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PROCEEDINGS

XI AIRAPT
International
Conference

NAUKOVA
DUMKA

HIGH
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SCIENCE
AND
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PHASE TRANSFORMATIONS IN THE FERROMAGNESIUM SILICATES AT HIGH PRESSURES AND TEMPERATURES

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Ferromagnesian silicates, containing some 10 mole % FeO, of olivine, pyroxene and garnet are believed to be the major constituents of the Earth's upper mantle. Furthermore, it is postulated that the Earth's deep interiors (the transition zone and lower mantle) consist of the various high-pressure modifications of these ferromagnesian silicates.

In pure magnesium end-member of these minerals, the first high-pressure modification (or phase assemblage) was reported by Sclar et al. [1], who claimed that $MgSiO_3$ (clinoenstatite) decomposes into Mg_2SiO_4 (forsterite) plus SiO_2 (stishovite) at 115 kbar and 650°C. This result, however, has not been confirmed by all subsequent studies, and it appears to be erroneous.

Ito et al. [2] reported that clinoenstatite decomposes into Mg_2SiO_4 (modified spinel) plus stishovite at 250 kbar and 1000°C, which then transforms to another mixture of Mg_2SiO_4 (spinel) plus stishovite at 280 kbar and 1000°C. At a pressure in excess of 500 kbar at 1000°C, an ilmenite form of $MgSiO_3$ was prepared by Kawai et al. [3]. All the pressures reported by these authors are probably overestimated, some by more than a factor of 2.

Ming and Bassett [4] reported the synthesis of a hexagonal form of $MgSiO_3$ at 250 kbar and 1000°C, which then decomposes into component oxides having the rocksalt and rutile structures at still higher pressures. These results, however, have been dismissed as due to misinterpretation of the X-ray diffraction data [5].

Liu [6] has synthesized an orthorhombic perovskite-type $MgSiO_3$ at about 300 kbar and 1000°C. This form is the most densely packed magnesium silicate yet known.

Recently, Sawamoto and Kohzaki [7] reported a distorted garnet phase of

$MgSiO_3$, which may be stable in the same pressure range as the ilmenite-type $MgSiO_3$, but at higher temperatures ($> 1500^\circ\text{C}$?).

With increasing pressure, in the temperature range 800-1500°C, the phase transitions of $MgSiO_3$ can be summarized as follows: clinoenstatite 15.2% modified "spinel" + stishovite 1.8% "spinel" + stishovite 2.0% "ilmenite" 7.0% "perovskite", where the percentages are the increase in density from one to the other calculated at ambient conditions.

Various attempts to determine the equilibrium boundaries for the phase transitions observed in $MgSiO_3$ have been made in the literature (see [8] for a detailed review). In general, this is a very different problem from the establishment of new phase transitions at high pressures and temperatures described above. Only after a new phase (or phase assemblage) is firmly established, does the determination of the stability field become meaningful. The T-P conditions for high-pressure and high-temperature synthesis of the new phase (or phase assemblage) are usually known only roughly. In determination of the equilibrium boundaries, however, precise T,P conditions have to be measured. Unfortunately, pressure calibrations at high temperatures are not well established at present. In addition, there are fundamental experimental difficulties in measuring both the high pressures and high temperatures simultaneously. Thus, one may regard the T-P boundaries determined at pressures below about 50 kbar as reasonable, those in range 50 to 150 kbar may be reliable, but only the sign of the boundaries may be determined for those above 150 kbar. Both the determined and proposed T-P boundaries of all phase transitions known in $MgSiO_3$ are delivered in Fig. 1 and the effect of Fe^{+2} on these transitions are shown in Fig. 2.

Magnesian garnet (pyrope) may be regarded as an intermediate composition along the join $MgSiO_3$ - Al_2O_3 . Liu [9] reported that pyrope transforms to an ilmenite phase at a pressure between 240 and 250 kbar at 1000-1400°C, which then crystallizes in an orthorhombic perovskite phase at pressures greater than 300 kbar [10]. This is the first instance of a silicate perovskite known. Thus, the high-pressure phase behavior of pyrope is as follows: pyrope 7.8% "ilmenite"

7.7% "perovskite", where the percentages have the same meaning as before. The effect of substituting 2Al^{3+} for $\text{Mg}^{2+} + \text{Si}^{4+}$ on the phase behavior of Mg_2SiO_4 is shown in Fig. 3, and that of Fe^{2+} for Mg^{2+} in garnet is shown in Fig. 4 (cautions should be exercised against the reliability of these T-P boundaries).

The first experimental results of the phase behavior of Mg_2SiO_4 were reported simultaneously by Akimoto and Ida [11], Kawai et al. [12] and Ringwood and Major [13], who all claimed to have synthesized a spinel phase of Mg_2SiO_4 at pressures between 150 and 230 kbar and at 700-1100°C. Although the X-ray diffraction pattern of this phase resembles a spinel structure, Ringwood and Major [13] noted that some complications were developed in the pattern and attributed it to a retrogressive product during quench. This complicated phase was later also observed in Co_2SiO_4 -II at high pressure and temperature by Akimoto and Sato [14], who also successfully indexed the complicated pattern of Mg_2SiO_4 in terms of the Co_2SiO_4 -II structure. This was suggested later to be a distortion of the spinel structure by Morimoto et al. [15] and Moore and Smith [16].

The true spinel form of Mg_2SiO_4 was probably prepared by Suito [17] at pressures greater than 220 kbar at 1000°C, but the complete conversion to this phase was reported by Ito et al. [18].

The so-called post-spinel phase of Mg_2SiO_4 was the subject of considerable attention in the geophysical literature for about a decade (see [8] for a detailed review). All possibilities for the post-spinel phase of Mg_2SiO_4 proposed on the basis of available data of analogue compounds were proved to be erroneous by the results of direct high-pressure studies of Mg_2SiO_4 and $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$ by Liu [19,20]. The post-spinel phase of Mg_2SiO_4 is still unique.

The direct experimental studies of the post-spinel phase of Mg_2SiO_4 were first reported by Kumazawa et al. [21], who concluded that Mg_2SiO_4 (spinel) decomposes into periclase and stishovite. This result was also confirmed independently by Ming and Bassett [22]. With further experimental studies, however, Liu [5, 19] found that neither Mg_2SiO_4 nor MgSiO_3 had a stability field consisting of periclase and stishovite at high pressures and temperatures. Instead, Liu [19]

has shown that the post-spinel phase of Mg_2SiO_4 is a mixture of MgSiO_3 (perovskite) + periclase which was observed earlier by him, but regarded as a post-oxide phase [23].

From shock-wave experiments, there appears no further phase transition in Mg_2SiO_4 which is denser than the mixture MgSiO_3 (perovskite) + periclase known in the highest pressures existing within the Earth's interior.

With increasing pressure, in the temperature range 800-1500°C, the phase transitions of Mg_2SiO_4 can be summarized as follows: olivine 7.9% modified "spinel" 2.4% "spinel" 10.7% "perovskite" + periclase. The T-P boundaries of the transition are shown in Fig. 5 and the effects of substituting Fe^{2+} for Mg^{2+} on these transitions are displayed in Fig. 6 (cautions should be exercised against the reliability of these T-P boundaries).

From the data shown in Figs. 2, 4 and 6, it is clear that Fe^{2+} substitutes readily for Mg^{2+} to form complete solid solutions in these silicates at low pressures. Except for the spinel phase, complete solid solutions between Mg^{2+} and Fe^{2+} do not exist in any other known high-pressure modifications of these minerals.

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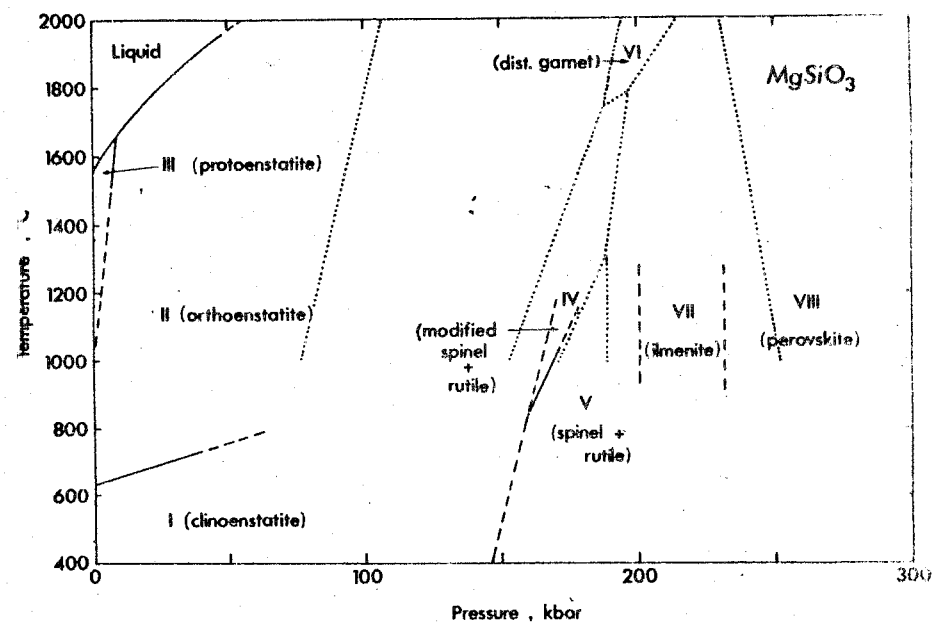


Fig. 1. Phase diagram of $MgSiO_3$.

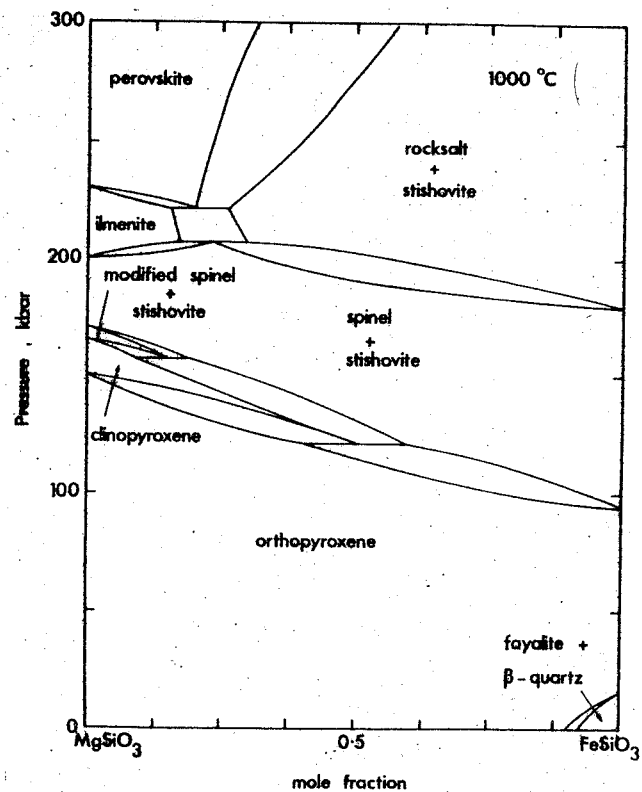


Fig. 2. Phase diagram of MgSiO_3 - FeSiO_3 .

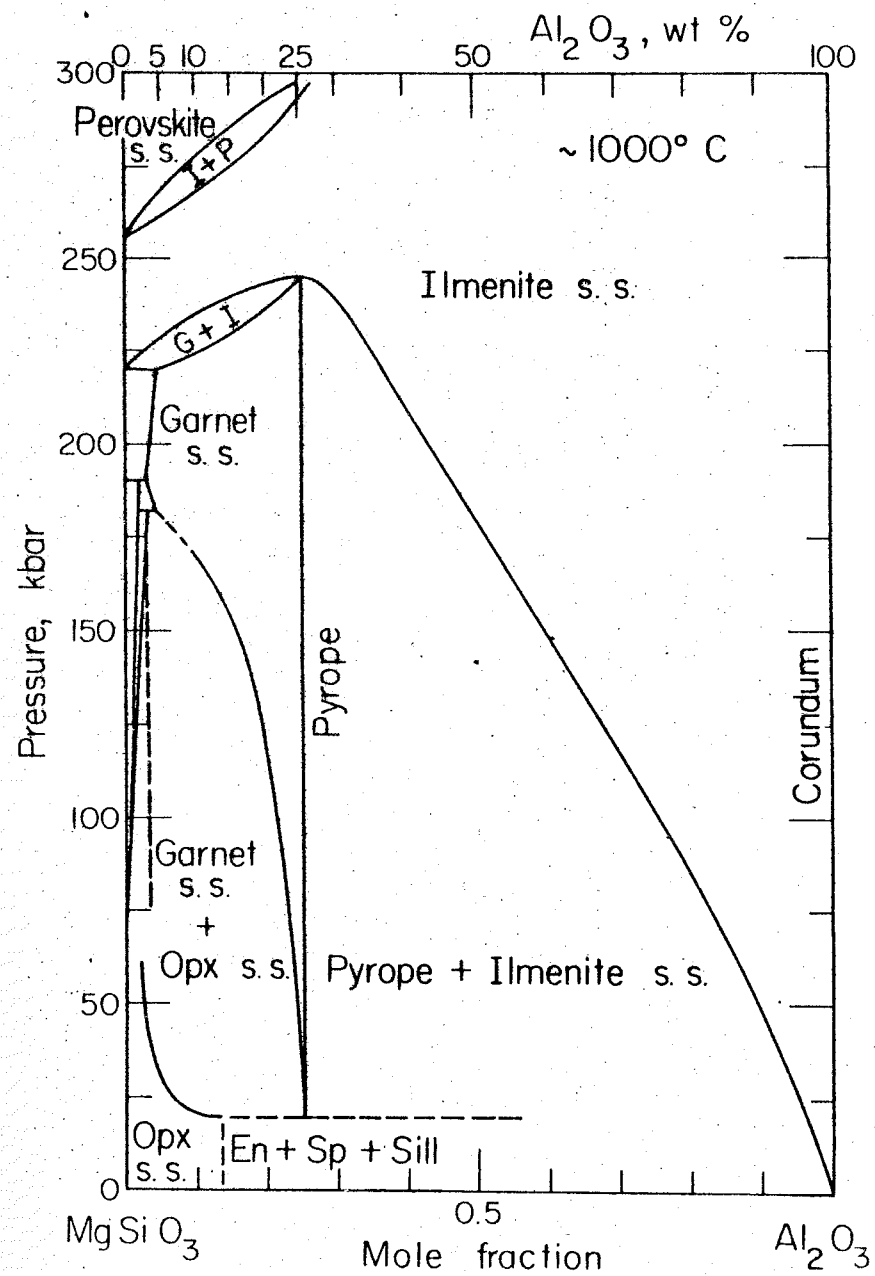


Fig. 3. Phase diagram of MgSiO_3 - Al_2O_3 .

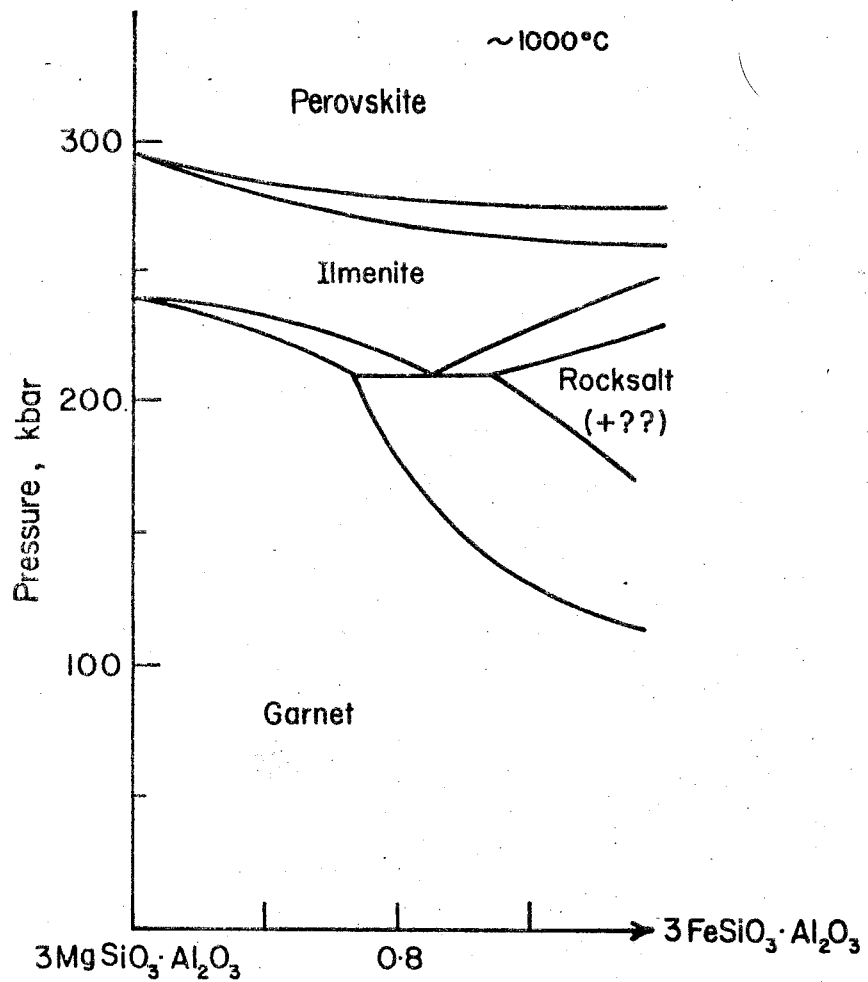


Fig. 4. Schematic phase diagram of pyrope-rich garnet.

