research. To overcome these limitations, we have designed a new high pressure set-up for *in situ* angle-dispersive X-ray diffraction studies under high (P,T) using the V7 type Paris-Edinburgh press. The V7 has a capacity of 450 tonnes, i.e. almost twice as the standard press, but still a weight of less than 80 kg. The ~ 20% larger overall dimensions allow to accommodate a two-stage multi-anvil system similar to the Stony Brook "T-cup system" which operates routinely to 25 GPa and 2500 K. The advantage of such a combined V7-T-cup system is its extreme compactness compared to all other multi-anvil systems currently existing on other synchrotron sources. The reduced dimensions and weight allow to transport it easily between laboratories and to install it in almost any experimental hutch within ~2 hours. It offers also the considerable advantage of being able to work with several presses simultaneously, i.e. carry out experiments with one cell whereas other presses are being prepared for the following measurements. We present this new high-pressure set-up as well as first results obtained in both off-line and on-line experiments at the ESRF [1].

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Determination of the Coefficient of Friction between Metal and Diamond under High Hydrostatic Pressure.

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Knowledge of the nature and magnitude of frictional forces is often important for fully interpreting the results of various types of experimental investigations of material rheology. One such example, depending on the experimental procedure, is the determination of yield strengths of materials under high pressure in the diamond anvil cell.

We have developed an experimental method to obtain the coefficient of friction between diamond and metal in the DAC [1]. A metal ring is compressed between the diamond anvils and its inner and outer diameters are measured as a function of the compression. Measured dimensions are then compared to the results of finite element simulations, in which the coefficient of friction is a free parameter. As an example, we apply the method to polycrystalline molybdenum up to a hydrostatic pressure of 6 GPa.

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Ruby pressure scale: revision and alternatives

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We have constructed equations of state of Cu, Ag, Au, Pt, W, MgO, NaCl, Al_2O_3 and diamond, which agree with modern shock-wave, ultrasonic, X-ray and thermochemical data in the temperature range from 10-20 K to the melting temperature and to compression x=0.6. We used the Bose-Einstein function [1] for the thermal part of the Helmholtz free energy, different forms (Birch-Murnaghan, Vinet, Holzapfel) for the cold pressure, the Al'tshuler et al. form [2] for the volume dependence of the Grüneisen parameter, and the Zharkov and Kalinin model [3] for the electronic contributions to the Helmholtz free energy. Intrinsic anharmonicity was described with equations of the Oganov and Dorogokupets [4] that provide correct low-/high-temperature behaviours. We show that neglect of intrinsic anharmonicity gives incorrect high-temperature thermodynamic functions of some solids at low pressure. Constructing an equation of state using only shock-wave data while neglecting zero-pressure measurements (heat capacity, enthalpy, volume, thermal expansion, compressibility) leads to a significantly distorted room-temperature isotherm (e.g., for Cu and Ag) and affects the calibration of the ruby pressure scale [5]. We have cross-checked the calculated room-temperature isotherms for these solids in order to derive a self-consistent pressure scale; particular attention was paid to high-temperature isotherms of Au, Pt, MgO and NaCl.

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Near infra-red Raman scattering and measurements of high P-T conditions.

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We will present a Raman spectrometer in the near infra-red dedicated to high pressure study in the DAC at high P-T conditions. This set-up has been built from a commercial Perkin-Elmer spectrometer. A 20 W YAG laser is used for the excitation. Essentially, the following modifications have been done: A new sample compartment for a micron control positioning of the sample and for doing micro-microscopy in transmission with two Mitutoyo NIR objectives; A new filtering system with 3 Notch filters so as to have access to the Stokes and anti-Stokes spectra; A visualisation of the sample under laser illumination; the insertion in the optical path of an optical transfer to a dedicated ruby fluorescence spectrometer.

First, it will be shown that the IR Raman spectroscopy offers some interesting possibilities at high pressure: a weak contribution of the fluorescence of the diamond to the Raman spectra; less photo-induced chemical effects; the possibility of bulk Raman measurements in semiconductors; Raman measurements much below the absorption edge of the diamond window even at very high pressure; the simultaneous Raman measurement over a broad spectral range.

Moreover, the use of a 20 W YAG laser allows to do laser heating of the sample up to the 2000K-3000K range. The possibility to perform spectroscopy in the range 1.7 μm – 0.9 μm under this laser excitation allows to do Raman and blackbody temperature measurements at the same time. Raman spectra of molecular systems under pressure have been obtained in the range 600K - 1300K. Above this temperature, the measurement of Raman signal is merged with blackbody radiation. A Raman spectrometer in the visible is now coupled to this IR setup to lessen the relative contribution of the blackbody radiation and hence extend the measurements in the 1600K range.

Synthesis of Boron Doped Diamond with Laser Heated Diamond Anvil Cell

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Recently the superconductivity was found in the boron-doped diamond synthesized at HPHT with toroid type high-pressure apparatus at 8–9 GPa, 2,500–2,800 K. [1] This initiates the new round of research fever on boron doped diamond. In this paper, boron-doped diamond has been synthesized from graphite mixed with different ratio of B_4C at high pressure high temperature (HPHT) using laser heated diamond anvil cell. The starting composition was transformed to diamond compound at pressure ~9GPa, 2200K-2600K as indicated by the in-situ x-ray diffraction pattern with synchrotron radiation source. Raman spectrum of the recovered specimen from HPHT state confirmed that boron has been doped into diamond lattice.

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Reversible pressure-induced structure changes in turbostratic BN–C solid solutions

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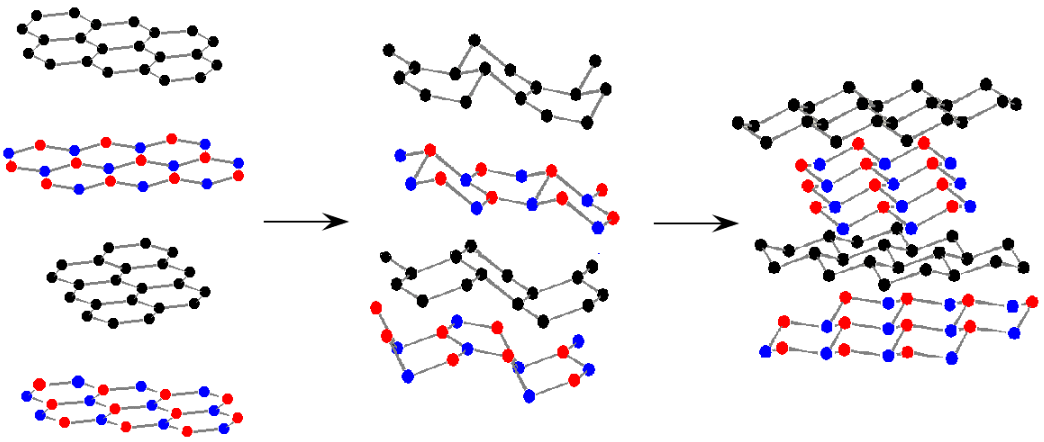
Graphite-like BN-C solid solutions are promising precursors for the high-pressure synthesis of novel superhard phases in the B–C–N system. Recently phase transitions of turbostratic graphite-like BC_2N up to 30 GPa have been studied in a DAC using X-ray diffraction with synchrotron radiation [1]. With the aim of explaining the observed evolution of diffraction patterns under compression at room temperature, we have performed the Rietveld analysis of the experimental patterns and simulated diffraction patterns of layered finite-size B–C–N clusters with lattice defects of various types [2].