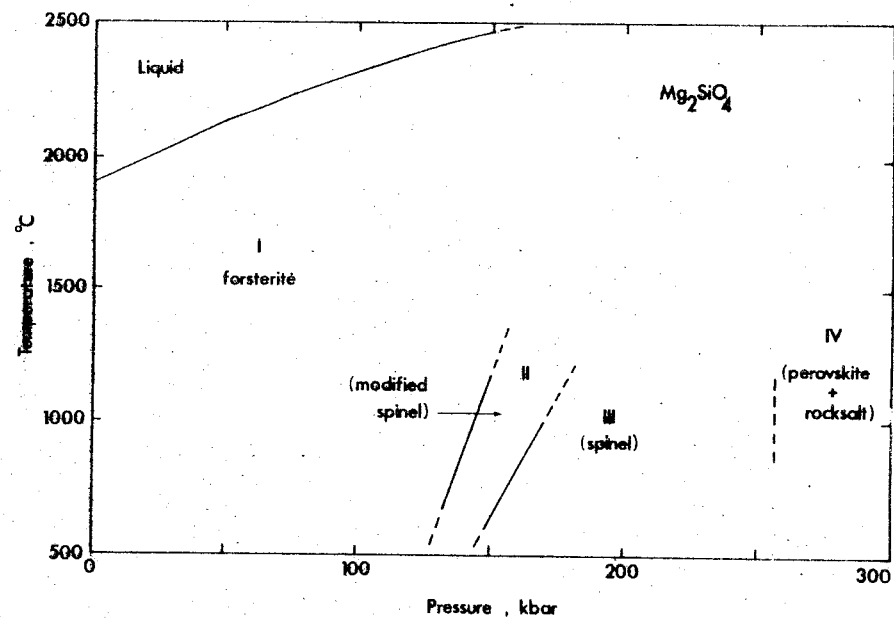


Fig. 5. Phase diagram of Mg_2SiO_4 .

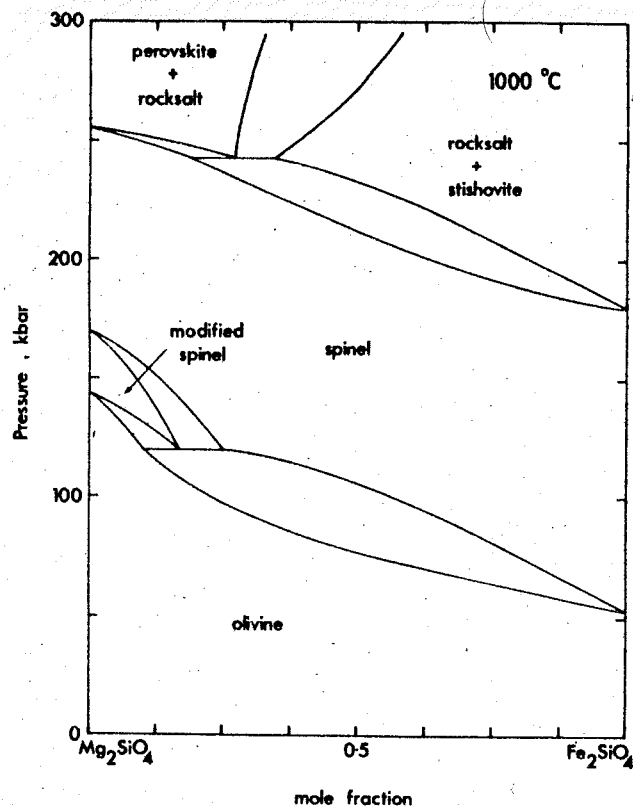


Fig. 6. Phase diagram of Mg_2SiO_4 - Fe_2SiO_4 .

PHASE EQUILIBRIA OF MULTICOMPONENT MINERAL SYSTEMS AT HIGH PRESSURES AND HIGH TEMPERATURES

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The substance of the Earth's upper mantle was essentially differentiated in the course of deep-seated magmatic processes. It is for the most part formed by peridotitic as well as pyroxenitic and eclogitic rocks [1,2]. The most deep-seated ones pertain to the garnet-peridotitic facies. Liquidus phase relations between the minerals of primary garnet lherzolite (compositional estimations are given in [1-3]) account for the regularities of the formation, evolution, crystallization of multicomponent silicate magmatic melts and petrogenesis of garnet-peridotitic mantle rocks.

The study on the real peculiarities of liquidus composition for the substance of garnet-peridotitic mantle is thus a key physico-geochemical problem. The investigation on the problem implies the study of the phase equilibria at the melting of multicomponent heterogeneous mineral systems under high pressures and high temperatures. It was started in the works [4-6].

The six-component system of oxides $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is fairly comprehensive to represent the real compositions of garnet-peridotitic mantle, 99% of its weight being determined. Major attention should be paid to the experimental study on the liquidus phase equilibria of the multicomponent system olivine-orthopyroxene-clinopyroxene-garnet which is an internal three-dimensional joint of the system of oxides.

For this study it seems expedient to use a more simple version of the system, so called standard system. With relation to mineralogy and concentration, the system forsterite (Fo)-enstatite (En)-diopside (Di)-pyrope (Py) approaches the standard. This system forms part of the system $\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ resulted from the basic six-component system of oxides by means of subtraction of isomorphous FeO and Na_2O components.

At first, it is advisable to review the experimental data available for present on the standard system Fo-En-Di-Py and construct the model of its isobaric liquidus as a three-dimensional

projection on the tetrahedron of compositions. Available are the melting diagrams of binary boundary systems (the review in /6/). Some of them such as the eutectic ones Fo-Di, Fo-Py and the pseudobinary one Di-Py were studied at 40 kbar. Others such as the eutectic systems Fo-En, En-Py, and the peritectic one En-Di were obtained by extrapolation to 40 kbar of the diagrams studied at lower pressures. A pressure of 40 kbar reported in this work reproduces the conditions of the garnet-peridotitic mantle. Based on the diagrams of the binary systems the liquidus relations in the boundary ternary systems of the standard system are given in Fig.1,a as a development of tetrahedron. Liquidus diagrams of the ternary systems were used for plotting the liquidus of the standard system (Fig.1,b), a number of the most important peculiarities of the binary systems En-Di and Di-Py being found.

First of all, the boundary system En-Di has a melting diagram of the IV Roseboom's type for limited solid solutions and is specified by the reaction $\bar{En}_{ss} + \bar{L} (\text{melt}) = Di_{ss}$ (minus sign over the phase symbol indicates that the phase abundance decreases within the given peritectic reaction). This reaction is responsible for the peritectic equilibrium $\bar{En}_{ss}, Di_{ss}, \bar{L}$ in the binary system En-Di and for the equilibria Fo, $\bar{En}_{ss}, Di_{ss}, \bar{L}$; $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$; Fo, $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$ in the ternary systems Fo-En-Di, En-Di-Py, and quaternary standard system Fo-En-Di-Py, respectively. Hence the temperature of the liquidus curve $Di_{ss}, \bar{L}$ in the system En-Di decreases with figurative compositional point moving outwards the peritectic point $\bar{En}_{ss}, Di_{ss}, \bar{L}$. A decrease in temperature of the same origin - is observed at the cotectics Fo, $Di_{ss}, \bar{L}$; $Di_{ss}, Py_{ss}, \bar{L}$, and Fo, $Di_{ss}, Py_{ss}, \bar{L}$ in the systems Fo-En-Di, En-Di-Py, and the standard system Fo-En-Di-Py, respectively.

Another system Di-Py (Fig.2,a) is featured by pseudobinary properties, En_{ss} appearing as a complementary phase, formation of Mg-pyroxenic and Ca-garnetic components and solid solutions Di_{ss} and Py_{ss} . Based on the analysis of the basic ternary system En-Wol (wollastonite)-Cor (corundum) the system Di-Py turned out to be the internal polythermal joint of the ternary subsystem $En_{ss}^o - Di_{ss}^o - Py_{ss}^o$ with some effective compositions of boundary phases (Fig.2,c). Therefore the joint Di-Py contains information on the liquidus of such a ternary system, namely on the nonvariant point $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$ (is plotted at the joint as a line), on the

univariant curves $\bar{En}_{ss}, Py_{ss}, \bar{L}$; $\bar{En}_{ss}, Di_{ss}, \bar{L}$, and $Di_{ss}, Py_{ss}, \bar{L}$ (are plotted as fields). What is of vital importance the peritectic nature of the nonvariant equilibrium $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$ and the descent of the univariant curve $Di_{ss}, Py_{ss}, \bar{L}$. This may be concluded from the relative disposition of the elements they are represented in the system Di-Py along the temperature axis.

For the liquidus of the standard system Fo-En-Di-Py it is significant that at 40 and 30 kbar the nonvariant point $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$ in the system $En_{ss}^o - Di_{ss}^o - Py_{ss}^o$ is situated on the different sides of the joint Di-Py (Fig.2,c). This also affects the melting diagrams of the system Di-Py: the fields $\bar{En}_{ss}, \bar{L}$ and $\bar{En}_{ss}, Di_{ss}, \bar{L}$ appear at 30 kbar (Fig.2,b). Therefore the liquidus of the standard system Fo-En-Di-Py at 30 kbar (Fig.1,c) is specified by the shift of $\bar{En}_{ss}, \bar{L}$ primary crystallization volume towards the plane Fo-Di-Py. The three-dimensional position of the univariant line $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$ is seen to change. The trace of the line appears at the plane Fo-Di-Py. The ternary system Fo-Di-Py itself should be considered as an internal joint (two-dimensional projection) of the quaternary system $Fo - En_{ss}^o - Di_{ss}^o - Py_{ss}^o$ with some effective boundary compositions and not as a boundary system. Thus any binary polythermal joint of such a two-dimensional projection belongs to all the quaternary system at a time. This fact was proved experimentally.

Thus, the distinctive features of the standard system Fo-En-Di-Py are as follows: the five-phase equilibrium Fo, $\bar{En}_{ss}, Di_{ss}, Py_{ss}, \bar{L}$; one of the four univariant four-phase curves the cotectic Fo, $Di_{ss}, Py_{ss}, \bar{L}$ descending with decreasing temperature. It is noteworthy that this system liquidus forms part of the liquidus of the system $Fo - \bar{En}_{ss} - Di_{ss} - Py_{ss}$ with some effective boundary compositions. As appears from the present review, the experimental study on the standard system is far from being concluded. But the inference we arrived at is proved by the study of analogous multicomponent systems. Some results of this are reported in this paper.

The ferriferous system $(Di_{80}Hed_{20})_{50}(Py_{80}Alm_{20})_{50} - Fe_{80}Fa_{20}$ (Hed - hedenbergite, Alm - almandine, Fa - fayalite) forms part of the five-component system of oxides $CaO - MgO - FeO - Al_2O_3 - SiO_2$. Like the analogous standard system it is the internal joint (projection) of the ferriferous system Ol-Opx-Cpx-Gr with some effective boundary compositions. That is why the polythermal joint $(Di_{80}Hed_{20})_{50}(Py_{80}Alm_{20})_{50} - Fe_{80}Fa_{20}$ belongs to the internal and

not to the boundary joint of the considered ferriferous quaternary system. The experimental study of the joint $(\text{Di}_{80}\text{Hed}_{20})_{50}(\text{Py}_{80}\text{Alm}_{20})_{50}-\text{Fo}_{80}\text{Fa}_{20}$ (Fig.3,a) discovers the five-phase peritectic equilibrium $\text{Ol}, \text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$ as well as three four-phase equilibria: the peritectic ones $\text{Ol}, \text{Opx}, \text{Cpx}, \text{L}$; $\text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$ and the cotectic one $\text{Ol}, \text{Cpx}, \text{Gr}, \text{L}$. The latter one decreases with decreasing temperature. Note that the five-phase equilibrium is univariant and not nonvariant due to the isomorphous ferriferous components of solid solutions. Hence, instead of a point it is depicted as a line along the temperature axis which looks like a short length in that ferriferous components are limited in concentration. Such a length corresponds to the field $\text{Ol}, \text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$ of a polythermal joint (Fig.3,a).

So ferriferous components forming part of a garnet-peridotitic system are responsible for the expansion of Opx, L primary crystallization volume and its shift along with the peritectic curve $\text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$ outwards the joint $\text{Ol}-\text{Cpx}-\text{Gr}$ like in the standard system at 30 kbar. Therefore the liquidus of the ferriferous system $\text{Ol}-\text{Opx}-\text{Cpx}-\text{Gr}$ looks like that of the standard system at 30 kbar (Fig.1,c). But the presence of ferriferous components produces a considerable decrease in liquidus and solidus temperatures.

The real liquidus of the garnet-peridotitic mantle to a reliable degree may be related to the liquidus of the system $\text{Ol}(\text{Fo}_{86}\text{Fa}_{14})-\text{Opx}(\text{En}_{84.5}\text{Fs}_{10.5}\text{Di}_3\text{Jd}_2)-\text{Cpx}((\text{Di},\text{Hed})_{60}\text{Jd}_{18}(\text{En},\text{Fs})_{22})-\text{Gr}(\text{Py}_{73.4}\text{Alm}_{16.6}\text{Gros}_{10.0})$ (Jd - jadeite, Gros - grossular). The boundary phase compositions of the latter one are specified by the system of oxides $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. These compositions are peculiar to the garnet peridotitic rocks the least depleted in Fe and Na components, as well as to the hypothetical rocks of the upper mantle. The experimental study at 40 kbar of the system $\text{Cpx}-\text{Gr}$ (Fig.3,b) which like the standard one is an internal polythermal joint brings to evidence that the composition of the real liquidus of the garnet-peridotitic mantle agrees well with the model given in Fig.1,b.

To sum up, the liquidus of the real garnet-peridotitic mantle is specified by the five-phase peritectic equilibrium $\text{Ol}, \text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$; two four-phase peritectic equilibria $\text{Ol}, \text{Opx}, \text{Cpx}, \text{L}$; $\text{Opx}, \text{Cpx}, \text{Gr}, \text{L}$, and two four-phase cotectic equilibria $\text{Ol}, \text{Opx}, \text{Gr}, \text{L}$; $\text{Ol}, \text{Cpx}, \text{Gr}, \text{L}$, the latter one being plotted as a curve descending with decreasing temperature.

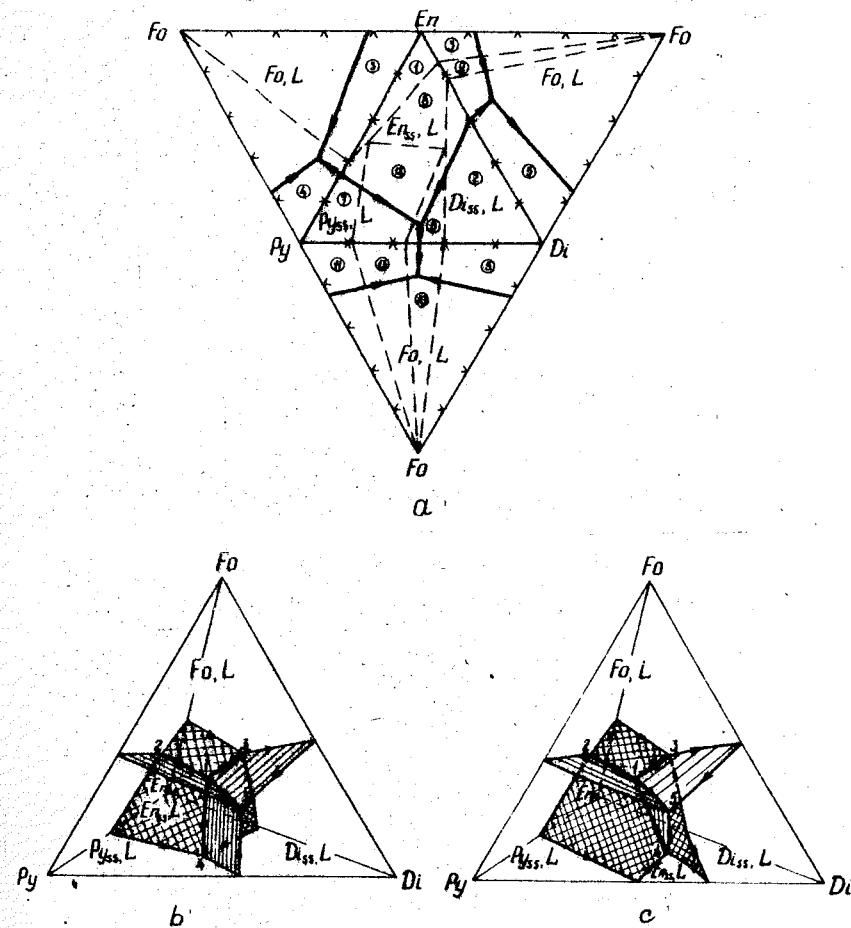


Fig.1. Liquidus model of the system $\text{Fo}-\text{En}-\text{Di}-\text{Py}$ as projected onto the tetrahedron of compositions:
a-boundary ternary systems at the development of the compositional tetrahedron at 40 kbar: liquidus - solid lines, solidus - dashed lines. Subsolidus: 1- En_{85} ; 2- Di_{85} ; 3- $\text{Fo}, \text{En}_{85}$; 4- $\text{Fo}, \text{Py}_{85}$; 5- $\text{Fo}, \text{Di}_{85}$; 6- $\text{En}_{85}, \text{Py}_{85}$; 7- $\text{En}_{85}, \text{Py}_{85}$; 8- $\text{Di}_{85}, \text{Py}_{85}$; 9- $\text{Fo}, \text{En}_{85}, \text{Di}_{85}$; 10- $\text{Fo}, \text{Di}_{85}, \text{Py}_{85}$; 11- $\text{Fo}, \text{En}_{85}, \text{Py}_{85}$; 12- $\text{En}_{85}, \text{Di}_{85}, \text{Py}_{85}$; 13- $\text{Fo}, \text{En}_{85}, \text{Di}_{85}, \text{Py}_{85}$;
b, c - liquidus of the system $\text{Fo}-\text{En}-\text{Di}-\text{Py}$ at 40 and 30 kbar, respectively. (1- $\text{Fo}, \text{En}_{85}, \text{Di}_{85}, \text{Py}_{85}, \text{L}$; 2- $\text{Fo}, \text{En}_{85}, \text{Py}_{85}, \text{L}$; 3- $\text{Fo}, \text{En}_{85}, \text{Di}_{85}, \text{L}$; 4- $\text{En}_{85}, \text{Di}_{85}, \text{Py}_{85}, \text{L}$; 5- $\text{Fo}, \text{Di}_{85}, \text{Py}_{85}, \text{L}$).

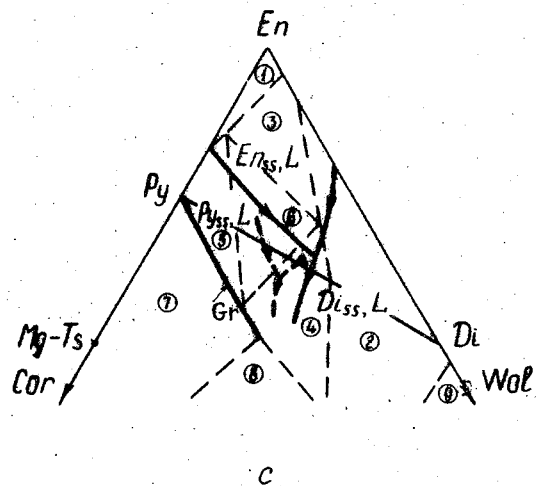
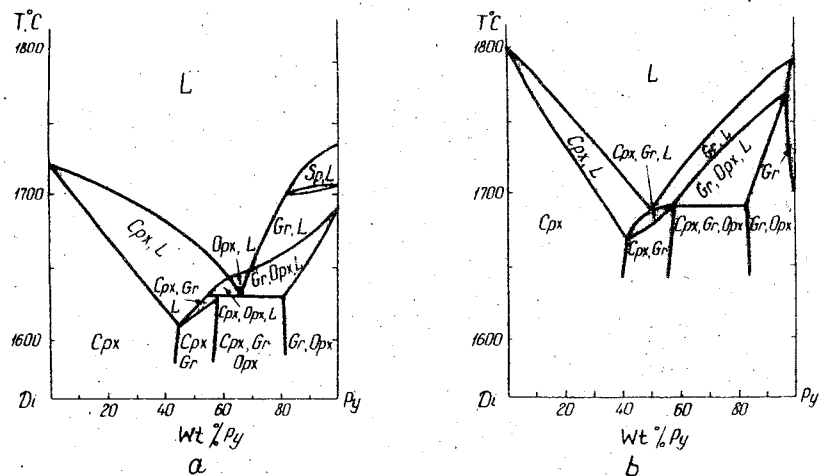


Fig. 2. Melting diagrams of the system Di-Py: a-30 kbar; b-40 kbar; c-fragment of the system En-Wol-Cor: liquidus at 40 kbar (solid lines), at 30 kbar (dashed lines). Subsolidus: 1-Enss; 2-Diss; 3-Enss, Diss; 4-Diss, Pyss; 5-Pyss, Enss; 6-Enss, Diss, Pyss; 7-Pyss, Cor; 8-Diss, Pyss, L; 9-Diss, Wol. Gr solid solutions Py-Gros; Mg-Ts - Tschermak molecular.

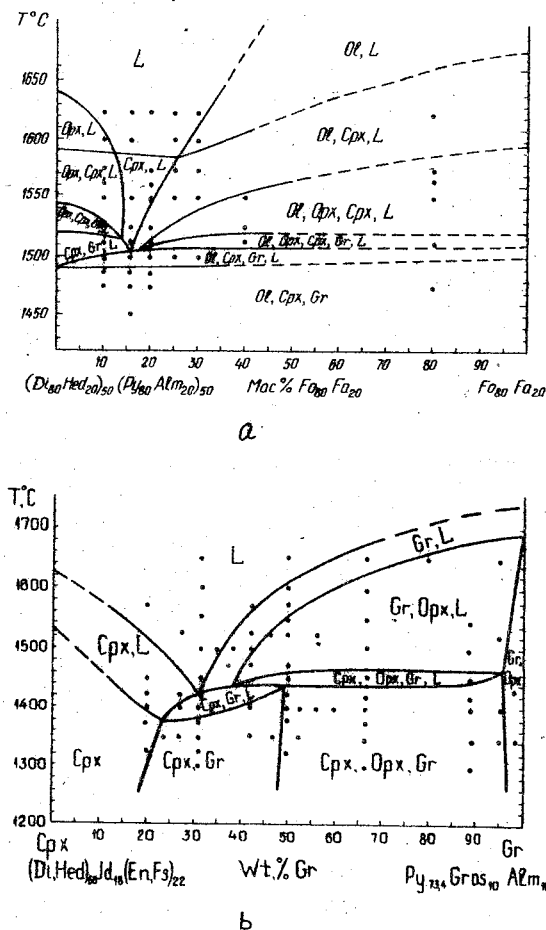


Fig. 3. Melting diagram of the multicomponent systems at 40 kbar: a - for the joint $(\text{Di}_{80}\text{Hed}_{20})_{50}(\text{Py}_{80}\text{Alm}_{20})_{50}\text{Fo}_{80}\text{Fa}_{20}$; b - for the system Cpx-Gr with typical of the real mantle compositions of boundary phases at 40 kbar. Experimental points are shown.

The information on the real peculiarities of liquidus composition for the garnet-peridotitic mantle contributes to the study of its fundamental characteristics. They form a base for the interpretation of the peculiarities of deep-seated magmatism processes and genesis of the Earth's upper mantle rocks.

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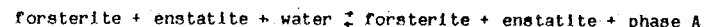
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THE "WATER LINE": ORIGINS OF THE OCEANS AND LOW-VELOCITY ZONE

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The "water line", below which H_2O is locked in solid phases A, B, ..., recently proposed by Liu [1] is a mineralogic reaction:



which exists where both Mg_2SiO_4 and H_2O (even if in minute amounts) coexist in the Earth's upper mantle, and was determined by experiments to have the boundary P (kbar) = $17 + 0.074 T$ ($^{\circ}C$) up to about 80 kbar. If the mantle contains some 10 mole % FeO , a linear extrapolation of the water line would intersect the water saturated solidus of a peridotite near 350 km (B' in Fig. 1). The linearity of the water line at these depths has been discussed in some detail by Liu [1] and the extrapolation of the solidus follows Hasebe et al. [2].

If the surface of the growing Earth was covered by large-scale "magma ocean" during accretion, then nearly all of the H_2O in infalling planetesimals is likely to be dissolved into the melts [e.g. 1,3]. It is conceivable that, shortly after accretion, the Earth's surface and at least its outer regions were covered by melts in the present model. The Earth may have a paleogeotherm such as XY shown in Fig. 1. On cooling, XY would eventually intersect the joint B' in Fig. 1. Thus, H_2O in the melts would be stored in phase A below the water line, and would remain in the melts above the water line. On further cooling, the melts move away from the water line and the paleogeotherm $X'Y'$ intersects the solidus at C and the water line at B'' . H_2O in the region $B''C$ would exsolve as free water which would, however, dissolve immediately in the melts above C if the melts are not saturated. Thus, the concentration of H_2O in the up-rising melts increases while the melts move further away from the water line. Eventually, when the whole Earth is solidified, all H_2O in the melts above B' has to be expelled from the Earth. The expelling of water from the Earth's interior would be a violent early degassing.

The surface temperature of the Earth at this stage is likely to be much higher than the critical point and/or the condensation temperature of H_2O at the proto-atmospheric pressure. H_2O thus produced in the proto-atmosphere would eventually condense to form the oceans when the surface cools down.

Quantitatively, one may make an estimate of the amount of H_2O evolved in the present model. Assume that the core has already formed at the end of the accretion whilst the outer regions of the Earth are still covered by "magma ocean". The total H_2O evolved above 350 km is calculated to be 2.9×10^{24} g if the melts contain 0.5 wt % H_2O . This is very close to the total inventory of H_2O (2×10^{24} g) in the near-surface geochemical reservoirs (hydrosphere + crust) of today's Earth estimated e.g. by Holland [3]. The difference may be accounted for by the escape of hydrogen during the Earth's history. The H_2O content in the melts used in the present model was estimated by assuming that the ratio of H_2O loss to H_2O available above the water line is the same for Earth as for Venus during the history of these two planets [4]. This value is consistent with that in the present mantle (0.5 wt %) estimated by Rubey [5] and with that in the deep-sea basalts (0.1 - 0.9 wt %) observed by Moore [6].

The low-velocity zone (LVZ) is a widely accepted feature of the Earth's upper mantle. The depths of LVZ were placed differently by different seismologists because of the non-uniqueness inherent in surface wave analysis. It is generally recognized, however, that (1) the LVZ exists somewhere between 50 and 300 km under the suboceanic mantle, (2) the evidence for the presence of an LVZ beneath the continents is much less convincing than for regions beneath the oceans and (3) the S-wave anomalies were about four times greater than the P-waves in the LVZ.

Formation of the LVZ has been generally ascribed to partial melting of mantle materials. However, there appear to be many difficulties associated with partial melting models which have not been appropriately addressed [1,7]. A different model which would overcome most of the difficulties arisen in [1,7] is given here.

In addition to the water line and solidus curve, the experimentally determined stability fields for amphibole and phlogopite are shown in Fig. 2. Also shown in

Fig. 2 are the oceanic geotherm and the thermal model of the descending lithosphere (dotted lines) proposed by Hasebe et al. [2].

According to Fig. 2, the oceanic geotherm intersects the water line having a 10 mole % FeO near 300 km (B), the stability field of phlogopite near 200 km (C), and that of amphibole near 100 km (D). The continental geotherm is not available in the model of Hasebe et al. [2]. By assuming that the continental geotherm passes by the region in the vicinity of C' in Fig. 2 where the stability field of phlogopite intersects the water line, the information available from Fig. 2 may be transformed into a diagrammatic sketch shown in Fig. 3. The water line and the stability fields for amphibole and phlogopite in the suboceanic mantle and the descending lithosphere shown in Fig. 3 are precisely what were given in Fig. 2. The same information for the subcontinental mantle and in the vicinity of the mid-ocean ridge shown in Fig. 3 is more suggestive. However, the directions of the variations of these boundaries in these regions are real.

In Fig. 3, free water above the water line must move upward, but it may not be able to escape easily because the concentration of H_2O in the mantle is likely to be low (~ 0.5 wt %) and because water may form vesicles and reside in the mantle. However, once the free water moves away from the water line, H_2O stored in phase A below the water line has to be evolved as free water across the water line, because the mineralogic control of the water line is an equilibrium reaction. Thus, it appears that water has been continuously, but slowly, supplied from underneath the water line in the mantle since the Earth was solidified. Free water thus produced would form phlogopite and amphibole once it reaches the stability fields of these minerals. Amphiboles occur in the mantle under both the oceans and continents, whereas phlogopite may occur mainly in the subcontinental mantle due to its high potassium contents. Thus, the free water zone may be extended from 300 km to 100 km in the suboceanic mantle, but limited in the region near 250 km, or may not exist at all, in the subcontinental mantle.

Seismic-wave velocities, S-waves in particular, would certainly be attenuated by travelling through the region containing free water, even in a minute amount,

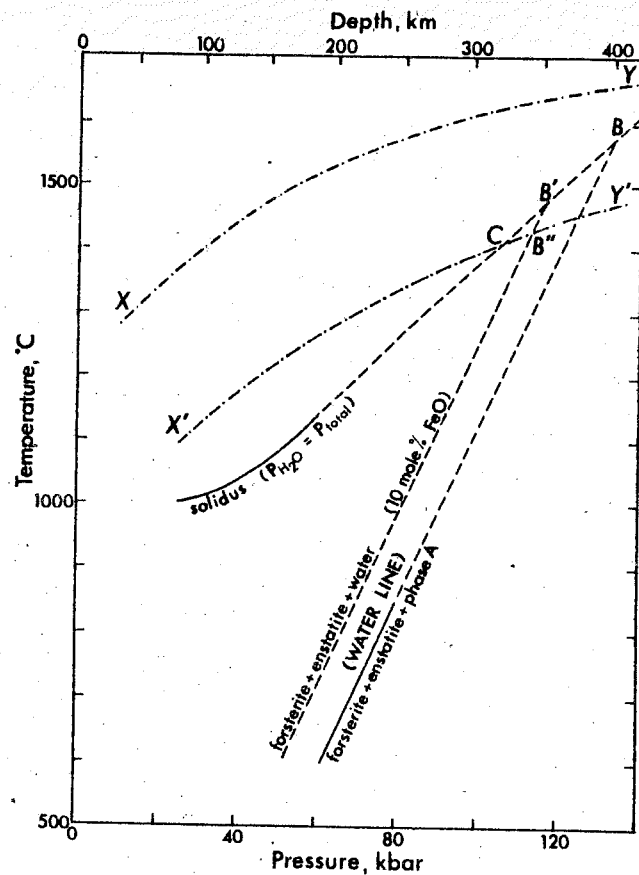


Fig. 1.
The water line and the solidus of a peridotite are compared with hypothetical temperature profiles (XY and X'Y') shortly after accretion of the Earth.

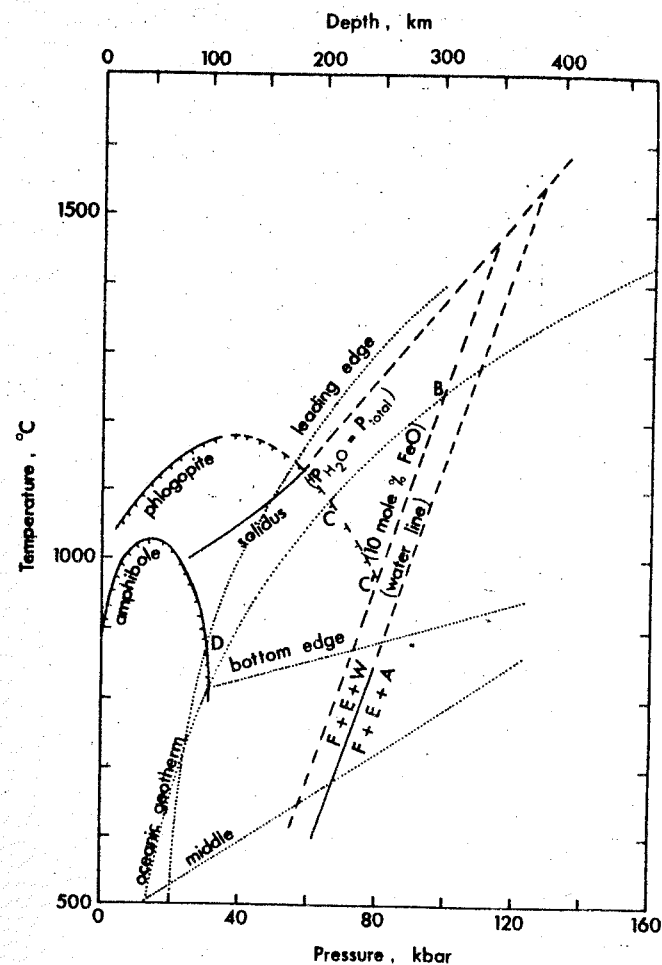


Fig. 2.
Experimentally determined water line, solidus of peridotite, and the stability fields of amphibole and phlogopite are compared with the oceanic geotherm and the thermal model of the descending lithosphere. Abbreviations: F, forsterite; E, enstatite; W, water; A, phase A.

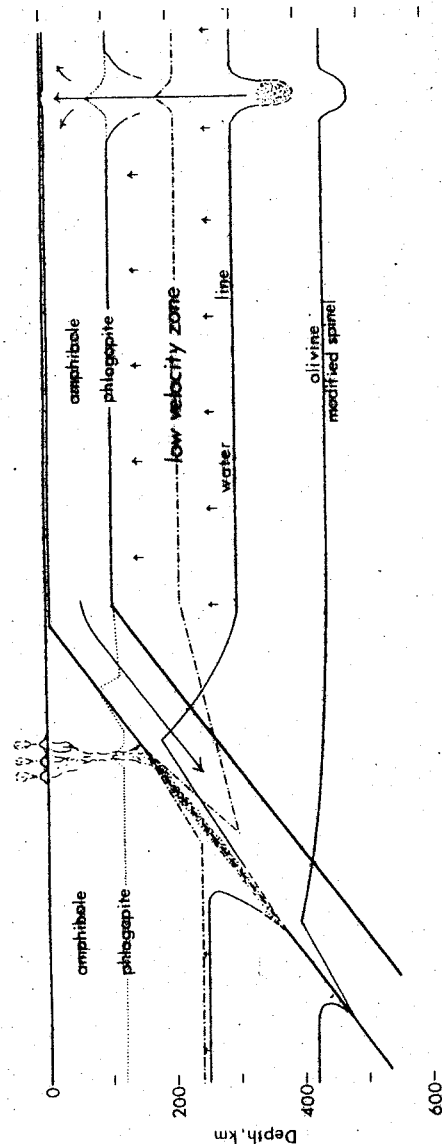


Fig. 3. Schematic diagram showing the stability fields of amphibole (dotted line) and phlogopite (chain line), the water line, and the olivine ↔ modified spinel boundary in different tectonic provinces of the Earth's upper mantle. Arrows indicate the flow of free water.

in the mantle. The depths of the free water zone in the suboceanic mantle (100 - 300 km) revealed in this study appear in quite good agreement with the depths of the LVZ derived from seismological observations. The different character of the LVZ between different tectonic provinces reconciles the different chemistry in these areas, which constrains both the depths and regions of the free water zone. In conclusion, regardless of the different tectonic provinces, this study suggests that the water line may be the probable cause and may be defined as the base of the LVZ, and that the LVZ itself is a zone containing free water in the mantle. The top of the LVZ is probably defined by the stability boundary of amphibole under suboceanic mantle and by phlogopite or other hydrous potassium silicates under subcontinental mantle.

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On the basis of the previously designed diamond anvil cell /1/ a complex of equipment and techniques for pressures up to 40-50 GPa and temperatures up to 400 °C has been developed permitting to get information on crystal chemistry and physicochemical processes in the Earth's interiors.

The compressibility and reversible phase transitions of minerals at high pressures were studied by X-ray diffraction. Exposure time for powder samples with diameter 200-300 μm at pressures up to 20.0 GPa was 50-70 hours when using traditional film technique. As was shown by preliminary experiments carried out at the Novosibirsk synchrotron radiation Centre with monochromatic synchrotron radiation and position sensitive detector the exposure time might be reduced up to several minutes /2/.

Compression of zincite ZnO was studied up to 20.0 GPa. The experiments were carried out with gasketed samples (gasket material is stainless steel) in hydrostatic conditions (methanol/ethanol-4/1). The pressure was determined by ruby luminescence R₁-line shift ($\sim 20 \mu\text{m}$ -size ruby chip was added to the sample). The accuracy was ± 0.1 GPa in hydrostatic conditions. Conventional film technique was used in these experiments. In Fig.1 the relative volumes of ZnO obtained in three different runs are plotted as a function of pressure to 12.0 GPa.