Our findings have shown that above 20 GPa a reversible diffusionless transformation of the initial turbostratic structure into disordered layered high-pressure phase takes place. The general mechanism of the process includes disordering in interlayer spacings, buckling of layers and abrupt change of interlayer spacings attributed to the formation of the disordered high-pressure phase consisting of close-packed buckled layers with a diamond-like structure (Figure).



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Phase transition of BC_3 under high pressure

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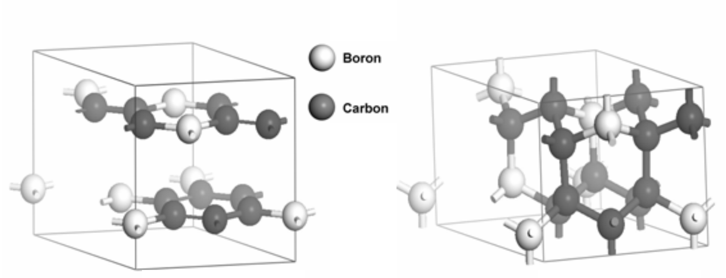
According to the work of M. L. Cohen *et al*, two structures of hexagonal BC_3 were identified to be stable. But their basic properties have not been investigated under high pressures. We employ an *ab initio* calculation on one of the proto lattice, which symmetry is CMCM. By full relaxation of the supercell and atoms inside, a meta-stable structure is found within the pressure ranges from 50GPa to 80GPa.

The original cell, shown in Fig1 (a), is composed of 2 layers of graphite-like structure. Each layer contains 8 atoms, 6 of which are carbon and the rest are boron. The total energies, electronic band structures, optical properties and the elastic properties are calculated when the system reaches equilibrium under pressures from 0GPa to 80GPa, by geometry-optimization using the quasi-Newton BFGS method at 0K. An indirect LDA band gap $E_g \approx 0.4$eV is observed at 0GPa, and when ambient pressure reaches 20GPa, the conduction band and the valence band overlap, suggesting that BC_3 of this structure transits from a semiconductor to a metal, but the lattice maintains stable before 50GPa. When the pressure increases higher, the lattice is distorted due to the strong interaction between the layers which induces symmetry transformation from CMCM to CMCA, as shown in Fig1 (b), meanwhile the bond type transforms from sp^2 to sp^3 hybridization. The bulk modulus increases from about 15GPa to more than 500GPa as the pressure increases.



(a) (b)

Fig.1 (a) Layered structure of BC3 at 0K and 0GPa.
(b) The structure of BC3 at 0K and 60GPa.

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The effect of the chemical environment on the kinectis of carbon phases formation at high-pressure and high-temperature

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The objective of this work was to investigate the effect of the chemical environment on the formation of carbon phases during the thermal decomposition of succrose ($C_{12}H_{22}O_{11}$) under high pressure. The samples were processed at 7.7 GPa in the temperature range from 900°C to 1700°C in a toroidal-type high pressure apparatus, during 15 min, inside the thermodynamic region of stability of the diamond phase. The samples consisted of pure succrose, succrose diluted in water, and mixtures of succrose + diamond powder, and diluted succrose + $NiCl_2$:$6H_2O$. The reaction products were analyzed by micro-Raman spectroscopy and by X-ray diffraction. The thermal decomposition of succrose under pressure favored the formation of graphite whose crystallinity depended on the chemical environment. The dilution of succrose in water difficulted the graphitization process. A small amount of metallic ions in the chemical environment modified the reaction product considerably, hindering the graphitization. The presence of pyrolised succrose enhanced the annealing of defects on micrometer sized diamonds promoted by the thermal treatment at high pressure.

High-pressure photo-luminescence spectra of BN single crystals doped with lanthanides

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Luminous cubic boron nitride (c-BN) single crystals, doped with Eu, Tb, and Sm, respectively, have been first synthesized using a temperature gradient method under high pressure [1]; the photo luminescence (PL) of Eu-implanted c-BN was once investigated at atmospheric pressure [2]. The Eu-doped c-BN single-crystal synthesized this time shows a strong and sharp peak at around 712 nm, which is due to an intra-4f electron transition of Eu^{3+}, $^5D_0$-$^7F_4$. Thus we have investigated the pressure change in the luminescence.

The high-pressure PL spectra have been measured using a diamond anvil cell. A single crystal with a dimension of about 50 x 50 μm^2 was put in a sample chamber with a mixture of methanol-ethanol (4:1 by volume) and a ruby ball. The pressures loaded on the sample were determined using the fluorescence of ruby.

The PL spectra were measured using an excitation wavelength of semiconductor lather (λ=400 nm). The pressure change in the peak frequency observed by loading up to 10 GPa is shown in Fig. 1. The frequency monotonously increases with pressure by a variation ratio, 0.275 nm / GPa, which is smaller than that of R1 of ruby [3].

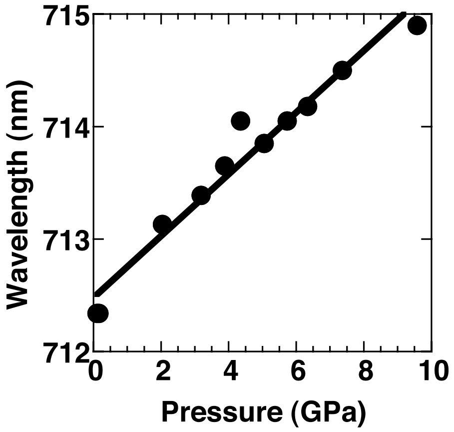

Fig. 1 Pressure change in the peak frequency of photo luminescence of c-BN:Eu.

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THE ALUMINUM-CARBON SYSTEM AT A PRESSURE OF 8 GPa AND DIAMOND SYNTHESIS

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To synthesize diamonds at high pressures, carbon – metal (metals) systems are used, melts of which dissolve carbon and ensure the nucleation and growth of diamond crystals. The presence of the stable diamond liquidus in the system at high pressures is the necessary condition for such a process to occur.

At atmospheric pressure the Al–C system is characterized by incongruent melting of the Al_4C_3 carbide according to the $L + C \leftrightarrows Al_4C_3$ peritectic reaction at 2150 ^oC. The carbon liquidus, which should become the diamond one at high pressures, is located in the higher temperature region. In the majority of systems, an increase in pressure causes the temperatures of peritectic and eutectic equilibria to increase. For the Al–C system, this behavior of the pressure dependence of the peritectic reaction temperature is bound to lead to a lowest temperature of diamond synthesis at 8 GPa, i.e. 2200-2250 ^oC.

In the present work, we have experimentally verified the parameters of diamond synthesis in the aluminum–carbon system. Electrolytic aluminum and natural graphite have been used as the initial materials. The experiments have been carried out in a toroid-type high-pressure apparatus with a working cell of diameter 20 mm. An indirect heating by a graphite heater was employed. In all the experiments, the pressure measured from the phase transformations of the reference substances at normal temperature was 8 GPa. It has been found that at this pressure the lowest temperature of the diamond synthesis in the Al–C system is 2100±50 ^oC. The diamond formation was registered in samples containing more than 50 at% of carbon. Thus, the decrease in the temperature of nonvariant three-phase equilibrium in the Al–C system is observed with increasing pressure, which is typical for systems having a considerable negative mixing volume. The Al-C phase diagram at 8 GPa has been thermodynamically calculated.

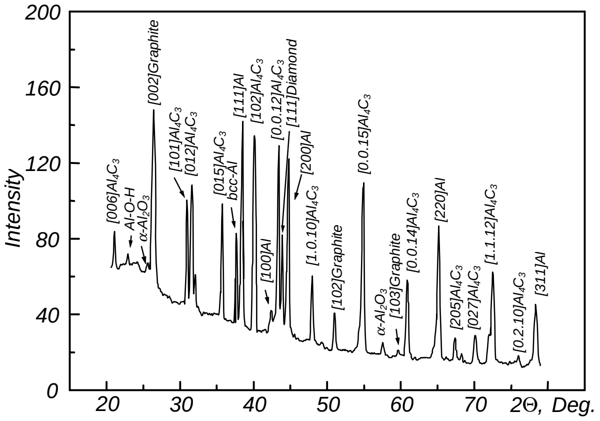

Fig. X-ray pattern of the sample (82 at.% C, 18 at.% Al) after treatment at 8 GPa and 2100^oC

Electrical, microstructural properties and calorimetry of superconducting boron-doped diamond

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Here we report experimental study of a new superhard superconductor, B-doped diamond. Superconductivity has been recently discovered in B-doped diamond, synthesized at high temperature and pressure [1], and in B-doped diamond films deposited by microwave plasma assisted chemical vapor deposition method [2, 3]. The diamond samples, synthesized at high pressures in the B_4C-graphite system, may contain less than 2-3 percent of only B_4C phase and are sufficiently large for electrical transport and magnetic susceptibility measurements. The maximum value of the lattice parameter of diamond synthesized in the presence of boron carbide was 3,578±0.001 Å. We investigated microstructure dependence of electrical and mechanical properties of boron-doped diamond. Our experiments showed the onset of a resistive transition to the superconducting state at about 9 K followed by a sharp transition to the zero-resistance state in the range 5.8-5.3 K for sample with maximum lattice parameter 3.578 Å. The correlation of physical properties, such as specific heat, electrical resistivity, and magnetic susceptibility, near the superconducting transition temperature is a clear evidence of bulk superconductivity in heavily boron-doped diamond samples.

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On cubic boron nitride formation in the BN–AlN system at high pressures and temperatures

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Since the first successful synthesis of cubic boron nitride (cBN) made by Wentorf 35 years ago, two principal mechanisms of cBN formation have been revealed: 1) direct solid-state conversion of graphite-like hexagonal BN (hBN) at high pressures and temperatures (8 GPa at 2000 K) and 2) cBN crystallization from BN solutions in different eutectic (or peritectic) melts above 4 GPa at temperatures of 1400-1700 K.

Very recently we have *in-situ* studied the BN–AlN system at pressures up to 8 GPa and temperatures up to 2200 K using angle-dispersive X-ray diffraction with synchrotron radiation. cBN formation in system has been observed starting from 5.3 GPa at temperatures above 1700 K that can not be explained by either of the mentioned above mechanisms. According to our results, in the whole *p*-*T* range under study, the formation of liquid in the BN–AlN system is not observed, therefore, the realization of the second mechanism is impossible. On the other hand, the threshold pressure of cBN formation in the system is too low for the direct solid-state hBN-to-cBN transformation, however, no evidence for formation of other crystalline or amorphous phases in the BN–AlN system has been found.

To explain the effect of AlN on the reduction of threshold pressure for hBN-to-cBN phase transformation, we have developed a simple continuum mechanical and thermodynamic model. Rigid particles of AlN do not change pressure in the neighborhood, but create non-hydrostatic stress state. Our estimates show that at pressure of 5.3 GPa, the radial stress (orthogonal to the particle surface) is higher by 2 GPa. Generally, an increase in radial stresses is proportional to the pressure. Deformation of hBN crystal lattice in the course of the phase transformation is also very anisotropic, with maximum compression in the *c*-direction. To estimate thermodynamic conditions of the phase transformation under non-hydrostatic stress state, a recently developed phase transformation criterion has been used. As the result, for hBN crystals with *c*-axes oriented along the normal to AlN particle, pressure in a standard phase transformation criterion has to be substituted by the radial stress. Thus, the observed difference between the radial stress and pressure explains the maximum possible magnitude of reduction (2 GPa) in threshold pressure of direct hBN-to-cBN phase transformation in the presence of AlN.

The strength of diamond

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Diamond is the hardest known material. However, the limits of diamond are not clear because its yield strength σ_y is not known. At room and lower temperatures diamond is a prototype of brittle solids, but signs of plastic deformation were observed during some experiments on indentation, sclerometric tests, and pressurizing diamond anvils. We report methods for reproducible plastic deformation of diamond and determination of yield strength. We squeezed a gasket between diamond anvils and thus concentrated the pressure at the center of the anvils. We precisely determined the beginning of the diamond yielding by measuring the pressure distribution over the anvils, and detecting a strong luminescence - a fingerprint of the plastically deformed diamond (Fig. 1). By using the theory of elasticity for this loading, we determined the maximum shear stress and hence the yield strength of diamond at room temperature σ_y = 130-140 GPa. This means in particular, that diamond is ~70-100 times stronger than hardened steel. Our findings may be used to extend the static pressure limit beyond the current value of about 300 GPa which is determined by yielding of diamond.

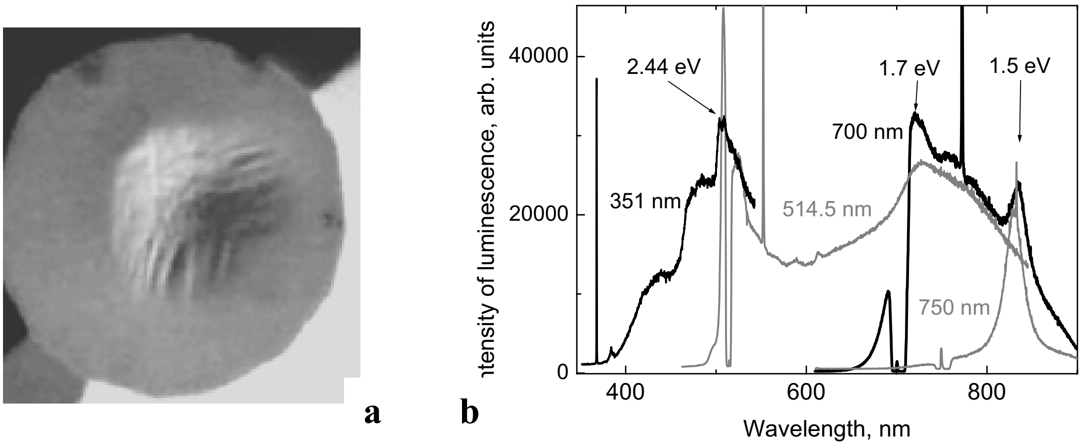

Fig. 1. Plastically deformed diamond. (a) Imprint at the culet of diameter 20 μm after pressurizing to 200 GPa. (b) Luminescence of a plastically deformed synthetic diamond (there is no noticeable luminescence from underformed diamond) excited with the marked laser excitation lines. There are characteristic bands at 2.44, 1.7, and 1.5 eV. Sharp lines in the spectra are the first-order Raman scattering of diamond, and absorption bands near the laser lines are due to the notch filters.