At low pressures zincite has hexagonal wurtzite type structure. At pressures near 8.5 GPa zincite transforms into high-pressure phase ZnO-II with cubic NaCl structure first discovered by quenching technique /3/. Transition pressure and $(\Delta V/V)_p$ at transition - 17.2 % agreed well with previous in situ X-ray measurements /4/. The compression of low pressure phase is described by Birch-Murnaghan equation with $K_0=134$ GPa and $K_0^1=4.8$, the later taken from /5/. The bulk modulus is in excellent agreement with ultrasonic value 139.4 GPa /5/.

The high pressure cubic phase ZnO-II transforms very slowly to the initial hexagonal phase when releasing pressure at room temperature and might be preserved at pressures as low as 4.0-5.0 GPa. Our data on ZnO-II compression (Fig.1) combined with the

V_0 value for this phase from /3/ permitted us to estimate the rough value of its bulk modulus $K_0=143$ GPa assuming $K_0^1=4.8$.

Our results on bromellite compression confirm the absence of phase transition to NaCl structure in BeO at pressures up to 20.0 GPa.

To investigate the behaviour of porous structures at high pressures /6/ the compression and Raman spectra /7/ of natural zeolite natrolite $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ were studied in various pressure transmitting media.

To characterize chemical bond under pressure and in particular to measure the energy gap at high pressures a spectroscopic equipment for optical absorption measurements on microsamples in the diamond cell in the region 400-800 μm was made. It includes luminescent microscope, prism monochromator, filament lamp, photomultiplier and registration system.

We have been studying chalcogenide glasses of composition As_2S_3 with some additives. They are met sometimes in nature, possess semiconductive properties and can be synthesized with different admixtures of the third component, allowing their properties to be altered purposively. For high pressure experiments glass microsamples uniform in thickness (about 4-5 μm) and 20-30 μm in diameter were chosen under interference microscope.

The mixture methanol/ethanol - 4/1 was used as reference liquid for measuring the transmission spectra. Spectra were collected without correction on reflectance. The transmission spectra of $\text{As}_2\text{S}_3\text{Ge}_{0.2}$ glass at pressures to 3.0 GPa are shown in Fig.2 in coordinates $I/I_e - \lambda$, where I is intensity of transmitted light, I_e - the intensity of light transmitted through the reference liquid, λ - wavelength of the incident light. The absorption edge of $\text{As}_2\text{S}_3\text{Ge}_{0.2}$ glass shifts to long-wave spectral region with pressure increasing, $d\lambda/dP$ being $\sim 40 \text{ nm/GPa}$, that is similar to the results got by us and in /8/ for pure As_2S_3 . Thus, in spite of slightly different initial value, the energy gap for glasses $\text{As}_2\text{S}_3\text{Ge}_{0.2}$ and As_2S_3 is decreasing by 0.53 ± 0.05 eV when increasing pressure from 1 atm to 3.0 GPa.

For geochemical studies it is very interesting to investigate the simultaneous influence of high pressure and temperature on a sample. To work at temperature up to 400 °C a simple modification of outer heater was used by us as well as a procedure of a simultaneous temperature and pressure measurement based on the shape of ruby luminescence R-lines. The preliminary study of

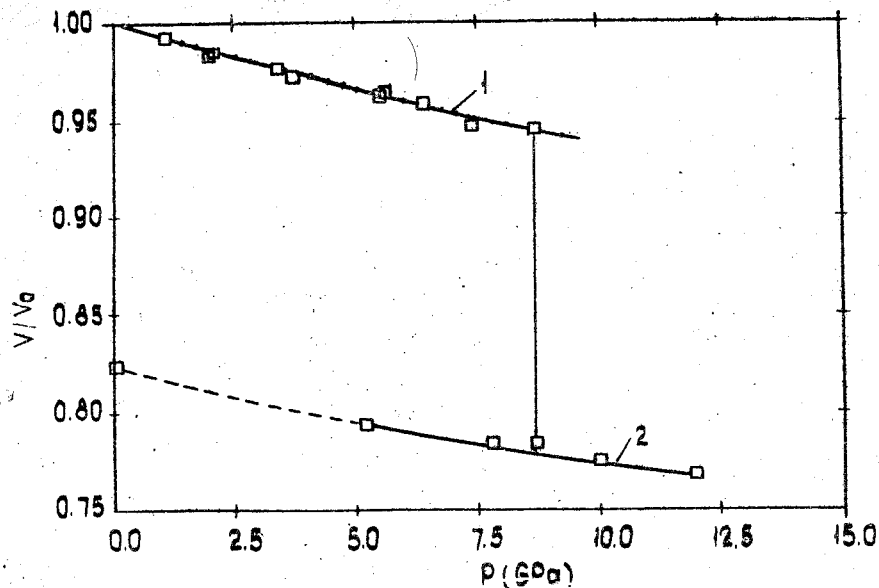


Fig.1. Compression curves of zincite ZnO phases: 1-low pressure hexagonal wurtzite phase; 2-high pressure cubic phase (NaCl type).

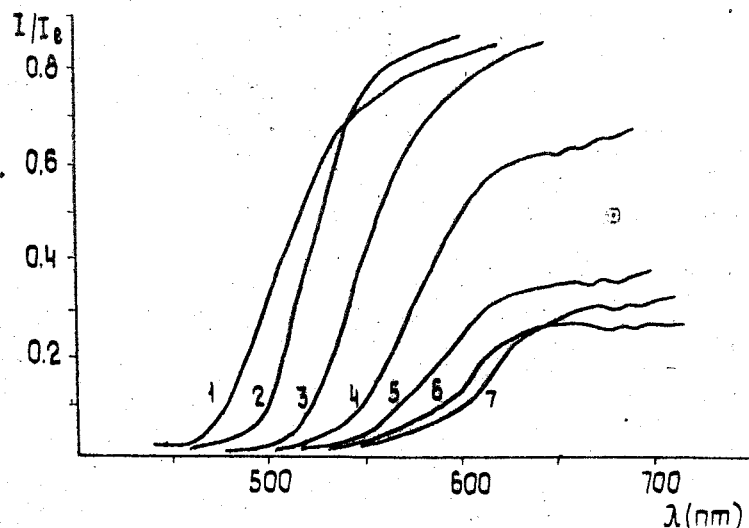


Fig.2. Transmission spectra of $\text{As}_2\text{S}_3\text{Ge}_{0.2}$ glass at different pressures: 1-1 atm.; 2-0.3 GPa; 3-0.8 GPa; 4-1.6 GPa; 5-2.1 GPa; 6-2.6 GPa; 7-3.0 GPa.

mineral-water systems was made in stainless steel gasket. We have observed the crystallization of high pressure unquenchable phases of KI with CsCl structure hydrates of CaCO_3 . Fine crystals of coesite were synthesized in $\text{SiO}_2\text{-H}_2\text{O}$ system at pressure 7.0-8.0 GPa and $T=450^\circ\text{C}$. At pressure about 3.0 GPa and temperature higher than 350°C recrystallization of waterless beryl crystals was observed in pure water resulting in alkali-free water-bearing beryl with anomalously high water content. The further development of outer heater system is under way in our laboratory. That will permit to increase temperature and pressure range to study phase equilibria of geochemical interest.

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HIGH - PRESSURE PHYSICS AND INTERNAL STRUCTURE AND
EVOLUTION OF PLANETS

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A successful attempt for the description of internal structure and possible evolutionary scenario of the planets requires the knowledge of many scientific disciplines like physics and chemistry or cosmic sciences as well as other modern research branches. During formation and evolution of the planets temperature and pressure vary in large intervals so that corresponding experiments have to cover this wide range to include the conditions beginning with the preplanetary nebula up to those in the deep interior of the giant planets. On the other hand, planetary observations offer a variety of data that can be used to construct relevant models for the description of planetary interiors. Measurements of seismic wave velocities, densities, of the gravitational field parameters etc. form the basis for a mechanical model of the planetary interior.

But this variety of possible models may be restricted taking into account results from high - pressure physics. It enables to connect structural and material distributions and properties with the mechanical model resulting for instance in a thermal model.

Since those models can only describe several special features of the whole phenomenon a satisfactory explanation of planetary evolution and interiors may result from the combination of several different models. This process of model construction, proof, and improvements is outlined in Figure 1. It connects planetology and geosciences with many branches of physics, chemistry etc. and improvements in any of these sciences result in model alterations

and amendments and so in a description that approaches reality more and more. High - pressure physics plays an important role in the investigation of the interior structure and evolution.

The first step in the evolutionary scenario is a condensation process in the preplanetary nebula. Assuming an appropriate temperature distribution in the nebula and a condensation scheme the differences between the two groups of planets - terrestrial and giant planets - become obvious. Figure 2 gives the phase diagrams of some materials important for the composition of the terrestrial planets. The evolutionary path starts in the preplanetary nebula at low pressures and temperatures ($200 \text{ K} \leq T \leq 1500 \text{ K}$; $0.1 \text{ Pa} \leq p \leq 100 \text{ Pa}$) and it proceeds along the indicated way of increasing temperature and pressure until it ends in a planetary adiabat given by the present state. The phase equilibrium curves indicate, that first - order phase changes will occur if the evolutionary path crosses these lines. Already the four curves (many other phenomena were omitted) give the impression that the evolution of the terrestrial planets is a very complicated process that involves a vast number of phase transitions. Since every transformation is accompanied by a loss of information it is rather difficult to conclude from the present state to early stages of the evolution as it is done in application of the actualistic principle.

Figure 3 gives a quite different picture for the evolution of the giant planets. The main constituent of the gaseous envelope that surrounds a small rocky core is hydrogen or a hydrogen - helium mixture. These compounds are not affected by as much phase transformations as the condensed materials. Only in the case of Saturn the present day adiabat crosses an equilibrium curve as indicated. So the knowledge about the interior and possible evolution of the

terrestrial planets is always restricted in comparison to a more detailed picture of the giant planets.

Coming back to the terrestrial planets the general picture of their present stage shall be outlined shortly. The present structure of all four planets of this group roughly may be described by three main parts: core, mantle and crust. Mantle and crust consist of a mineral assemblage and due to increasing pressure and temperature several different phase transitions will occur with increasing depth. So the mantle itself is not homogeneous but layered and laterally structured. Another important fact that should be regarded is that interaction between different components of the assemblage significantly alters the behaviour as it is observed for instance in the silicate - water system where the slope of the melting curve is changed from a positive value for the dry system to a negative one in the low pressure region. Here high - pressure physics offers a lot of possibilities to study these variations and to include this knowledge into improved models.

Core formation and evolution are ruled by the melting behaviour of iron or various iron compounds forming the core. Light alloying elements like sulphur shift the melting curve to lower temperatures. These elements also give rise to the occurrence of other effects, for instance the existence of a miscibility gap in the Fe - S system leads to the assumption, that the planets's magnetic field could be generated by separation between sulphur - rich and - poor liquids and the resulting release of gravitational energy.

The evolution of the terrestrial planets shall be characterized by the main processes only. Condensation in the preplanetary nebula is followed by accretion processes. The release of gravitational and radioactive energy leads to increasing temperature. After melting of the iron fraction core formation starts. The difference in

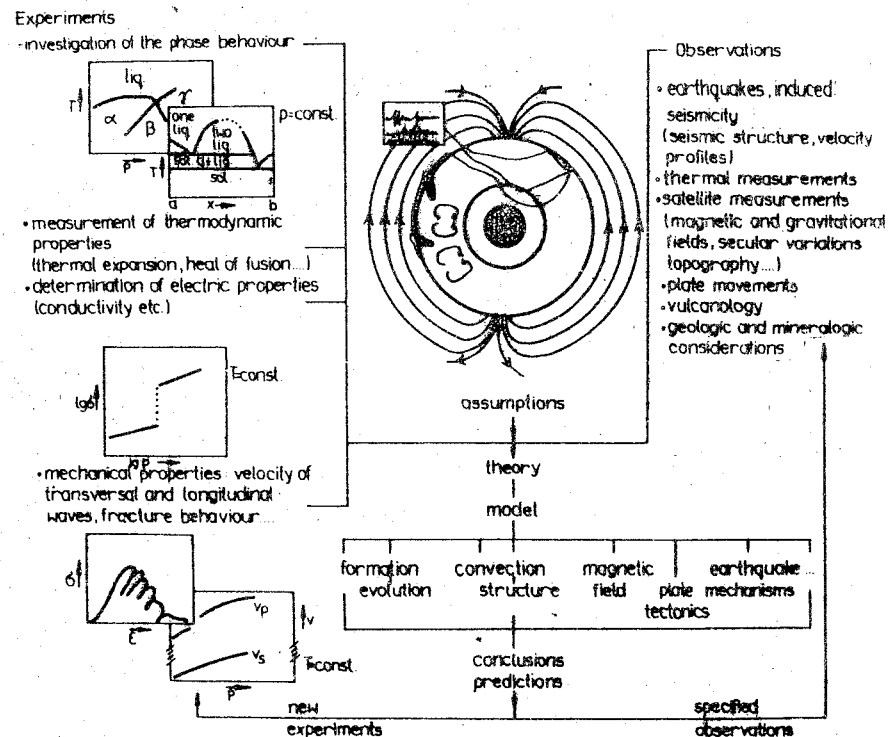


Fig. 1.
Connections between high - pressure physics and geosciences.

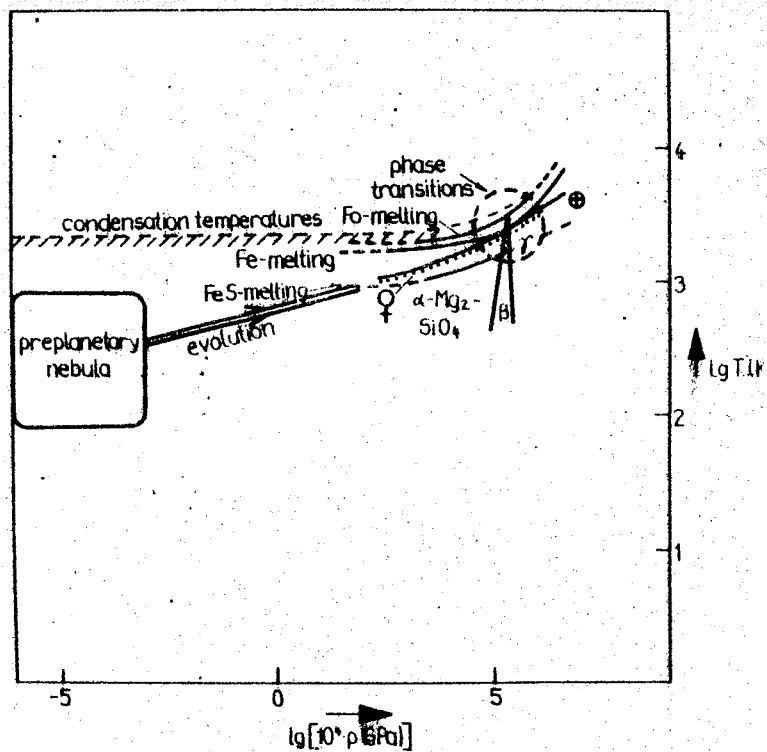


Fig. 2.
Evolution of the terrestrial planets in the pressure -
temperature plane
($\oplus$, $\ominus$: adiabats of Earth and Venus, respectively).

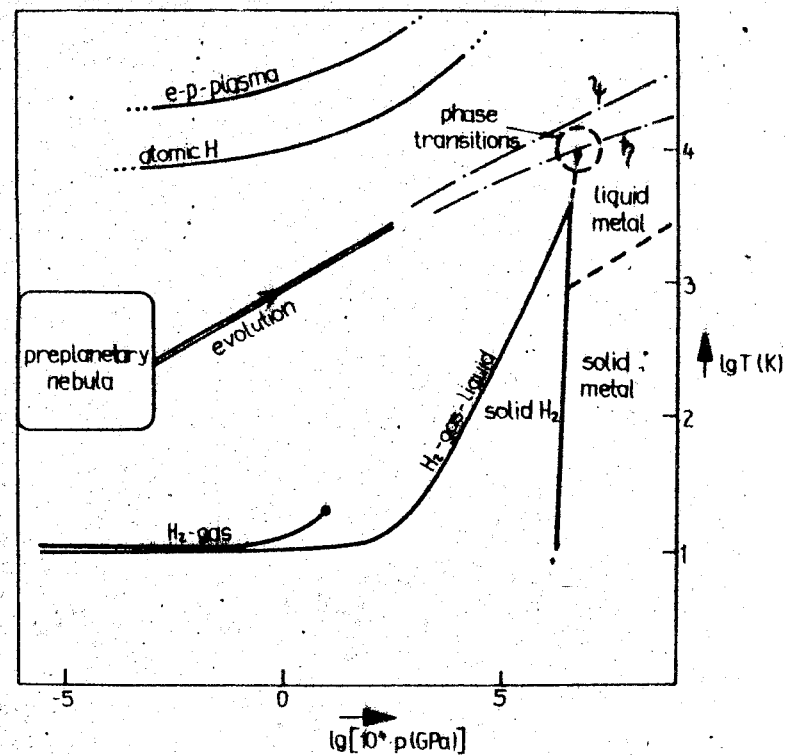


Fig. 3.
Evolution of the giant planets in the pressure - tempera-
ture plane
(♃, ♄: adiabats of Jupiter and Saturn, respectively),

the potential energy between beginning and end of this process is converted into thermal energy that heats up the planet. The present structure evolves as result of intense convective cooling of the mantle that proceeds up to now. When the temperature in the core reaches a certain value so that the adiabat intersects the core melting curve, inner - core formation starts. Mantle cooling removes energy so that decreasing temperatures in the core lead to further growth of the solid inner core until it reaches its present size. This process continues into the future.

So the present structure is a product of long - lasting and large scale processes. The task of geosciences in connection with high - pressure physics is to search for a relevant description of the present structure and the evolutionary way that lead to it. The models worked out up to now reflect only some features of the complex nature, but better laboratory experiments designed to study material behaviour under extreme pressure and temperature conditions and new observations of the planets may lead to important improvements.

PHYSICO-CHEMICAL PROPERTIES OF FLUID-MAGMATIC SYSTEMS AT HIGH TEMPERATURE AND HYDROGEN PRESSURES

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A high gas pressure apparatus equipped with a special H₂-reactor /1/ was used to study the H₂ diffusion mobility and solubility in magmatic and model melts, their viscosity, as well as the effect of H₂ pressure on the albite (NaAlSi₃O₈) melting. Temperature was measured with accuracy of ± 5 °C and the relative uncertainty in measuring pressure was ± 1 %.

The method of falling sphere filled with radioisotope Co⁶⁰ /2/ was used to study the viscosity of the albite and andesite melts. The viscosity was measured within the relative uncertainty of ≤ 10 %. Experiments were run at P up to 2 kbars and T=1200 - 1400 °C. It was found that the viscosity of the albite melt virtually did not change under H₂ pressure whereas the viscosity of andesite melt at H₂=2 kbars and T=1200 °C decreased by 45 % as compared with that at argon pressure. The decrease is caused by the dissolution of H₂O formed in the reaction of H₂ with variable-valence elements of the melt (ferric, ferrous, etc.) /1/.

A modified method of redox colour indication was used to study H₂ diffusion mobility in melts and glasses (albite, eutectic diopside-anortite-Di₅₇An₄₃, picrite) /1/. The relative uncertainty in hydrogen diffusion measurements was less than 25 % within the P-T range up to 5 kbars and at 750-1300 °C. Some of the results obtained are summarized in Fig.1. These data in particular show that under isoviscous conditions, H₂ diffusion mobility in magmatic melts is by two orders of magnitude higher than that of H₂O, K₂O, Na₂O and by seven orders of magnitude higher than that of the diffusion mobility of silica and alumina. It has been also found that hydrogen diffusion is unsteady in low-viscous (about 70-100 P) magmatic melts containing variable-valency elements. In this case hydrogen diffusion into the melt, gives rise to the thermo-capillary convection (Marangoni's convection /3/) controlled by surface tension gradient at the hydrogen - melt interface (Fig.2*). This gradient presumably develops in the melt as a result of the reaction between H₂ and variable-valency elements which is accompanied by local heat release at the diffusion front and the appearance of the concentration gradient. In this case,

* The Figure is given at the end of the book

the rate of the convectional mass transfer in the melt ($\sim 10^{-3}$ cm/s) is by more than two orders of magnitude higher than the rate of H_2 steady-state diffusion ($\sim 5 \cdot 10^{-6}$ cm/s). H_2 solubility in the melts of various compositions (Ab, $Di_{57}An_{43}$ - eutectic, gabbro-norite, basalt, andesite) was studied at P_{H_2} up to 5 kbars and T up to 1300 °C. Isobaric quenching technique was used which involved hydrogen diffusional dissolution through the melt-hydrogen boundary. To determine the hydrogen equilibrium concentration in the melts, isobarically quenched glasses were subjected to thermal degassing in He atmosphere. The released H_2 was analysed on a CHN-1 gas analyser. The isothermal hydrogen (1300 °C) solubility in the albite melt is shown in Fig.3. It is seen that H_2 solubility (mass %) is about two orders of magnitude lower than that of H_2O , and about twice as high as the solubility of carbon dioxide; it satisfactorily obeys Henry's law for the dissociated solution, within the accuracy range of 10 rel.%. Hence, to a first approximation hydrogen dissolution in the albite melt is accompanied by H_2 dissociation. However, establishing the exact pattern of H_2 dissociation during its dissolution and diffusion in magmatic melts under high pressures is a subject of further investigation.

The effect of high H_2 pressures on the melting temperatures of rock-forming minerals was studied by the quenching method with temperature, increasing from low values to the melting point. The procedures and methods have been discussed elsewhere. In the P-T diagram, the system albite - hydrogen is compared with the systems albite - water and albite - carbon dioxide. It follows from these data that, according to the solubility, the effect of increasing hydrogen pressure on the decrease in the albite melting temperature is lower than that of water pressure, but greater than the effect of carbon dioxide pressure.

The albite melting temperature is 80 ± 10 °C lower at the hydrogen pressure of 5 kbars than under the argon or lithostatic pressures. The analysis has shown that the hydrogen pressure relationships of hydrogen solubility in the albite melt and the albite melting temperature are thermodynamically consistent.

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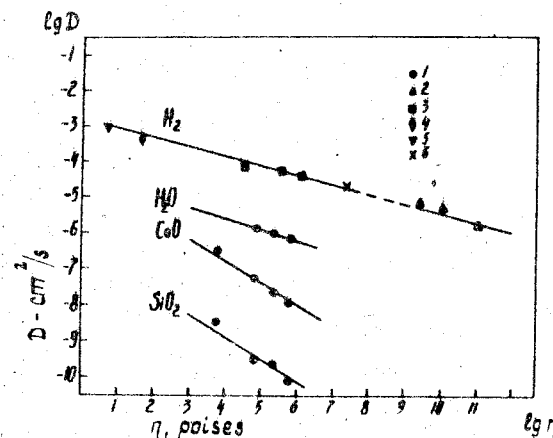


Fig.1. The relation between the diffusion mobility of some components and viscosity of a water - albite melt (glass): 1-water - albite melt, $P_{H_2O}=P_g$ /1/; 2-albite glass+0.05 wt% of CO_2 , $P_{H_2}=180$ MPa; 3-lead-containing albite melt (from below upwards 5, 10, 20 wt% of PbO respectively), $P_{H_2}=P_g=20$ MPa, $T=1200$ °C; 4-eutectic melt ($Di_{57}An_{43}$ + 10 wt% of PbO), $P_{H_2}=20$ MPa, $T=1300$ °C; 5-meimechite melt, $P_{H_2}=20$ MPa, $T=1300$ °C; 6-albite melt at a liquidus temperature of 1100 °C (4-6 - calculated values).

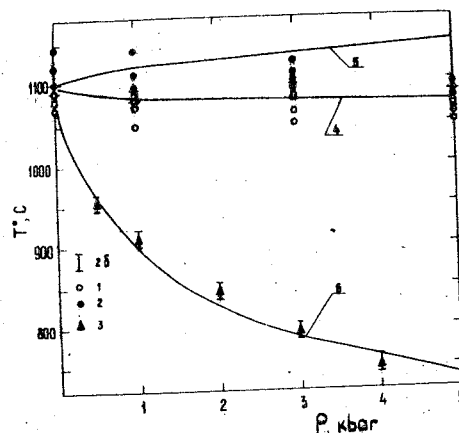


Fig. 3. Isothermal (1300 °C) H_2O solubility in an albite melt: 1, 2-experimental data, molecular weights of the albite melt are 64,55 and 262,2 g/mol respectively; 3-uncertainty range of ± 5 rel%.

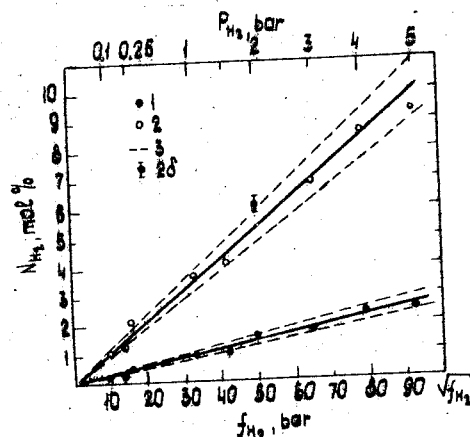


Fig. 4. Pressure effect on the albite melting: 1-albite; 2-albite + melt; 3-liquidus point under H_2O pressure according to the data /4/; 4-the melting under H_2 pressure; 5-the melting at lithostatic pressure and under CO_2 pressure /5/; 6-the melting under H_2O pressure based on the data /6/.

INVESTIGATION OF THE ELEMENT BEHAVIOUR IN PROCESSES OF INTERACTION OF VAPOUR AND MAGMATIC MELTS UNDER HIGH PARAMETERS

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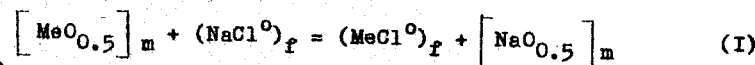
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Information on the regularities of element distribution between magmatic melts and fluids (supercritical water-salt solutions) under high T-P parameters is of great importance for our conceptions key-problems in geochemistry, and first of all in ore- and petrogenesis.

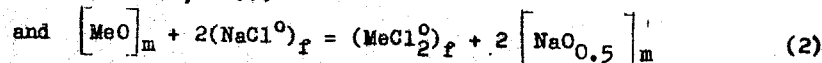
To-day physical chemistry has no sufficient base both experimental and theoretical for solution such kind problems. Experimental investigations are connected with essential difficulties. The peculiarities of fluid-melt equilibria include practically full association of electrolytes under parameters of experiments: $T > 1000K$, $P > 100 MPa$ and the probability of fluid desintegrating in two phases: vapour and liquid.

Distributing of petrogenic elements .

As it was shown /1-3/ an exchange of petrogenic elements occurs and corresponding reactions may be expressed by following equations (fluid = NaCl-solution)



where $Me = K^+, H^+ \dots$



where $Me = Ca^{2+}, Mg^{2+}, Fe^{2+} \dots$

Indexes f and m relate to the fluid and the melt phases correspondingly.

Exchange reaction constants data are following by various authors: $k_{K-Na} = 0.61-0.74$, $k_{Ca-Na} = 0.25-0.38$, $k_{Mg-Na} = 0.1-0.16$ /1-3/.

The same sequence of data is observed for petrogenic cation exchange also in "dry" system salt-magmatic melt /4/. It is rea-

reasonable to emphasize that k_{K-Na} data are practically of the same value both for albite and granite melts /3/.

Distributing of Cl-ion

Cl-ion is an universal and predominant component of magmatic fluids and determines the behaviour of other elements (ore elements). Therefore the discovery of the regularities of Cl-ion distributing is one of important problems in geochemistry.

On data /1,3/ Cl⁻-distributing curve may be considered as representative of two parallel effects, each of them predominant in different intervals of Cl⁻ concentrations. By low concentrations (up to 0.5-1 mol/kg Cl⁻ proportionally distributes between phases and the slope of radial line represents the influence of the melt nature on Cl solubility. In coincidence with this indication petrogenic oxides may be divided roughly in two groups: with positive (Na₂O, K₂O, CaO, FeO) and negative (Al₂O₃, SiO₂, MgO) influence on Cl solubility. Essentially that the correspondence Cl⁻ behaviour in water-salt and dry salt is observed. It means the same character of influence of melt composition on Cl⁻ solubility takes place /4,5/.

For high concentrated Cl⁻ solutions the distributing curves represent thermodynamic properties of fluids, in the first place nonideality up to the desintegrating of fluids with formation of vapour and liquid phases. This regularity may be more complicated by process of cation exchange. Thus low position of Cl-distributing curve on Fig.1 in the system Ab-KCl-H₂O in comparing with Ab-NaCl-H₂O is a consequence of K-Na exchange process in the first system, and as the result this system approaches to the composition Or-KCl-H₂O /1/, and fluid in its turn, KCl-H₂O, is far from ideality more then NaCl-H₂O under same conditions.

Distributing of ore elements

For ore elements are important problems of distributing elements in fluid-melt equilibria and forms of species of elements in fluid phase. The treatment of experimental data includes the analysis of the distributing coefficient, K_{Me}^P , formulated as ratio of element concentrations in both phases, as a function of Cl⁻ concentrations. This approach is based on the idea that chlorides are predominant forms of the most number of elements in fluids. For Pb, Cu, Mo follows that Pb²⁺ is transported in fluid

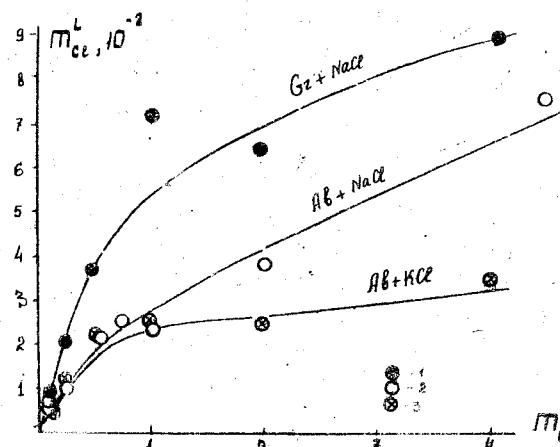


Fig.1. Ion Cl⁻ distributing between fluid and melt, 1173K, 300 MPa: 1-granite-solut. NaCl; 2-albite-solut. NaCl; 3-albite-solut. KCl.

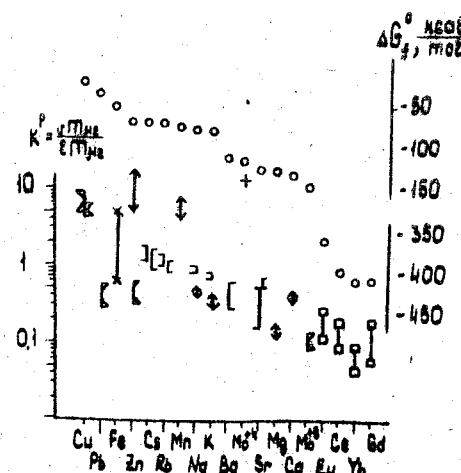


Fig.2. K^P as a function of standard free energy data of oxides formation.

phase as $PbCl_2^0$, Cu^+ - as $CuOH$ by low and as $CuCl$ - by high concentrated Cl^- solutions, Mo^{6+} - in form of hydroxide complexes.

There is much data on ore element distribution in literature, but they are hardly comparable because of differences in parametrical and methodical conditions, melt compositions etc. Some generalizations of experimental data may be done on the basis of correlations /6/. On Fig.2 available data K^D for melt elements are represented as a function of free energy data of forming their oxides under standard conditions. It is seen that a correlation takes place. This correlation permits to estimate even with some caution distributing coefficient values for not yet investigated elements by fluid composition $NaCl+H_2O$. The information of such a kind may be sometimes fruitful.

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ORE FLUID FORMATION: DISTRIBUTION OF ORE SPECIES BETWEEN FLUID AND MAGMATIC MELT AT HIGH PRESSURES AND TEMPERATURES

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One of the possible mechanisms by which the ore fluid can form involves extraction of ore material from a magmatic melt by the fluid developing during magma crystallization or decompression as well as by the ascending deep-seated fluid. This mechanism has been tested in an experimental study where two groups of ore species with different geochemical properties (rare metals Mo, W and base metals Pb, Zn) were partitioning between the melt of natural akchataussky granite and fluids of varying composition and acidity-basicity (750-900 °C, P=1-50 kb).

Experiments were run on high-pressure apparatus described in detail elsewhere /1/. It will be noted that the analytical methods thus far used in fluid composition determinations do not allow the simultaneous analysis of all ore, petrogenetic and volatile species in the fluid. Complete analysis of the quench fluid first became possible with the method developed by the present authors /2/. Experimental results were given in /3,4/. Runs were performed at 750 °C, 1 kb pressure. The experimental scheme is largely based on the extraction of ore species from the melt by a fluid. In this technique, the resulting coefficients of component partitioning between fluid and melt ($K_{partit.} = C_{fl}^i / C_{melt}^i$) are lower than their true values because the system does not achieve complete equilibrium. For Pb and Zn (run durations of 7 days) which have a relatively high diffusion coefficients in the granitic melt, comparison with the results of Urabe and Holland /5,6/ who introduced Pb, and Zn into the system via fluid has shown that the true and experimental $K_{partit.}$ are the same order of magnitude. In contrast, the diffusion coefficients of Mo and W are about 2 orders of magnitude lower than those of Pb and Zn (run durations 1 day) with the result that the experimental $K_{partit.}$ were too low. Assuming they are underestimated by the same order of magnitude in all solutions, consider the dependence of $K_{partit.}$ for MoO_3 , WO_3 , PbO and ZnO on the composition, concentration and pH of the starting solutions. The extraction of Mo, W, Pb and Zn

by the fluid phase was found lowest in a purely water fluid and HF acidic solution. The extraction increases considerably in fluids containing acids (HCl), alkalies (NaOH) or salts (NaCl, KCl). Note that the extraction of Mo and W in the 0.5 M solutions increases in the order NaCl, HCl, NaOH to reach a maximum in the alkaline NaOH solution ($K_{\text{partit.}} = n \cdot 10^{-1}$). On the other hand, increasing acidity and chloride concentration in the starting solution favours the maximum redistribution of Pb and Zn into the fluid (in 0.5 - 1 M NaCl or HCl solutions $K_{\text{partit.}} = n$). Increasing the NaCl concentration in the starting solution has been found to improve considerably the extractive power of the fluid. At 15-30% NaCl, the extraction becomes maximal. The data for Pb and Zn show that a concentrated salt fluid with 75 mass% NaCl is capable of extracting 4-7 times the amount of based metals extracted by a 3% NaCl solution ($K_{\text{partit.}} = 10-15$ or higher). An increase in the temperature from 750 to 900 °C does not have a marked effect on the W and Mo partition coefficients whereas a pressure increase from 1 to 5 kb makes the extraction raise sharply (about 2 orders of magnitude for W in a purely water fluid). The analysis of petrogenic species showed that the presence of Cl in the fluid leads to a marked debasification of the granitic melt.

In consideration of the underestimated $K_{\text{partit.}}$ for Mo and W, the distribution of these species in the solution was studied experimentally by introducing them into the system via the fluid (1M NaCl + MoO₃ WO₃). Again, the system did not attain equilibrium but the resulting $K_{\text{partit.}}$ were too high, 2.5-5 times the true values. It appears that the true $K_{\text{partit.}}$ should lie somewhere between the values obtained with Mo and W introduced into the system through the melt and through the fluid. A set of special experiments at 750 °C, 1 kb showed that the true $K_{\text{partit.}}$ are within 0.8-1.5 in a 1M NaCl solution. In a complex model fluid, 1M NaCl + 0.1M HCl, at the same temperature and pressure the order of magnitude of the true $K_{\text{partit.}}$ for Pb and Zn is about 10.