The stability of methane clathrates above 1 GPa

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During years 2005-2008, the Cassini spacecraft will provide infrared remote sensing images of Titan's surface, the largest satellite of Saturn. Understanding the relationships between Titan's atmosphere and surface as observed by Cassini, and the deep interior, requires an accurate knowledge of the phase relations in the methane-water system. One of the key parameter for understanding Titan's dynamics and history is the methane clathrate stability curve at pressures above 200 MPa.

The methane clathrate stability curve in the pressure range [0-2 GPa] is studied using an optical sapphire anvil cell coupled with a LabRam Raman spectrometer. Samples of CH_4-H_2O mixtures are enclosed in a 1 mm hole drilled in a pre-indented 60 µm thick stainless steel gasket. The sample is loaded at 77K in a system which provides a rough control of the stoechiometry (±10%).

Pressure measurements are carried out using a diamond pressure sensor which has been calibrated against the melting curve of pure ice (Figure 1). This sensor has been preferred to ruby in the pressure range below 2 GPa because the position of the Raman peak depends only weakly on temperature. Furthermore, diamond does not react with the aqueous fluid which acts as a pressure medium. As a contrary, it has been observed that chromium diffuses from ruby to liquid medium so that pressure measurements with the ruby technique are inaccurate.

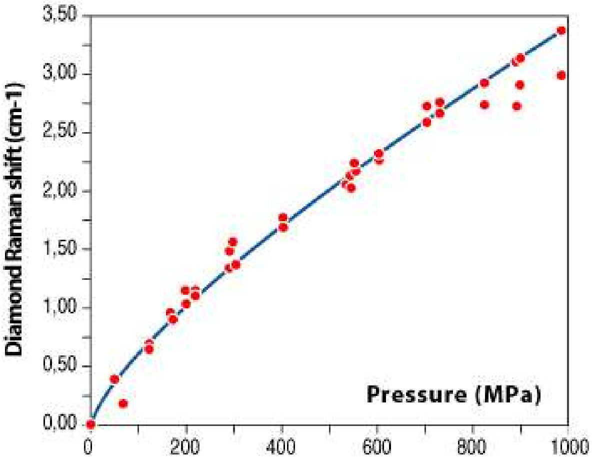

Fig. 1: *The pressure dependance of the diamond Raman peak in the moderate pressure range [0-1 GPa] relevant for Titan.*

A synthesis of both previous and new data on the CH_4-H_2O system will be proposed. First, the dissociation curve at high pressures will be reconciled with previous data from petroleum research at moderate pressures. Second, the phase boundary between low pressure methane clathrates (structure I) to an hexagonal structure II (expected around 1 GPa) will be studied. Implications of this work for understanding the nature of methane reservoirs within Titan will be shown.

Direct measurement of the equation of state of liquid water under pressure

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We present a novel experimental technique to determine the equation of state of compressed liquids. Both interferometric and photographic methods are used for direct volume determination at a given pressure.[1]

Direct measurements of the equation of state of water are reported at room temperature. Measurements have been performed in a cubic zirconia anvil cell (*CZAC*) using copper as gasket material. The pressure is determined by the standard ruby fluorescence method. Our results are compared to recent experimental results of the high pressure equation of state of water over the whole liquid range [2].

We also present a model that relates the pressure profile in the anvil cell with the elastic properties of the gasket material. We confirm that a detailed study of the pressure behavior of the gasket allows to obtain the compressibility of the sample by comparison of the pressure profile in the absence of sample. This model seems to be very promising, because it allows to obtain information about the equation of state of the sample by simply measuring the pressure profile on the gasket.

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Fluorescence of oxygen under pressure.

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Raman spectroscopy of molecular systems under pressure has been used mainly to investigate the low energy excitations, like vibrational modes. However, when the incident photon energy is matching an electronic transition, electronic processes can be observed in the spectra, such as the absorption band edge or luminescence bands, and their intensity can largely overcome the one of the Raman signal. Generally the first excited states of simple stable molecules lie in the UV range, i.e above the absorption threshold of diamond (>2.5 eV). Interestingly, the oxygen molecule has an electronic transition ${}^3\Sigma_g^- \rightarrow {}^1\Delta_g$ in the near-infrared region, very near the YAG laser photon energy. The transition is spin-forbidden but can occur in a bimolecular process where one molecule is excited in the ${}^1\Delta_g$ state and the other undergoes a spin flip. We have excited oxygen samples under high pressure with a YAG laser and measured the luminescence spectra in the near infrared. Our measurements show a rapid increase of the luminescence intensity of O_2 up to 2 GPa related to an increase of the bi-molecular process due to the increase of density. Above 2 GPa, the intensity of the luminescence starts to decrease, because the mechanism of electronic desexcitation becoming less effective compared to other process (phonon). This is confirmed by the observation of a thermal lens in the solid above 6 GPa. Finally the total disappearance of the luminescence in the ε phase could be related to a dramatic change of the absorption band. This YAG induced fluorescence could have direct application for novel high pressure material synthesis with O_2 by using O_2 as a reactant because it is well-known that the oxygen molecule is highly reactive in the ${}^1\Delta_g$ state.

High-Pressure High-Temperature Brillouin Study of Liquid water

Fangfei Li, Qiliang Cui, Zhi He, Qiang Zhou, Guangtian Zou

The recently reported structural transformations occurring to water from the low-density (LDW) to high-density (HDW) regimes have been studied by in situ Brillouin scattering at temperatures up to 230 ^{0}C and at pressures up to 5GPa. We find a discontinuity response of the sound velocity of water as pressure increases at ambient temperature (300K), while the velocity increases with pressure smoothly at higher temperature. The result of this study demonstrates the possible thermodynamic stable regime of the high-density water existing, which consists with the theoretical calculation. Proper calculations have been made to complete the conclusion.

The properties of water at high pressure and temperature are of fundamental interest in physics, chemistry, and planetary sciences. Besides the variety of ice polymorphism existing under different conditions of pressure and temperature, some have pointed out that near ambient conditions the liquid water process two different structures as LDW and HDW, but exact regimes and nature of these two forms are still controversies. An amount of experimental work such as Raman scattering, neutron diffraction, and X-ray diffraction have been carried out to investigate this phenomenon, we first attempt to study it by Brillouin scattering which is sensitive to density change, and draw a conclusion.

Stability of filled ice structure of methane hydrate and existence of a post filled-ice structure

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Understanding of the structural changes in gas hydrates under pressure has been advanced by recent studies. The cage structures of gas hydrate containing the guests smaller than methane transform to a filled ice structure Ih (FIS-Ih) under higher pressure [1]. The stability of these cage structures almost correlates to guest size and pressure [1]. On the other hand, the retention of the filled ice structure are various among the hydrates; The FIS-Ih of methane hydrate survived up to 40 GPa [2], while the others decompose below 6 GPa. According to a theoretical study, FIS-Ih of methane hydrate remains under the pressure higher than 80 GPa, accompanied by symmetrization of hydrogen bonds [3]. The present study intends to examine whether a possible post FIS-Ih of methane hydrate exists or not above 40 GPa and to examine how the FIS-Ih can be kept under such high pressure.