It has been inferred from the experimental results that solutions separating from the magma are capable of extracting ore material, even from intrusions with clarse concentrations, in amounts sufficient for commercial deposits to develop. The concentrations of ore species, in-particular Pb and Zn, in the experimental acidic chloride solutions have been found to correlate with the ore species contents in natural thermal springs and gas-liquid inclusions at the hydrothermal stage of ore deposition.

The dynamics of the thermal field and fluid separation evolution has been calculated using the experimental $K_{\text{partit.}}$ values for W to evaluate the extent of ore species extraction, transfer and mode of deposition. It is believed that the process can give rise to large deposits but for commercial ore bodies to form it is necessary that a set of faults, fractures and fluid-conducting structures appear in an environment most favourable for deposition.

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SOME PROBLEMS OF P-T STUDIES OF PHYSICAL PROPERTIES OF ROCKS

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The cognition of physico-chemical conditions of mineral matter formation and evolution and prediction of changes of its state and composition at great depths is closely related with multilateral petrophysical studies under respective laboratory PT-situations of the experiments / 1-3 etc. /.

Some intensification of the experimental studies of physical properties of rocks under simultaneous high PT effect is observed. These studies are mostly made in isobaric or isothermic regimes. However, the fact that the lithospheric mass changes P and T simultaneously with depth according to the general laws with some regional (sometimes appreciable) deviations prompted the authors to elaborate a method of programmed modelling used in studying mineral matter physical properties with taking deep P-T regimes of concrete geological bodies into account. This enables us to approach the experimental P-T conditions to the real ones of the interior. E.g. the generalized laboratory experimental data obtained by the above method conclude possibility of significant differences of elastic characteristics of compositionally similar rocks in different deep PT situations. In other words, the effect of the PT conditions on the changes of the elastic

properties of rocks is not less than that of the general composition and numerical proportion of their minerals. Zones of elastic wave velocity decrease and increase whose nature is defined by thermodynamic conditions of respective depth have been revealed and thermobaric zonality of the distribution of the mineral matter elastic characteristics of the upper lithosphere for large and compositionally uniform crustal blocks has been established.

A great role is assigned to systematic development of new instruments and methods to realize programmed petrophysical PT studies including improvement of necessary PT equipments and digital devices, automatization of the experiments and data processing, increase of measurement accuracy, optimization of experiment duration and sample size etc. on the basis of great experience acquired and respective methods.

At present, the laboratory data on changes of physical properties of rocks in high PT regimes is still often insufficient for wide generalization and presentation in form of analytical relations or detailed schemes. Its amount is restricted due to difficulties in preparation and performance of the experiments. This gap can only be filled by modernization of the technology of specialized PT-experiments. One should always increase their purity, provide high representativity of the mineral bodies used and unify the existing methods and instruments.

Thus, the progress of the laboratory petrophysical studies made in different model PT regimes of the Earth's crust and upper mantle is first of all due to expanding the experimental high P-T range in new or previous improved apparatus, enabling imitation of their simultaneous effect at different depths. Important is elaboration of modern universal automatic systems recording even

very little changes in experimental PT parameters and physical properties considered. Increasing sample size permit to exclude some possible sample ununiformities in the experiments immediately. This method has its merits and defects. Particular requirements are set as to modernization of the special PT chambers for thermobaric studies of elastic, density, electric, magnetic, thermal, deformation-stability and other physical and mechanical characteristics of mineral bodies in thermodynamic situations of their polymorphic and phase transitions including hard-phase transitions and melting.

In general, in the high P-T petrophysics as one of the fundamental Earth's physics trend the main activities to be intensified are

- the theoretical and experimental studies of the nature and laws of general and regional deep blockwise changes and relations of physico-mechanical and other physical properties of the mineral matter of the lithosphere and deeper Earth's parts considering its geostructure, genesis and subsequent natural and historical transformations;

- modelling composition and state of geologic media at different depths for different regions based on the analysis of modern theoretical data, petrophysical PT-experiments, the whole body of geologic-geophysical and petrologic-geochemical data, time and scale factors, water- and gas saturation, rheologic features and anisotropy of mineral associations etc.;

- finding and thorough studies of the causes of various changes of physical characteristics under extreme PT-conditions with taking their transformations at macro- and microlevel rigorously into account;

- search for essentially new methods (including non-linear ones) in combining PT-petrophysical and other studies;

- intensive improvement of present and construction of new special equipments, instruments and methods, wide automatization of experiments by use of control processors;

- elaboration of universal methods of the application of laboratory thermobaric petrophysical experimental data in interpretation of observations of different geophysical fields, processes and phenomena, solving geophysical exploration and mining problems, projecting and realization of ultradeep borehole drillings and mines etc.;

- synthesis of modern geoscience information, experimental PT-data, respective theoretical calculations and construction of combined petrophysical sections (models) of the interior.

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MEASUREMENT OF ULTRASONIC WAVE VELOCITIES IN FUSED
QUARTZ UNDER HYDROSTATIC PRESSURES UP TO 6.0 GPa

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Abstract

A new method for the measurement of ultrasonic wave velocities in small samples with a diameter of 3.0 mm and lengths of 1.5 - 2.0 mm under hydrostatic pressure has been developed, using a split-sphere type high-pressure apparatus. A pulse-echo-overlap method was adopted for the measurement of the wave velocities.

The longitudinal and shear wave velocities in fused quartz have been measured under pressures up to 6.0 GPa at room temperature.

The longitudinal and shear wave velocities decrease with increasing pressure and have a minimum velocity at pressures of 2.3 GPa and 2.6 GPa, respectively. At pressures higher than those of the minimum velocities, the longitudinal wave velocity increases, and the shear wave velocity also increases, but only very slightly.

From the velocity measurements the elastic moduli, the compressibility and the Debye temperature were calculated as a function of pressure.

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Introduction

In the last twenty years, a large number of measurements on the ultrasonic wave velocities of solids have been carried out under high pressure for the interest of geophysics and physics. However, the maximum pressure in most of the measurements has been limited to less than 3 GPa.

For the geophysical interest, in particular it is necessary to develop a new method for measuring ultrasonic wave velocities accurately under higher pressure and at high temperature in order to investigate the elastic properties of earth materials.

Recently we have tried to develop a new method for the accurate measurement of ultrasonic wave velocities in small samples under hydrostatic pressure higher than 10 GPa, using a split-sphere type apparatus. This time we have succeeded in measuring the longitudinal and shear wave velocities in fused quartz up to 6.0 GPa.

It is well known that fused quartz has anomalous properties under pressure. Bridgman [1] first found that the compressibility of quartz glass increases with increasing pressure but that there is a reversal of the curve of compressibility at about 3.5 GPa.

Some investigations of ultrasonic wave velocities in fused quartz under pressures up to about 2 GPa showed that the longitudinal and shear wave velocities decrease with increasing pressure [2, 3, 4, 5].

Kondo et al. [6] measured the ultrasonic wave velocities

in fused quartz up to 3.0 GPa using a Kennedy-type piston cylinder apparatus. They reported that the elastic moduli of fused quartz decrease nonlinearly to a minimum value at 2.1 - 2.5 GPa and thereafter increase with increasing pressure.

Kozuki et al. [7] also measured the longitudinal wave velocity in fused quartz up to about 5 GPa using MA 8 high-pressure apparatus.

Schroeder et al. [8] studied the Brillouin scattering in amorphous-SiO₂ under hydrostatic pressures in a diamond anvil cell to 13.3 GPa. They reported that the elastic wave velocities, elastic constants and compressibility of amorphous-SiO₂ show anomalous behavior as a function of pressure and that the compressibility increases with increasing pressure then decreases beyond a critical pressure of around 2.5 GPa.

The purpose of this paper is to report the experimental method for the measurement of ultrasonic wave velocities in small samples in the form of cylinders with a diameter of 3.0 mm and a length of 1.5 - 2.0 mm using a split-sphere type apparatus, and to report the results of the measurement of the longitudinal and shear wave velocities in fused quartz under pressures up to 6.0 GPa at room temperature.

Experimental procedures

The fused quartz used in the present study was obtained from Toshiba Ceramics Co. Ltd. The density was $\rho_0 = 2.200$ g/cm³. The samples were prepared in the form of cylinders

having a diameter of 3.0 mm and lengths of 1.5 - 2.0 mm. The parallel ends were polished and planed.

The ultrasonic buffer rod, which was made from cylindrical brass having a diameter of 3.5 mm and lengths of 2.0 - 2.5 mm, was used. It was also polished and planed.

The transducers of lithium niobate (LiNbO₃) were used for the measurement of longitudinal and shear wave velocities. They were cut in the form of disks with a diameter of 3.0 mm and thicknesses of 0.15 - 0.25 mm. The one end was plated with gold by vacuum evaporation to act as an electrode. The other end was bonded to one of the buffer faces with Cyanoacrylate resin.

Once assembled, the sample, the buffer rod and the transducer were set into a cylindrical Teflon capsule with the liquid pressure medium and closed up tight as shown in Fig. 1. In the present experiment, silicon grease was employed as the liquid pressure medium. As silicon grease has the phase change at about 1 GPa, some attentions should be paid to the determination of pressure. The detailed discussion is given elsewhere [9].

Ultrasonic wave velocities were measured by the pulse-echo-overlap method. The errors in the measurement of ultrasonic wave velocities were estimated to be less than 0.1 %.

In order to determine the pressure dependences of the ultrasonic wave velocities, the dimensional changes of the sample under pressure were calculated by using the method described by Fritz [10].

A split-sphere type apparatus [11] was used in the present high-pressure experiment. The sample assembly of an octahedron made from pyrophyllite with a 19 mm edge-length is shown in Fig. 2.

The pressure was calibrated up to 6.0 GPa against the load pressure by using the calibration curve obtained from the registrance change of Ca (0.70 GPa), Bi (2.55 GPa), Tl (3.67 GPa) and Yb (4.00 GPa). The errors of the pressure measurement were estimated to be less than 2 %.

Results and discussions

The pressure dependence of the longitudinal and shear wave velocities in fused quartz at room temperature is shown in Fig. 3. The longitudinal and shear wave velocities under atmospheric pressure have been found to be 5967 ± 5 m/s and 3758 ± 3 m/s, respectively.

The longitudinal and shear wave velocities, first, decrease with increasing pressure and reach a minimum velocity at 2.3 GPa and 2.6 GPa, respectively. Beyond these pressures, the longitudinal wave velocity increases with increasing pressure in accordance with the normal solid behavior, while the shear wave velocity only increases very slightly with increasing pressure-up to 6.0 GPa.

Kondo et al. [6] reported that the longitudinal and shear velocities decrease nonlinearly with increasing pressure up to 2.4 - 2.6 GPa, after which they increase with increasing pressure up to 3.0 GPa, and that there exist minimum values

for both velocities. Kozuki et al. [7] also reported that the longitudinal wave velocity reaches a minimum at 3 GPa. The present results agree well with the result of Kondo et al. The attenuation of the ultrasonic waves was observed at pressures between 1.5 GPa and 3.0 GPa in the present study.

The variations of the elastic moduli (Bulk modulus : K , Young's modulus : E , and Shear modulus : G ,) with pressure, which were calculated from the present ultrasonic data, are shown in Fig. 4. These reach a minimum at 2.0 - 2.5 GPa. These results agree with the results of Kondo et al. [6].

In Table I, the elastic moduli and their first pressure derivatives are listed with those of the other investigators [2, 3, 4, 6, 12].

The variation of the compressibility in fused quartz with pressure is shown in Fig. 5. It is seen that the compressibility increases with increasing pressure and has the maximum at 2.0 GPa then decreases with increasing pressure in accordance with the normal solid behavior. In Fig. 6, this result is compared with the result obtained from Brillouin scattering measurement by Schroeder et al. [8]. The two curves shows a similar tendency with pressure up to 6 GPa. However, our value is smaller than that of Schroeder et al. This seems to be due to the differences of the high-pressure apparatus and the experimental methods.

The variation of the Debye temperature in fused quartz with pressure is shown in Fig. 7. It, first, decreases with increas-

Table I. Elastic moduli and their first pressure derivatives for fused quartz

Authors	Temperature (°C)	G (GPa)	K (GPa)	dG/dP	dK/dP	Reference
Bridgman	30	----	37.1	----	-6.4	/12/
McSkimin	25	31.2	36.8	-3.20	-5.9	/2/
Bogardus	25	31.3	36.7	-3.15	-6.3	/3/
Peselnick et al.	25.5	31.2	36.5	-3.25	-6.15	/4/
Kondo et al.	20	31.0	36.9	-3.37	-5.31	/6/
Present work	24	31.1	36.9	-3.34	-5.12	

ing pressure and has the minimum at 2.4 GPa, after which it increases with increasing pressure. From this result, the Debye temperature of fused quartz at atmospheric pressure is determined to be 493°K. This value agrees with the values of 495°K after Anderson [13] and 491°K after Kieffer [14].

The physical explanations of the anomalous properties of fused quartz have been given in other papers [6, 8, 15].

Fritz [10] reported the quite similar behavior to that of fused quartz for a commercial glass-ceramic (Corning Pyroceram 9608) at pressures up to 2.6 GPa. His result suggests that there may be other materials which have such anomalous behavior as fused quartz. If such anomalous behavior as fused quartz is found under pressure in the materials of geophysical interest, some interesting comments will be made about the elastic properties of the earth's interior.

Conclusion

The longitudinal and shear wave velocities in very small samples of fused quartz have been measured with accuracy under pressures up to 6.0 GPa. Using these ultrasonic data, the elastic moduli, the compressibility and the Debye temperature of fused quartz have been calculated as a function of pressure.

Acknowledgements

The authors would like to thank Dr. Y. Akahama and Mr. Y. Kozuki for their helpful discussions.

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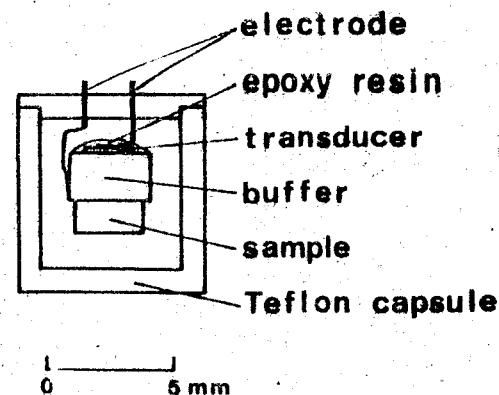


Fig. 1. Cross section of the liquid cell for ultrasonic velocity measurements.

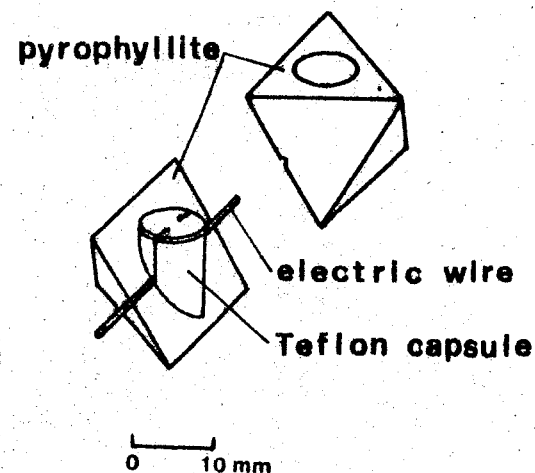


Fig. 2. Sample assembly.

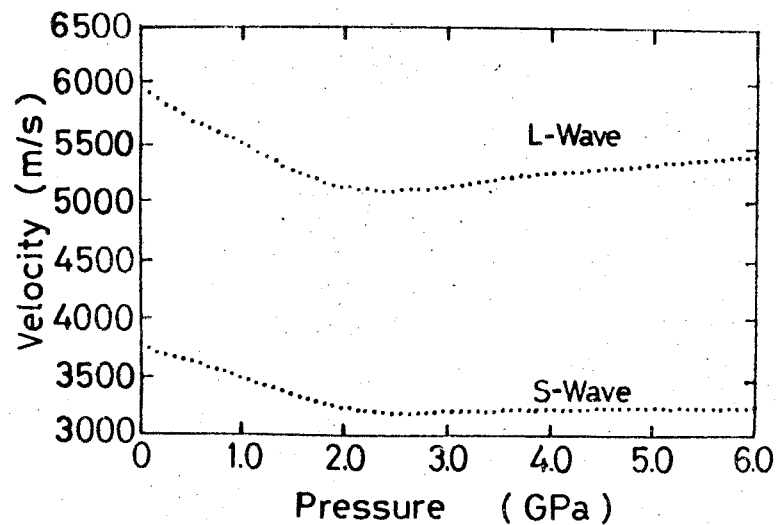


Fig. 3. Variations of the longitudinal and shear wave velocities in fused quartz with pressure.

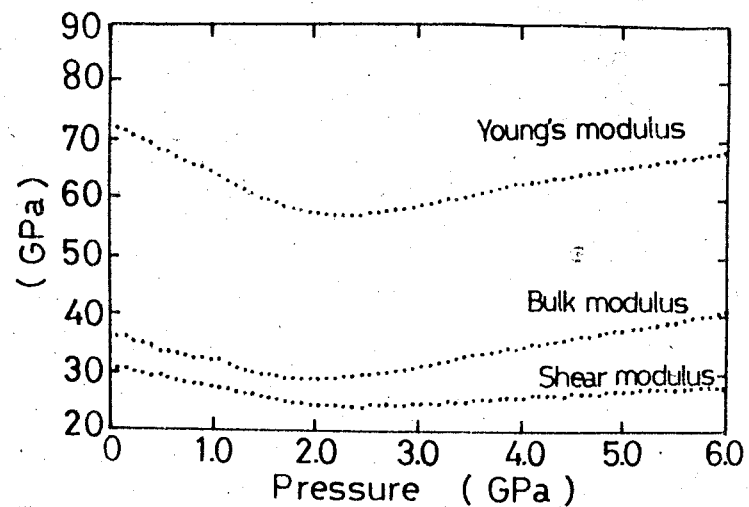


Fig. 4. Variations of the elastic moduli (Bulk modulus : K , Young's modulus : E , and Shear modulus : G) in fused quartz with pressure.