The in-situ x-ray diffractometry and Raman spectroscopy performed in the pressure range from 0.1 MPa to 86 GPa revealed a transition from the FIS-Ih to a high-pressure form at 40 GPa. That XRD pattern was indexed as a orthorhombic structure. The vibration modes of methane molecules were split at about 20 GPa without any change in the XRD pattern. And, the vibrations showed softening, comparing to those of solid methane. The observed changes in the intramolecule vibrations suggest increased attractive interactions between the methane molecules and also between the methane and water molecules. This interaction can result in additional stabilization of the FIS-Ih under such high pressure.

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Close-packing and H-bonding in ice and water under extreme conditions

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The structure of amorphous ice under pressure has been studied by molecular dynamics and in-situ neutron diffraction. The starting low-density phase undergoes significant changes as the density increases, and at ρ=1.51 g/cm^3 our calculated $g_{OO}(r)$ is in excellent agreement with our experimental data obtained at 1.8 GPa and 100 K on very high density amorphous ice (VHDA) made at 150K. The analysis of orientational distributions reveals that dense amorphous ice is characterized by major distortions of the tetrahedral geometry, and that the structural changes on densification can be interpreted as a trend towards a disordered closed packed structure [1]. The onset of the angular distortions is driven by temperature and explains the existence of two high-density forms of amorphous ice, HDA and VHDA [2]. A similar study, although very difficult from the experimental point of view, has been conducted on hot liquid water up to 700 K and 6.5 GPa. The analysis of the experimental data and of the classical and Car-Parrinello simulations shows that water under these conditions behaves more and more as a simple liquid [3].

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Structural and vibrationnal studies of solid ammonia

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Like water, ammonia is a major member of the group of simple hydrogen-bonded molecular ices. The study of its high-pressure properties is first of natural interest due to its abundance in the solar system, especially in the Jovian planets. Ammonia also presents a fundamental interest in condensed-matter physics as a H-bonded solid. Hydrogen bonds are weaker in ammonia than in water since 3 H atoms share a single lone pair (instead of 2 H sharing 2 lone pairs in the case of H_20). Whereas the symmetric state of water ice has been observed experimentally, the symmetrization path in ammonia appears more complicated. First, the phase diagram is barely known above 10 GPa. The structure of phase IV has been a longstanding issue: first identified by X-ray diffraction as hexagonal close-packed [1], neutron diffraction experiments [2] revealed an orthorhombic structure with space group $P2_12_12_1$. The stability of phase IV at higher pressure has also been subject to discussion for a long time : the presence of new phases has been suggested by Raman, Brillouin [3] and IR [4] experiments. But these results are confusing (what are the transition pressures ?) and incomplete (what is the nature of these new phases ?).

As a matter of fact, previous structural studies on ammonia under pressure have all been hampered by the problem of making a good powder. We decided to overcome this by using single-crystal samples. We performed X-ray diffraction experiments up to 120 GPa and polarized Raman scattering on single crystals up to 70 GPa at low temperature. The use of single crystals allowed us to observe for the first time both very weak diffraction peaks and Raman modes and measure their evolution with pressure. The comparison between NH_3 and ND_3 showed significant isotopic effects. We will present and discuss the new structural and vibrationnal informations we obtained on the high pressure phases of ammonia.

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Phonon dispersion of ice under pressure

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We report measurements of the phonon dispersion of ice I*h* (ordinary ice) under pressure to 0.5 GPa, at 140 K, using inelastic neutron scattering. They reveal a pronounced softening of various low-energy modes, in particular those of the transverse acoustic phonon branch in [100] direction and polarization in the hexagonal plane. We demonstrate with the aid of a Born - von Kármán model that these anomalous features in the phonon dispersion are at the origin of the negative thermal expansion coefficient in ice below 60 K. Extrapolation to higher pressure shows that the mode frequencies responsible for the negative thermal expansion approach zero at ~ 2.5 GPa, which explains the known [2] pressure-induced amorphisation in ice. These results give clear experimental evidence that pressure-induced amorphisation in ice I*h* is due to a lattice instability.

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Lattice vibrational Raman spectra in sI phase of methane hydrate under high pressure

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The cubic sI phase of methane hydrate (MH) is well known to exist up to 0.9 GPa at room temperature [1,2], and to be composed of two small and six medium host water cages per unit cell. Recently, Baumert *et al.* [3] have found the localized guest methane vibrations inside the medium cage at 40 cm^{-1} by the inelastic x-ray spectra at 100 K and the theoretical calculation. However, such vibrations in host cages are not yet identified by Raman spectra. Therefore, the purpose of this study is to investigate the lattice vibtational Raman spectra of partially deuterated methane hydrate (PDMH; CH_4-5.75D_2O) by comparing with those of MH and to identify the vibrations of guest molecules and host cages.

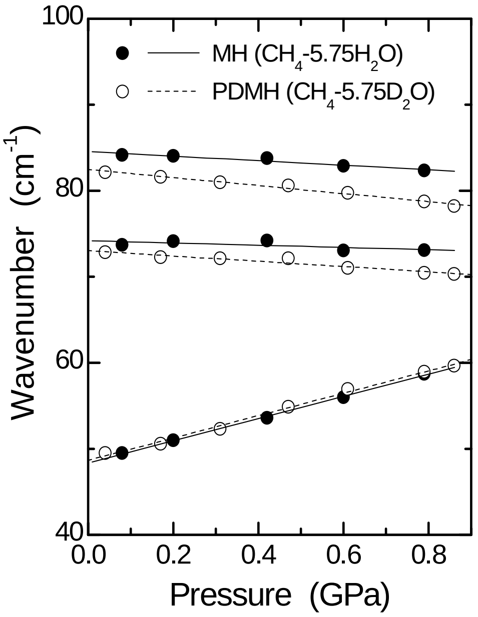

Fig. 1. Pressure dependence of Raman frequency shifts of methane hydrate (MH) and partially deuterated methane hydrate (PDMH) below 100 cm^{-1} at 296 K.

Raman spectra of MH and PDMH up to 0.9 GPa were measured for the lattice vibrational region between 30 cm^{-1} and 500 cm^{-1} at 296 K. With the exception of the peak at about 50 cm^{-1}, Raman frequencies of PDMH are about 3% lower than those of MH (see Fig.1) because of the substitution of D_2O, which suggests that these signals are basically attributed to the host-cage vibrations. On the other hand, the peaks of MH and PDMH around 50 cm^{-1} should be the vibrations of guest methane molecules in the medium water cages, since these peaks have almost the same frequency and the characteristic pressure dependences.

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Hydrogen-bonded substances under high pressure: Ultrasonic study of the low temperature phase diagrams of methanol, ethanol and H_2O ice

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Methanol and ethanol are reasonably among the model objects that can serve to study the nature of interatomic interactions in condensed systems with hydrogen bonds. Unlike water, which is also hydrogen-bonded substance, alcohols are much less studied, experimental data on their pressure-temperature diagrams and high-pressure physical properties being scanty [1-3]. We present a detailed ultrasonic study of the low-temperature phase diagrams and elastic properties of methanol and ethanol under pressures up to 1.2 GPa in the temperature range from 90 to 300 K, comparing those with the similar data for ice [4] considering as a system with the stronger hydrogen bonds.