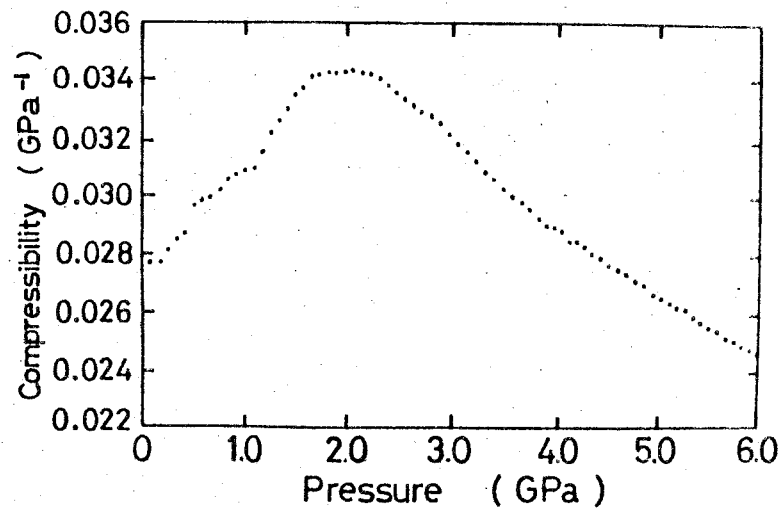


Fig. 5. Variation of the compressibility in fused quartz with pressure.

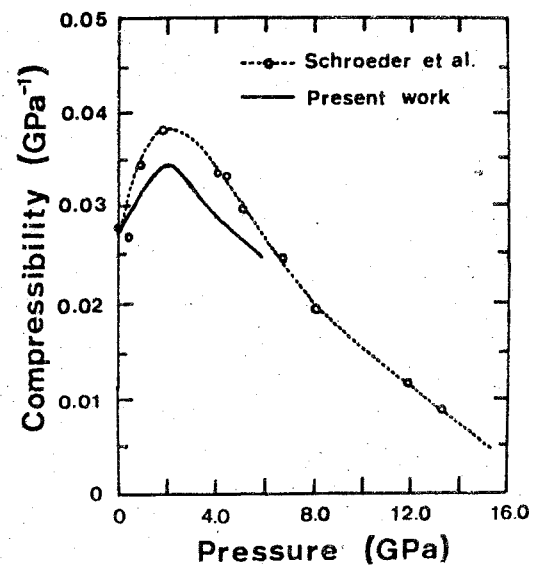


Fig. 6. Comparison of the present value of the compressibility with that of Brillouin scattering measurement by Schroeder et al. [8].

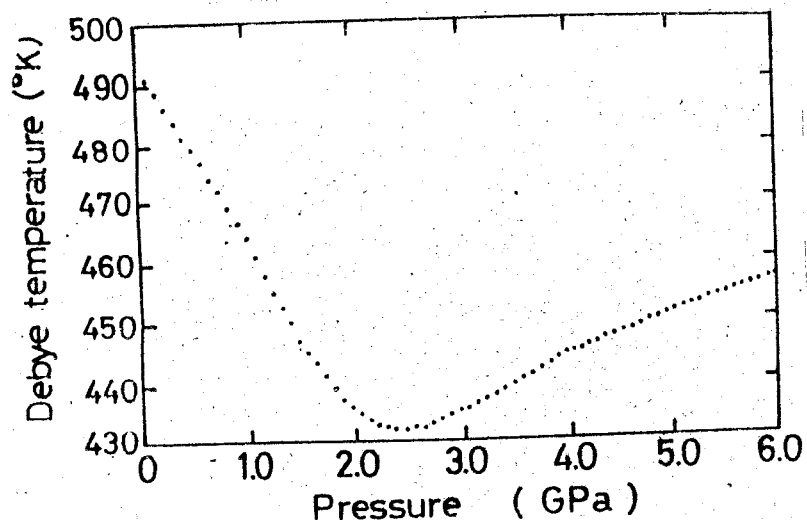


Fig. 7. Variation of the Debye temperatures in fused quartz with pressure.

ELECTRICAL CONDUCTIVITY OF GRANITOIDES FROM CZECHOSLOVAKIA UNDER HIGH TEMPERATURES

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Electrical properties are extremely useful in the study of the interior of the Earth, from near-surface surveys to find oil and minerals, through the deeper crustal sounding techniques used to study large geothermal systems and roots of volcanoes or earthquake zones.

Invariably, recourse must be made to laboratory-based petrophysical models in order to interpret the field electrical parameters in terms of more geological interest such as a temperature profile, ore deposit size, or depth of basement. Unfortunately, although electrical properties are extremely useful in being highly sensitive to subtle changes within the Earth, they are also complicated to interpret due to the great number of parameters which can influence equal changes.

In this paper we are studying the temperature dependence of the electrical conductivity of granitoides from the territory of the West Carpathians with comparison of the electrical conductivity of other granitoides. The dependence of the electrical conductivity of granitoides from the West Carpathians on pressure up to 2 GPa is discussed in the paper Lebedev et al. (see abstracts of this conference).

Generally granites and granitoides are rocks containing > 10% of quartz. They create 95% of intrusive rocks of the Earth's crust. Quartz, K-feldspar (orthoclase, sanidine, microcline) and plagioclase are three main rock forming minerals which are completed by micas (biotite, muscovite) and amphibole.

Cylindrical samples of 20 mm in diameter and 25 mm in height were prepared and the electrical conductivity of rocks was measured within the temperature range of 200 - 1000 °C by two electrode method. All measurements were performed in the argon atmosphere (8 l/hour) under partial pressure of oxygen of 10^{-1} Pa. The temperature during the experiment was measured by means of NiCr-Ni thermocouple and the Thermoprogramik LP 839 guaranteed

the linearity of the heating rate of $10^{\circ}/\text{min}$. The contact of the sample was treated with a solution of "glossy Pt and carbon". More details on the laboratory technique and rock-sample preparation can be found in /1/. The method and data were checked by repeated measurements and by comparing with results obtained by other methods /2-4/.

Fig. 1 shows the comparison of the average electrical conductivity (N = number of samples) as a function of temperature of granitoides from the West Carpathians (full line) with the average electrical conductivity of granites and granitoides obtained from /5/, granites, diorites and slates from /6/ and with less numerous measurements by various authors /7-9/ on the same types of rocks. This set of data obtained by various authors and in various laboratories cannot be homogeneous regarding the experimental conditions. However, individual curves of the average electrical conductivities fairly well agree. Fig. 1 shows that electrical conductivity of granitoides from the West Carpathians is comparable to conductivities of granitoides from various geographical areas. The less conductive are the old precambrian granites from Indian Subcontinent. Their low conductivity is influenced by the factor of the geological age, which was discussed in /9/. The electrical conductivity of granites studied in /7/ is dominantly controlled by temperature and free water content. The influence of free water on the electrical conductivity decreases with increasing temperature. Hydrostatic and lithostatic pressures, structurally bound water and partial pressure of oxygen have little effect on the behaviour of electrical conductivity according to /7/.

The average conductivity curve of granitoides from the West Carpathians (full line in Fig. 1) exhibits four temperature intervals of different behaviour of electrical conductivity. Up to $\sim 300^{\circ}\text{C}$ the dehydration of free water affects the conductivity by opening the pore structure. It results in a decrease of electrical conductivity. On the other hand, the rapid increase of conductivity with the increase of temperature is observed in the interval of $300-600^{\circ}\text{C}$. In the vicinity of 600°C the α - β transition of quartz took place and also a significant dehydration of crystalline water (OH^- group) from the original lattice of tourmaline was proved /10/. However, the volume of tourmaline in granitoides is small, it is necessary to point out, that also other physical-chemical processes and their combination are ope-

rating. Therefore, the determination of the cause of the change in the behaviour of the electrical conductivity at $T=600^{\circ}\text{C}$ is not clear up to now. However, a comparison of behaviour of electrical conductivity during heating and cooling cycles suggests that this change is irreversible. On the contrary, the electrical conductivity in the interval $600-800^{\circ}\text{C}$ increases with the temperature relatively slowly. Above $T = 800^{\circ}\text{C}$, a visible acceleration of the electrical conductivity increase is observed with increasing temperature, which may be connected to the β - $\rightarrow$ tridymite phase transition of quartz according to /11/. The comparison of heating and cooling shows this change probably will be reversible.

Fig. 2 demonstrates the dependence of the electrical conductivity of granitoides from the West Carpathians on the content of SiO_2 . Samples containing more SiO_2 are less conductive in the whole interval of temperature. The difference in conductivity for sample No.2022 (74.53% SiO_2) and sample No.2004 (48.64% SiO_2) at $T = 900^{\circ}\text{C}$ is about two orders of magnitude. This negative influence of less conductive SiO_2 on electrical conductivity (for broad scale of rocks from more than 300 localities) was already proved by the statistical principal component method in /12/.

Conclusion : Analysis of electrical conductivity of 23 granitoides from the West Carpathians showed that in the interval of temperatures $200-1000^{\circ}\text{C}$ their conductivity agrees well with conductivity of granitoides from various geophysical areas. Four temperature intervals ($T < 300^{\circ}\text{C}$, $300-600^{\circ}\text{C}$, $600-850^{\circ}\text{C}$, $> 850^{\circ}\text{C}$) of various behaviour of electrical conductivity were determined. Since the electrical conductivity of granitoides is complexly influenced by many factors, it has not been possible to determine unambiguously causes responsible for changes in behaviour of conductivity with increasing temperature. However, the negative influence of SiO_2 content in samples on their conductivity has been unambiguously proved during the whole interval of temperatures.

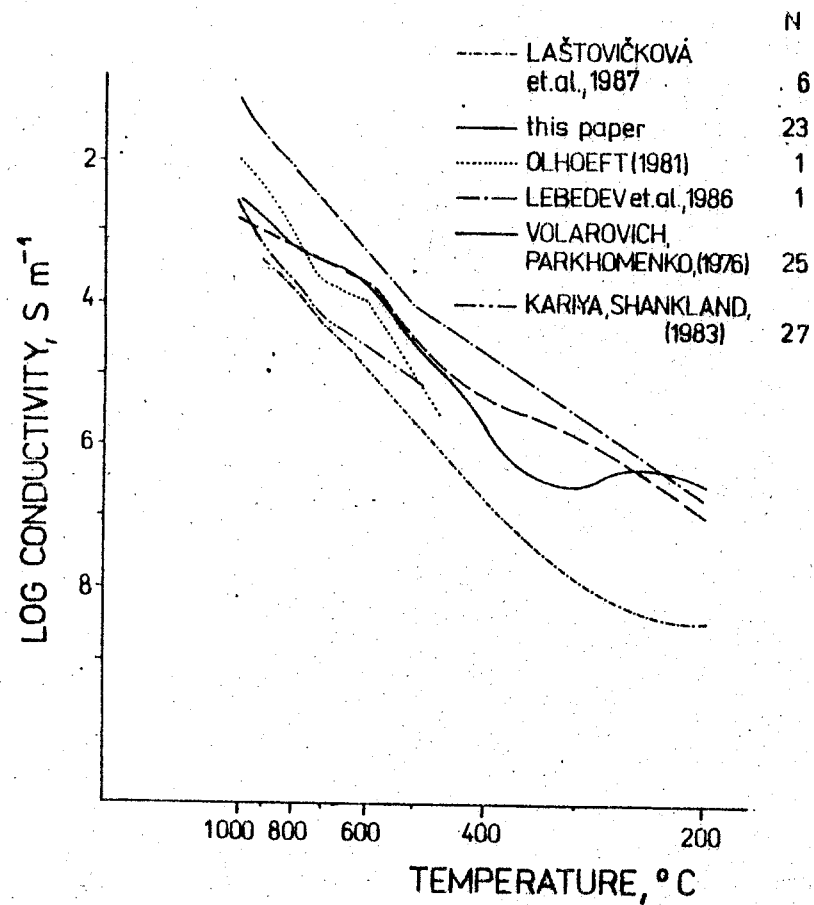


Fig. 1. Electrical conductivity of granitoides as measured by various authors between 200-1000 °C.

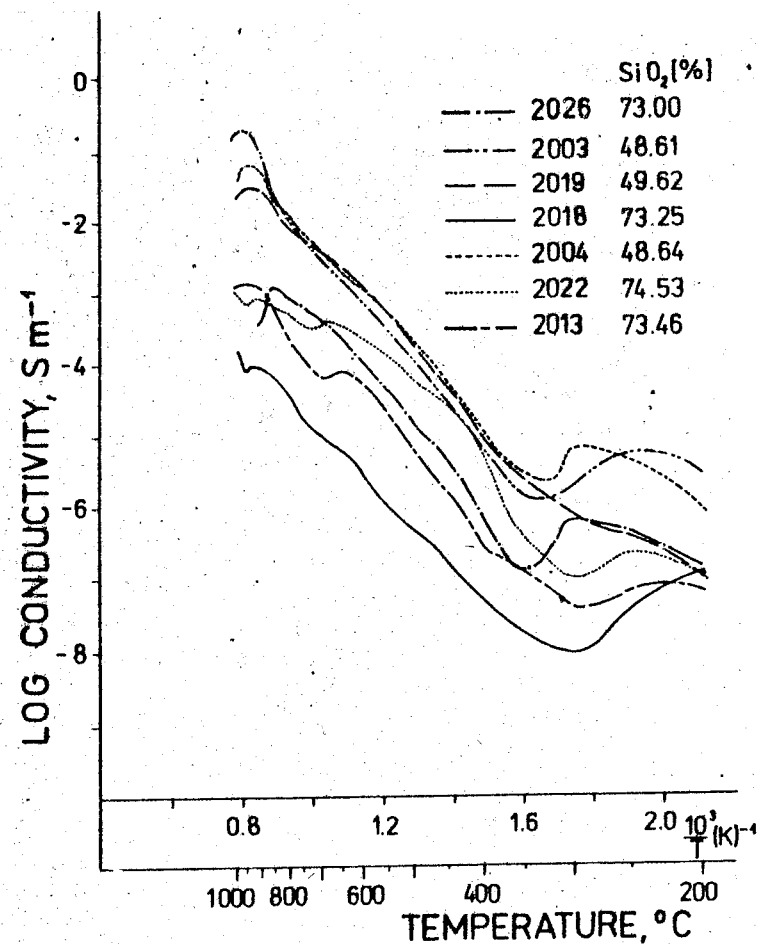


Fig. 2. Electrical conductivity of the West Carpathians granitoides with different content of SiO₂.

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MAGNETIC ANISOTROPY OF ROCKS AND MAGNETITE INDUCED BY UNIAXIAL PRESSURE

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I. Introduction

As regards magnetic properties, in a first approximation rocks may be visualized as a non-magnetic matrix with randomly distributed ferrimagnetic grains. If the concentration of the ferrimagnetic minerals is p , the measured magnetic susceptibility is determined by the relation /1/

$$K = pK_1 [I + (I - p)NK_1], \quad (I)$$

where K_1 is the intrinsic susceptibility of the ferrimagnetic mineral and N is the demagnetization factor. The relation (I) indicates that the changes in susceptibility and the related changes in anisotropy due to pressure may essentially be caused by two processes: by the change of the intrinsic susceptibility, or by the change of the demagnetization factor. The elastic deformation is mostly responsible for reversible changes of the anisotropy of intrinsic susceptibility K_1 . The physical mechanisms relating to these changes are the rotation of the spontaneous magnetization and the displacements of domain walls /2/.

The experimental study of susceptibility in the region of elastic deformations was carried out under uniaxial pressure e.g. /3/, /4/ and to a lesser extent under hydrostatic pressures /5/. The disadvantage of all these experiments is that they are restricted to the measurement of the pressure changes of directional susceptibilities and the degree of anisotropy could only be estimated. To be able to determine anisotropy completely, we built a uniaxial deformation chamber which can be placed inside the sensing coils of the bridge for measuring the susceptibility anisotropy /6/. The results of the measurements of the changes of the magnetic anisotropy due to uniaxial pressure are presented.

2. Results and discussion

The measurements were made on samples of basaltic rocks and of polycrystalline magnetite. The effective stress acting on the sample in the chamber was determined tensometrically using Young's modulus of the rocks. The magnetic susceptibility of the samples at a fixed pressures was measured in KLY-2 digital kappabridge with an accuracy of 0.6%. The intensity of the A.C. magnetic field was 300 A/m. The susceptibility anisotropy were calculated on the basis of measurements of 15 directional susceptibilities at each pressure value. The degree of anisotropy was characterised by $P=K_1/K_3$, the shape of the susceptibility ellipsoid was described by lineation $L=K_1/K_2$ and foliation $F=K_2/K_3$. K_1 is the maximum, K_2 intermediate and K_3 minimum susceptibility.

As the pressure increases, the degree of anisotropy changes appreciably. This applies especially to basalts with relatively small degree of anisotropy in undeformed conditions ($P \sim 1.05$). Under applied pressure of 60 MPa the degree of anisotropy increases to $P \sim 2.5-2.8$. The largest part of the changes of P due to uniaxial pressure are reversible with respect to the applied stress. The decrease or increase of the degree of anisotropy with pressure depends especially on the mutual orientation of the susceptibility ellipsoid in the undeformed condition and of the directional stress. This can be seen in Fig. I where the three directional susceptibilities have been plotted as functions of stress. In the interval of small uniaxial stresses, these functions are approximately linear. The susceptibility parallel to the stress decreases in all cases and, on the contrary, the susceptibility perpendicular to the stress is observed to grow. This behaviour is typical of the ferrimagnetic minerals with a positive magnetostrictive constant. The behaviour of the directional susceptibility inclined at the angle of 45° to the direction of stress is interesting. All samples display a decrease of this quantity with increasing stress, however, the rate of decrease is smaller than for the parallel susceptibility.

The method used to measure the anisotropy enabled a series of directional susceptibilities to be measured under constant loads of the sample. Besides the parallel susceptibility, two susceptibilities were measured in directions inclined at 45° relative to the stress and four perpendicular to the stress. These measurements clearly show that only the orientation of the directional susceptibility relative to the stress is the decisive factor.

One of the characteristics frequently used in rock magnetism is the mean susceptibility $\bar{K}$ which is defined as $1/3(K_1+K_2+K_3)$. As can be seen in Table I, the mean susceptibility decreases systematically with increasing uniaxial pressure. At 60 MPa the decrease of $\bar{K}$ amounts to about 10% of the original value in unloaded condition. However, a more detailed study would be required to explain the physical causes of these changes.