The experiments were carried out in the high-pressure low-temperature ultrasonic piezometer [5]. For methanol, we have established the exact boundary of the α-β crystal-crystal phase transition and found a week anomaly of density and longitudinal ultrasonic velocity in the liquid phase at temperatures 230 to 250 K and pressures 0.2 to 0.6 GPa, which is likely can be associated with the structural changes to the more dense liquid phase with the increase of pressure. Still, there is questionable an existence of the α-β-liquid triple point. A nature of structural changes in the liquid phase should also be clarified by direct *in situ* methods. In general, methanol demonstrates more complicated phase behavior under pressure in contrast to ethanol, phase diagram of which is quite simple in the studied pressure-temperature area. We associate the differences in the phase diagrams of methanol and ethanol to the stronger hydrogen bonds in methanol and to simpler structure of its molecules. The last trend is directly illustrated by H_2O water, which has one of the simplest molecule, the strong hydrogen bonding, and quite complicated phase diagram. We present a detailed ultrasonic study of the transitional phase diagram of H_2O ice [5], providing new insights into the mechanism of crystal-to-amorphous and amorphous-amorphous transformations.

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High-pressure liquid-solid phase transition and meltline for Water

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In connection with recent isentropic experiments on water where a functionally graded impactor in a light-gas gun is used to systematically probe the high-pressure meltline for water, hydrodynamic simulations of water undergoing a pressure-induced phase transition into its ice phase are presented. From a well defined set of initial conditions, the liquid system is isentropically compressed into its solid phase, thus a mitigating first-order phase transition occurs during which the energy of the system increases. Specifically, the simulations use a tabular single phase equation of state (EOS) for each phase. To mitigate between the single-phase EOS's of the system during mixed phase intervals, a thermodynamic linear mixing scheme is used. In this scheme a time constant is related to the phase transition rate which incorporates the underlying effects of kinetics. The simulation models in one dimension the entire experimental setup, accounting for the wave interactions throughout the impactor and target. The calculated results are directly compared with particle velocity records from the experiment.

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under contract W-7405-Eng-48.

Polymeric nitrogen

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Our recent results on nitrogen at megabar pressures will be reviewed. The transformation of molecular nitrogen to a single-bonded atomic nitrogen is of significant interest from a fundamental stand point and because it is the most energetic non-nuclear material predicted. We synthesized it directly from molecular triple-bonded nitrogen at temperatures above 2000 K and pressure above 110 GPa with the help of a novel arrangement of the laser-heated diamond cell [1]. Using x- ray and Raman scattering we have identified this as the long sought after polymeric nitrogen [2] with the theoretically predicted cubic gauche structure (*cg*-N) [3], Fig. 1. Its bulk modulus $B \approx 300$ GPa is characteristic of strong covalent solids. This crystalline phase is different from the amorphous nonmolecular nitrogen [4] obtained at the cold compression.

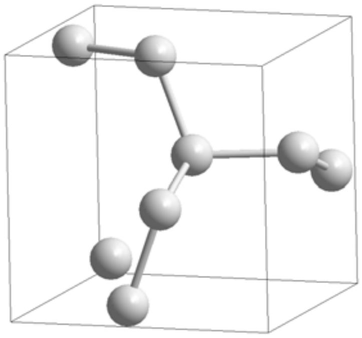

Fig. 1. Cubic gauche structure of nitrogen. The primitive cell is shown. Each atom of nitrogen is connected to three neighbors with three single covalent bonds

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20th AIRAPT and 43th EHPRG Meeting

The high-pressure synthesis and effect on structural and electrical properties of $SrCrO_3$ perovskite

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Abstract

As an important materials systems of strongly correlated electron system, the 3d transition metal oxide (TMO) has received growing interests due to unusual physical behaviors ranging from high Tc superconductivity, to CMR, to the metal-insulator transitions[1]. Pressure has play significant role in either the new materials synthesis of TMO with special valence[2] or the close packed perovskite related structures, as well performed in copper oxide superconductors[3] Chromium (IV) oxides with ABO_3 perovskite structure are rare at ambient pressure due to the unusual electronic distribution of Cr^{4+}, and these compounds only can be synthesized under high pressure high temperature (HPHT). We synthesized polycrystalline $SrCrO_3$ sample under high temperature high pressure through improved methods. X-ray diffraction (XRD) pattern indicated all peaks could be indexed with cubic crystal symmetry. *In-situ* high-pressure energy dispersive XRD measurements with the diamond-anvil cell (DAC) using synchrotron radiation showed the crystal structure of $SrCrO_3$ was stable under pressure up to 30GPa. According to the Birch-Murnaghan equation of state, we obtained a large bulk modulus about 280GPa for $SrCrO_3$. The result of the resistance versus pressure relationship showed the sample has an electronic structure phase transition at 10GPa. The possible reason causing the pressure behavior will be discussed.

Key words: transition metal oxide, high pressure synthesis, high pressure measurements, electronic phase transition, diamond anvil cell, synchrotron

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C. Q. Jin High Pressure Research **24**, 399-408(2004)

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High-pressure structural behavior of nanocrystalline germanium

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At ambient conditions, Ge has the cubic diamond-type structure with space group $Fd\bar{3}m$ (227). The room-remperature semiconductor-to-metal transition I→II has been extensively studied using resistance measurements, x-ray diffraction, shock-wave techniques and quenching. The Ge-II modification has a tetragonal structure of the β-Sn type with space group $I4_1/amd$ (141). In the present work, using XRD, we have studied the equation of state and the I–II transition of nanocrystalline Ge with crystallite sizes 13, 49 and 100 nm. The experimental results are given below:

Sample	Lattice constant a_0 (Å)	Bulk modulus B_0 (GPa)	Transition pressure P_{tr} (GPa)	–ΔV/V (%) at transition
Bulk	5.6576[a]	75[b]	8.0(5)[c] – 10.5(2)[d]	19.4(9)[c]
100 nm	5.660(2)	88(3)	11.5(3)	17.5(3)
49 nm	5.659(3)	92(3)	12.4(3)	17.3(3)
13 nm	5.645(5)	112(3)	16.4(3)	17.3(3)

[a] Literature data, [b] Ref [1], [c] Ref. [2], [d] Ref. [3].

It is seen that the smaller the particles, the higher the bulk modulus and the transition pressure. A theoretical model for the high-pressure behavior will be presented. Since a large fraction of the atoms reside in the grain boundaries of the nanophase material, it is clear that the interface structure plays a significant role in affecting the physical properties of these materials.

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Hydrothermal Synthesis of Silver Nanoparticles

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Hydrothermal techniques have been widely used in materials processing, crystal growth, waste treatment, and so on. In recent years, techniques of hydrothermal synthesis have been developed by the combined use of other chemical processes such as electrode reactions and crystallization. In this study, we have examined hydrothermal synthesis of Ag nanoparticles by reducing Ag^+ ions in the presence of polyvinylpyrrolidone (PVP).

Aqueous solutions of $AgNO_3$ (3 mM) and PVP (30 g dm^{-3}) were injected into the high-pressure optical cell equipped with two sapphire windows (optical path = 1 cm) by a HPLC pump at various flow rates (0.2, 0.5, 1.0 $cm^3 min^{-1}$) and pressure was kept at 40 MPa by a back-pressure regulator. Temperature was controlled using a jacket-type heater surrounding the cell. Absorption spectra of aqueous solutions at hydrothermal environments were measured in situ by a spectrophotometer. Prepared Ag colloidal solutions were subjected to TEM observations.

Absorption spectra of aqueous $AgNO_3$/PVP solutions measured at 40 MPa and at temperatures higher than 250 °C are characterized by the broad band developing around 400 nm, which is attributed to the surface plasmon band of Ag nanoparticles. This observation indicates that PVP acts as a reducing agent as well as a protective agent for the formation of silver nanoparticles under hydrothermal conditions. The peak wavelength of this absorption band is blue-shifted with increasing flow rate, indicating the decrease in the average size of Ag nanoparticles, which is consistent with TEM observations.

The effect of hydrothermal treatment on the photocatalytic activity of TiO_2 nanoparticles

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The improvement of photocatalytic activity of TiO_2 has been a subject of extensive studies. It is therefore important to investigate the correlation between the photocatalytic activity and bulk and surface properties. Hydrothermal treatment has been used in the reformation of inorganic materials. In this study, we have examined the effect of hydrothermal treatment on the photocatalytic activity, crystal structure, surface condition and morphology of TiO_2 nanoparticles.

TiO_2 nanoparticles were synthesized by controlled hydrolysis of titanium isopropoxide according to the method of O'Regan&Grätzel[1]. TiO_2 colloidal solutions (1.6×10^{-5}M) were continuously injected by a HPLC pump into a high-pressure cell at various flow rates (0.2, 0.5, 1.0 cm^3min^{-1}). Pressure was kept at 40 MPa by a back-pressure regulator, and temperature was controlled using a jacket–type heater. The morphology of TiO_2 nanoparticles was observed by TEM, and the crystal structure was analyzed by electron diffraction method. The photocatalytic activity was examined by the photoreduction of silver ions and the oxidative degradation of thiacyanine dye as model reactions. It has been demonstrated that the shape, size and the photocatalytic activity of TiO_2 nanoparticles are considerably changed as a result of hydrothermal treatment. Phase transition of crystal structurein in TiO_2 nanoparticles is observed for hydrothermal treatment at 300°C, 40MPa, $0.2cm^3min^{-1}$.

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HiPCO single-wall carbon nanotubes under pressures up to 50 GPa: Electrical properties

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Abstract:

Single-wall carbon nanotubes (SWNT) produced by HiPCO method and purified by thermal oxidation in air have been studied by impedance spectroscopy. The purity of nanotubes was estimated as 99% [1]. The dc conductivity measurements were carried out at temperatures 77-450 K. High pressure has been generated in the diamond anvil cell (DAC) with anvils of the "rounded cone-plane" type made of synthetic carbonado-type diamonds. These anvils are good conductors, permitting measurement of the resistance of samples placed between the anvils in the DAC by using the anvils as the electrical contacts to the sample.

The activation energy of the SWNT was estimated from the temperature dependences of resistivity. Temperature dependences of HiPCO SWNT resistivity were plotted and analyzed. Activation energy dependences of pressure were analyzed.

This work was supported in part by grant BRHE EK-005-X1 (Ural research educational center "Advanced materials").

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High-Pressure structural study on meso-carbon micro beads using hydrogen pressure-transmitting medium

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Meso-carbon micro beads (MCMBs) are spherical carbon particles having 300 nm in deameter on the average [1]. According to the transmitting electron microscope image, each particle of MCMB is composed by micro-graphites, taking a helical structure like a rose flower. The inner structure of MCMB has gaps and spaces between the micro-graphits, which is different from that of *G* ball: concentric, closed and solid particle [2]. Such an opened-structure is expected to have the hydrogen storage capacity. Then the pressure change in volume of MCMBs has been investigated by x-ray diffraction measurements using a diamond anvil cell with the hydrogen pressure-transmitting medium.

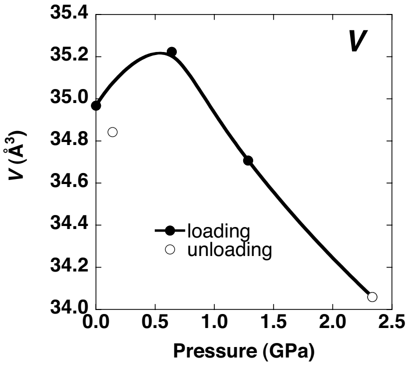

Fig. 1. Pressure changes in volume of MCMB using H_2 pressure medium at room temperature.

Figure 1 indicates the pressure change in volume of MCMBs in hydrogen gas atmosphere at room temperature. The *a*-axis length shows a 0.8 % increase at 0.7 GPa; additional pressurization causes the decrease. On the other hand c-axis length monotonously decreases with increasing pressure. In consequence the volume shows a passing expansion by 0.7 % at 0.7 GPa. Such a volume expansion suggests that MCMBs have the hydrogen storage capacity.

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Electrical properties of nanocrystalline *ZrO_2* at high-pressure

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We studied correlation between the sizes of crystallite and resistance ZrO_2 at the pressures 22 - 50 GPa and temperatures 77 - 400 K. Nanocrystalline praseodymium doped zirconia powders were produced using a microwave driven hydrothermal process under pressures up to 8 GPa. Nanopowders of zirconia with Pr in solid solutions having Pr contents of 0.5 mol %. The bulk material sample of zirconia having Y_2O_3 contents of 5 mol %. Size of crystallites changed from 10 to 500 nm.

The dc resistance measurements were carried out in a diamond anvil cell rounded cone-plane type.

At a pressures of about 30-37 GPa the ZrO_2 resistance decreases by 3-4 orders of magnitude. It's found that the transition pressure of ZrO_2 depends on crystallite size.The smaller the crystals the smaller the transition pressure. The reduction of transition pressure was observed to 10 nm. However at 10 nm the transition pressure rises steeply.

It is possible to suspect, that the surface effects essentially change ZrO_2 conductivity mechanism at high pressures.

At the pressure of about 40-48 GPa anomalies in the pressure dependence of the resistance and of the parameters which depend on the concentration, mobility, and activation energy of the charge carriers are found. This permit to suppose the high-pressure induced phase transformation at 40-48 GPa.

Furthermore we obtain that the activation energy depends on the crystallite size. The smaller the crystals the higher activation energy.

We studied relaxation processes inZrO_2 under the high pressures and the room temperature.The analysis of experimental data has shown that the time function of electric resistance most precisely described by exponential function. It can be seen, that relaxation times depend on pressure and crystallite size.

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Raman study of pressure screening effects in double-wall carbon nanotubes

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Carbon nanotubes have attracted intense scientific interest due to their fascinating - essentially one dimensional - electronic and vibrational band structure, their unique mechanical properties as well as the prospect for numerous applications. In this work, the pressure response of double-wall carbon nanotubes (DWCNTs) prepared by the peapod conversion process [1] has been investigated using the Raman spectroscopic technique. The pressure dependence of the observed Raman bands in DWCNTs suggest that the existence of the outer tubes results in a screening of the applied pressure on the inner tubes, while the latter provide structural support against pressure induced deformation of the outer tubes compared to the single-wall carbon nanotubes (SWCNTs) [2]. Moreover, the irreversibility in the relative intensities of the radial and tangential peaks attributed to the outer shells upon pressure release reveals the existence of residual pressure-induced deformations, in analogy to those observed earlier in SWCNTs [2].

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Raman scattering measurement of diamond anvil to 300 GPa: Pressure determination method in the multimegabar range

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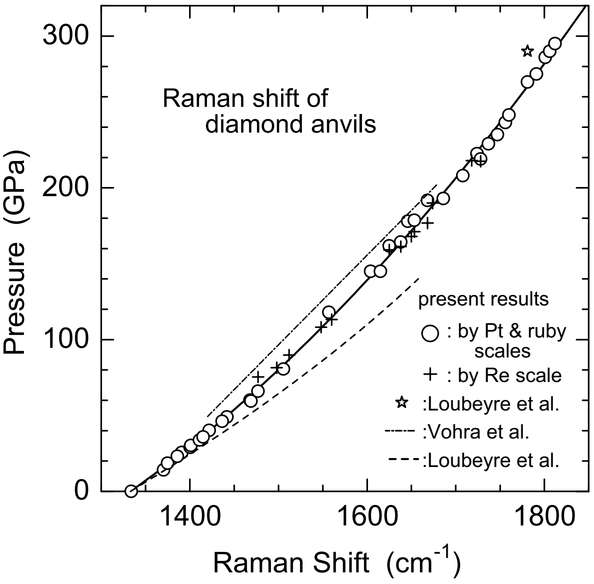
With the recent advance of the material research under ultra-high pressure, extending to 300 GPa, new convenient method for the laboratory-based pressure determination in the multi-megabars pressure region has been desired. At present, a strong candidate would be the first-order Raman mode of diamond anvils. Hanfland and Syassen[1] proposed the availability of the diamond anvil Raman measurement for pressure determination. They found that the high-frequency edge of the Raman band came from the culet face and the edge frequency exhibited a linear pressure dependence. However, the pressure range of the proposed dependences is limited. For the application to pressure determination, problems of the accuracy and the consistency among loading conditions still remain.

In this study, the first-order Raman spectra of diamond anvils used in a gasketed high-pressure cell have been measured at pressure up to 300 GPa. The high-frequency edge of the Raman band, which corresponds to the Raman shift of the culet face, is represented by a function of pressure in the sample chamber up to 300 GPa (shown in Figure). The dependence is almost independent on loading conditions. The application of the pressure dependence for pressure determination up to the multi-megabars pressure region is proposed [2].



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Calibration of pressure sensors for high pressures and temperatures

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The results of three sets of optical and x-ray diffraction experiments with a diamond anvil cell (DAC) are presented: externally heated DAC with a variety of pressure gauges (^{12}C, cBN, Sm:YAG, and $SrB_4O_7:Sm^{2+}$, Au) to 95 GPa and 900 K, laser and internally heated DAC in cBN to 40 GPa and 1900 K, and silica (including nano-materials) to 30 GPa at 295 K.

We have extended the room-temperature calibration of Sm:YAG in a quasi-hydrostatic regime up to 100 GPa. The ruby scale is found to systematically underestimate pressure at high pressures and temperatures compared with all the other sensors. On this basis, we propose an alternative high-temperature ruby pressure scale that is valid to at least 100 GPa and 850 K.

Raman spectroscopy in the diamond anvil cell (DAC) has been used to determine the pressure dependence of the zone-center transverse optical phonon at high temperatures. First-principles theoretical calculations of the phonon frequency and of the equation of state were performed within the local density (LDA) and quasi-harmonic approximations to 80 GPa and 2000 K. Alumina and argon were employed as pressure media. Phonon frequencies were measured up to 1700 K to 40 GPa and 2300 K to 26 GPa. We find that the measured temperature dependence of the phonon frequency becomes less pronounced under pressure, as predicted by calculations performed on the basis of the Debye-Grüneisen model. On the basis of our data we derive a high temperature pressure scale for cBN.

Raman spectra of compressed silica show an irreversible change of frequency, which depends on the maximum pressure attained. This information provides local pressure history at high resolution (<1 micron) and over a broad range of pressure (3 – 30 GPa), which is important for a number of applications (e.g., shock waves). We have calibrated this shift for bulk and nanomaterials to 30 GPa.

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The pressure sensor systems in optical cells below 2 GPa.

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High pressure optical cells have first been devoted to high and very high pressure studies. But in the last ten years, both diamond and sapphire anvils cells have also been used in the moderate pressure range below 1 GPa in many research fields such as biology, chemistry, pharmacology, Earth sciences, and food processing. In these different fields where a ,combination of both temperature and pressure constraints is common, the pressure calibrant which may be used by every one is still to be found. Present studies are made using various pressure sensors depending on the experimental constraints. This paper presents a rapid review of the different techniques commonly used in the moderate pressure range below 1 GPa. Two main classes of pressure sensors can be distinguished: organic or inorganic.

The class of organic sensors is commonly used in life sciences because it provides a relatively good accuracy on pressure measurements. Furthermore, their rapid response to pressure changes allow *in situ* kinetic measurements. Sensors can be proteins or other organic chromosphores. Unfortunately, these sensors cannot be used at very low temperature or at high temperature. In general their use must be devoted to studies where water is in its liquid state. Three common organic sensors are presented in Table 1.

The inorganic pressure sensors commonly used at moderate pressure are ruby, diamond, and quartz. Ruby is the worst because its pressure dependance is very weak and it cannot be used in many liquid samples since Cr^{3+} diffuses in the liquid. Diamond and quartz are inert and can be used in a very large temperature range for any kind of samples. The accuracy of these sensors is quite low (around 50 MPa) and the response to pressure variations is too slow for biologic studies.

CALIBRANT	*Ruby*	*Diamond*	*Quartz*	*Photosynthetic bacteria*	*Green Fluorescent Protein*
Spectroscopy	Visible	Raman	Infrared	Fluorescence	Fluorescence
Pressure shift	Very low	Low	Moderate	High	High
Temperature range	Low to moderate	Low to High	Low to High	Moderate	Moderate
Response to excitation	Slow	Slow	Slow	Rapid	Rapid

Table I: Principal characteristics of the common pressure sensors used beow 1 GPa in optical cells

An Optical Pressure Gauge for Multimegabar Pressures Calibrated to 300 GPa

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Abstract

The accurate measurement of pressure by a straight-forward and inexpensive optical procedure has been needed in the multimegabar region since static prtessures over 216 GPa, 361 GPa, 416 GPa and 560 GPa were obtained in the diamond anvil cell. Here, a simple optical pressure gauge based on the Raman shift at the center of a diamond tip at the diamond-sample interface is calibrated against a primary gauge (Pt isotherm at 300 K from shock data) to 300 GPa, thus enabling researchers who do not have a synchrotron to conveniently measure pressure with an optical scale from 50 to 300 GPa. Comparison is made with other available data.

Structure evolution and electrical property of the copper nitride under high pressure: the possible pressure calibrator

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Copper nitride Cu_3N crystallizes into anti-ReO_3 type structure of space group Pm3m. At ambient pressure and temperature, Cu_3N is a cubic without distortion. Six Cu atoms form an octahedron around one N atom, while two octahedrons connecting each other through their vertex atom of Cu, forming a 3-dimensional crystal lattice. Comparing with the normal ABO_3 type perovskite, there is no any atom at the A-site in the lattice of Cu_3N, which will enable rotations of these NCu_6 octahedrons. So the Cu_3N can be relatively easy to compress. We conducted *in situ* high-pressure x-ray energy dispersive diffraction experiment on Cu_3N using DAC technique with synchrotron radiation to study the series of phase transition. Also we did the *in situ* measurements of resistance versus pressure to see the conductivity evolution. Crystal structure transformations were observed in Cu_3N in the pressure range up to 39.2 GPa. We found a sharp drop of resistance with applied load an indication a pressure induced metallization which may be adopted as a pressure calibration[1].

Reference:
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