Table I. Changes of the mean susceptibility $\bar{K}$ due to uniaxial pressure

Uniaxial pressure (MPa)	Magnetite Mean susceptibility $\bar{K}$ (SI)	Basalt (A) Mean susceptibility $\bar{K}$ (SI)	Basalt (B) Mean susceptibility $\bar{K}$ (SI)
0	2.598	0.131	0.123
30	2.501	0.120	0.113
60	2.442	0.115	0.108
0	2.616	0.132	0.124

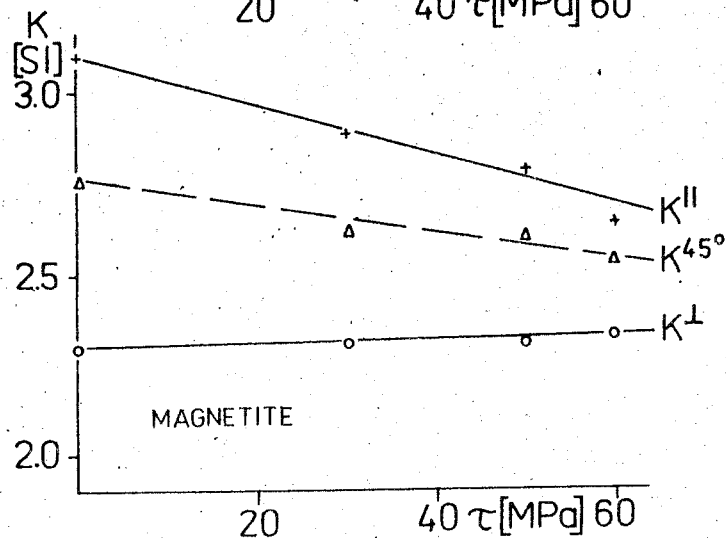
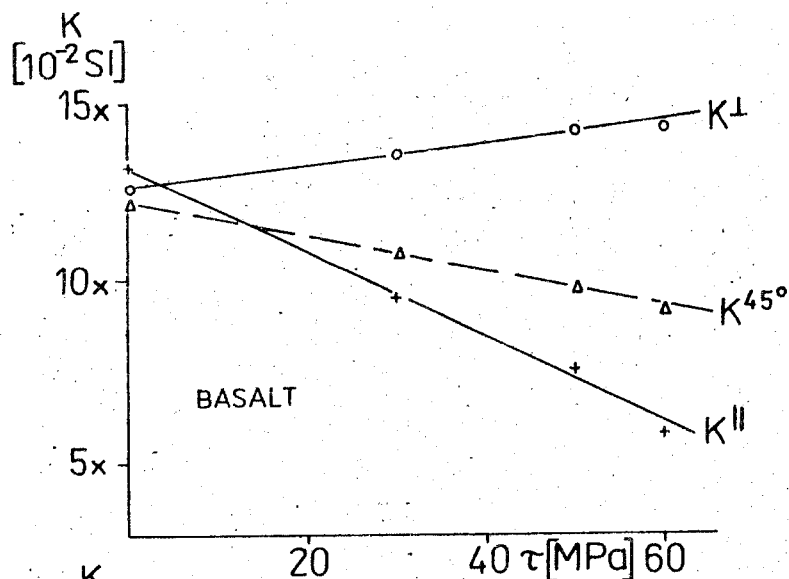
The reversible changes of the anisotropy of the intrinsic susceptibility due to directional external stress can be explained theoretically in terms of the mechanism of reversible rotation of spontaneous magnetization. According to this model, under small stresses and for materials with a positive magnetostrictive constant the changes of the directional susceptibilities with stress can be expressed as [2/

$$K'' = K_0 [1 - \beta'' \tau], K^{\perp} = K_0 [1 + \beta^{\perp} \tau], \beta^{\perp} \approx 1/2 \beta'', \quad (2)$$

where K_0 is the initial value of the susceptibility in unloaded condition, and β'' and $\beta^{\perp}$ are constants. The changes of the directional susceptibilities we measured under stresses $\tau \sim 50-60$ MPa and, consequently, also the changes in anisotropy agree well with this model. Constants β'' and $\beta^{\perp}$ determined for the basalts and magnetite are given in Table 2. However, in all cases the ratio $\beta^{\perp}/\beta''$ is considerably smaller than the theoretical value.

Table 2. Constants β'' and $\beta^{\perp}$ for the direction parallel and perpendicular to the pressure and the initial values of degree of anisotropy P_0

Sample	P_0	$\beta'' (10^{-3} \text{MPa}^{-1})$	$\beta^{\perp} (10^{-3} \text{MPa}^{-1})$	$\beta^{\perp}/\beta''$
Magnetite	1.37	2.1	0.2	0.1
Basalt (A)	1.04	9.2	2.3	0.25
Basalt (B)	1.05	8.3	1.9	0.23



Magnitudes of three different directional susceptibilities
vs. stress τ .

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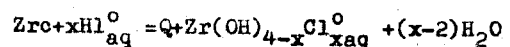
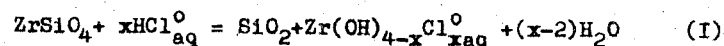
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ZIRCON ($ZrSiO_4$) STABILITY IN THE HYDROTHERMAL SYSTEM
 $ZrO_2-SiO_2-H_2O-HCl$ AT 400-600 °C AND 1 kb

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The incongruent solubility of zircon (Zrc) in the system
 $ZrO_2-SiO_2-H_2O-HCl$ yielding quartz (Q) according to the reaction



has been studied over the temperature range 400-600 °C and
 P=1 kb. The equilibrium constant for this reaction is

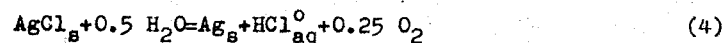
$$K_p = \frac{[Zr(OH)_{4-x}Cl^0_x]}{[HCl^0]^x} \quad (2)$$

where the expression in brackets denotes the activity of the
 complex. The solution being diluted, the H_2O activity coefficient
 is assumed unity. Since the complexes $Zr(OH)_{4-x}Cl^0_x$ and HCl^0
 are electroneutral compounds in the solution, their activity co-
 efficients may also be set equal to unity. Therefore, expression
 (2) can be rewritten

$$K_p' = \frac{m_{Zr(OH)_{4-x}Cl^0_x}}{m_{HCl^0}^x} \quad (3)$$

where m is the molar concentration of the complex.

The concentration m_{HCl^0} in the solution was controlled
 using the Frantz and Eugster method /1/ which employs the Ag-AgCl
 buffer. Under the run conditions this pair gives rise to the
 reaction:



The equilibrium constant for reaction (4) is:

$$K_p'' = m_{HCl^0} f_{O_2}^{0.25} \quad (5)$$

Equations (4) and (5) show that, at designated T and P, the con-

centration of the undissociated HCl^0 complex in the solution
 will be strictly as specified, provided the oxygen fugacity of
 the system was fixed.

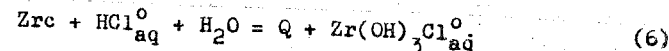
The modified method /1/ used in the present experiments ma-
 kes it possible to attain equilibrium from two directions (Fig.1).
 The experiments were carried out on hydrothermal apparatus /2/.

Using this technique, it is possible to control simultane-
 ously, within the same capsule, the oxygen fugacity (owing to
 the single oxygen buffer), the HCl^0 equilibrium concentration
 and the concentration of Zr_{aq} in the fluid (in the presence of
 Q) at specified T and P.

Equilibrium was considered attained once the HCl^0 concentra-
 tion of the fluid in the Pt $\phi=3$ mm capsules had equalized,
 $lg m_{HCl^0}$ did not differ greater than ± 0.06 log units, and the
 difference between the Zr_{aq} concentration of the fluid in two
 other Pt capsules ($\phi=4$ mm) did not exceed $\pm 0.07 lg m_{Zr_{aq}}$.

The oxygen fugacity was fixed by the buffers Co-CoO, Ni-NiO,
 $Fe_3O_4-Fe_2O_3$. There were three series of runs (by the number of
 oxygen buffers) for three isothermal sections: 400, 500 and
 600 °C. The pressure was held constant at P=1000 bar throughout.
 To obtain accurate m_{HCl^0} and m_{Zr} values, the runs were recy-
 cled repeatedly. The temperature t_{aq} was measured accurate to
 ± 5 °C, pressure to ± 50 bar. A total of more than 100 experiments
 have been run.

The results from the study are presented in Figs.1 and 2.
 In the diagram of Fig.1 the zircon solubility in the presence of
 quartz is shown as a function of the molar concentration of in-
 dissociated HCl^0 complex in the solution for T=400, 500 and
 600 °C, P=1 kbar and the oxygen buffer pairs Co-CoO, Ni-NiO,
 $Fe_3O_4-Fe_2O_3$. The diagram shows that zircon has retrograde solubi-
 lity - it increases with decreasing oxygen fugacity and increas-
 ing HCl^0 concentration in the solution. It is noteworthy that the
 three isotherms have the same slope close to 45°. Therefore, re-
 action (1) can be rewritten as



Based on K_p' and reaction (6), the Gibbs free energy was
 calculated for $Zr(OH)_3Cl^0$ at 400, 500 and 600 °C, P=1 kbar:
 ΔG_f ; 400 °C, P=1 kb = -283,274 $\pm$ 1.04 kcal/mol; ΔG_f ; 500 °C,
 P=1 kb = -269,966 $\pm$ 1.01 kcal/mol; ΔG_f ; 600 °C, P=1 kb = -258,140 $\pm$ 1.04
 kcal/mol.

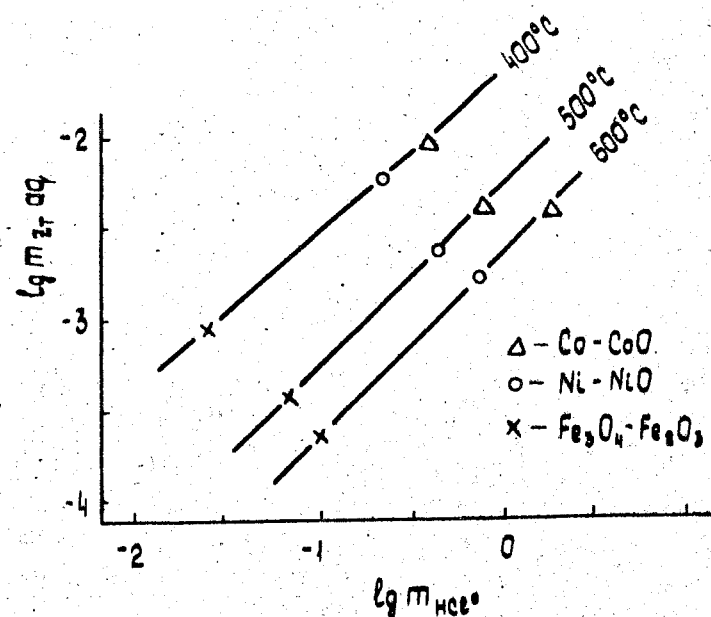


Fig. 1. Solubility of Zr in the HCl^0 aqueous solution at 400, 500, 600 °C, $P=1 \text{ kb}^{\text{aq}}$ in the presence of Q.

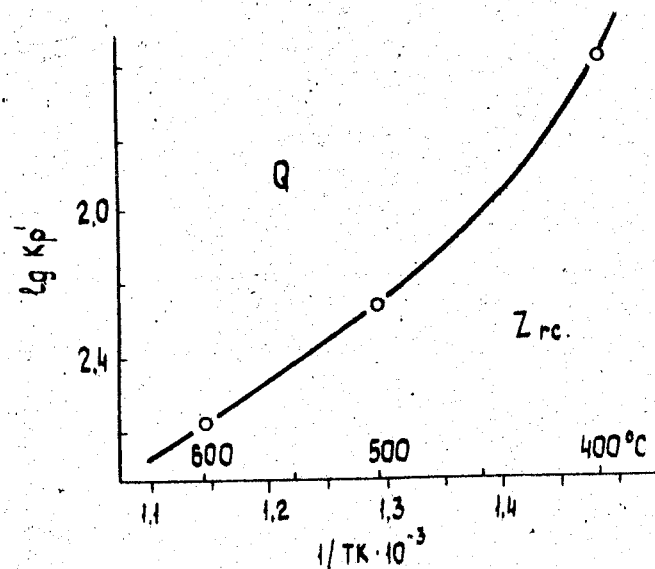


Fig. 2. Stability fields of Zrc and Q depending on $\lg K_p'$ and T

The stability fields of zircon and quartz are given in $1/TK$ versus $\lg K_p'$ diagram (Fig. 2) at $P=1 \text{ kbar}$. The monovariant line of zircon solubility, constructed from reaction (6), has a positive slope. The quartz stability field lies in a higher-temperature region than that of zircon. The experimental results were processed on a computer using Karpov's program [3] to correlate the above thermodynamic constants. The data presented in the diagrams can be used to evaluate the conditions for dissolution, transfer and deposition of zircon under natural hydrothermal conditions.

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KINETICS AND MECHANISM OF COESITE TRANSFORMATION IN LOW PRESSURE SiO_2 MODIFICATION

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Polymorphic transformation of synthetic coesite has been studied in the dry system at atmospheric and high pressure. The initial coesite was synthesized on a split-sphere apparatus at $P=50-55$ kbar and $T=1050^\circ\text{C}$. The coesite unit cell parameters are: $a=7.1392(4)\text{\AA}$, $b=12.3706(5)\text{\AA}$, $c=7.1728(4)\text{\AA}$, $\beta=120.324(5)^\circ$. The experiments were carried out in a shaft furnace under atmospheric pressure and on a piston-cylinder apparatus under high pressure. The quantitative determination of coesite content in the samples was made on the basis of integral reflexes intensity by X-ray doping method of defining initial coesite phase.

At $P=1$ atm coesite transformation into cristobalite occurs reconstructively with the formation of an intermediate uncrySTALLINE phase, structurally characterized only by the short range order and manifested by X-ray diagram as the diffusive reflections in the angle range $(2\theta): 20 - 24^\circ$ and $34-38^\circ$ (CuK_α). Microscopic study has shown that the initial coesite transformation initiates mainly from the surface, deepens inside the grain and results in the pseudoisotropic product rim.

The experimental results obtained at atmospheric pressure, are given in Table 1. We controlled only the quantitative coesite content, so the defined kinetic principles characterize the

first stage of the process, that is coesite transition into the intermediate phase.

Formally the kinetic behaviour can be well described by the Avrami-Erofeev equation and on the base of the geometrical model of the "contracting volume" as well. To take account of the process microscopic character, it was the last model used for interpretation, in which the transformation control is performed by processes on the interface:

$$1-x=(1-\frac{Gt}{R})^3, \quad (1)$$

where x is the product content, G is the mean line speed of interface propagation, R is the particle radius. The kinetic analysis was done accounting the sample granulometric features, valued by optical and electron-microscopic study. The particles as a first approximation were regarded as spherical and were characterized by the average conventional radius (Table 2). The kinetic equation with grain size dispersion corrections is presented as:

$$1-x=\int_0^\infty F(R)\cdot\Phi(R,t)dR, \quad (2)$$

where $F(R)$ is granulometric form of distribution, $\Phi(R,t)$ is the kinetic function (1). To determine the unknown parameter G in (1) within the table granulometric distribution, we solved the equation:

$$\frac{\partial}{\partial G} \left[\sum_j X_j^3 - \sum_i N_i \Phi(R_i, t_j)^2 \right] = 0$$

where X_j is the experimental values of coesite content at t_j exposure, N_i is a number of particles of R_i size. The differential function is a sum of squares of differences between experimental and calculated from the equations (1) and (2) values of coesite content.

The line rate of interface propagation is calculated for

$T=1250, 1300, 1350$ and 1400°C and at these temperature meanings $G=4.416\cdot 10^{-8}, 1.591\cdot 10^{-7}, 6.855\cdot 10^{-7}, 1.906\cdot 10^{-6}$ cm/sec, respectively. Coesite transformation rate dependence on temperature characterized by the change of $\ln G$ value in connection with the reverse temperature, is linear with the high correlation coefficient ($R=0.998$): $\ln G(\text{cm/sec})=26.211(0.8) - 65.77(1.27)\cdot 10^3/T(^{\circ}\text{K})$. The apparent activation energy (E) is $130.6(2.5)$ kcal/mol. On the basis of the defined kinetic constants, the extrapolation shows that even at considerable exposure ($n\cdot 10^2-10^3$ hour) and grain size 1 mm the temperatures not less than 1000°C are necessary for the initial steps of polymorphic transformation.

At $P=20$ kbar under conditions of quasihydrostatics the rate of coesite transformation is considerably increasing. The complete transformation in the temperature range $800-875^{\circ}\text{C}$ takes place at experimental exposure of 3-20 hours. In this case the kinetic dependences are more complex. It may be explained by a number of the additional factors - deviatoric stresses, plastic deformation - appearing in the sample with high pressure. The coesite transition into the stable quartz goes through the intermediate unordered phase, which content is decreasing relative to crystalline phases. Apparently, when pressure increasing, there is a change in relation of rates of the coesite transformation elementary stages (coesite $\rightarrow$ transitional phase and transitional phase $\rightarrow$ reaction product), as the formation of the loopy phase in comparison with those of the crystalline transitional one, becomes less advantageous.

In conclusion, the coesite transition at the atmospheric pressure can be described as the process, controlled by the rate of propagation of the reaction interface. At $T < 1000-1050^{\circ}\text{C}$ the low transformation rate gives the opportunity of coesite metastable keeping in pre-face conditions. At lower tempera-

Table 1. The experimental conditions on coesite annealing and the results of quantitative analysis ($P=1$ atm)

$T(^{\circ}\text{C})$	t (hours)	X_{Co}	$T(^{\circ}\text{C})$	t (hours)	X_{Co}	$T(^{\circ}\text{C})$	t (hours)	X_{Co}
1100	1	100	1300	2	42.77	1350	1	19.93
1200	1	95.0	1300	4	26.73	1350	2	6.48
1250	1	83.16	1300	7	11.00	1350	4	4.09
1250	2	74.00	1300	12	6.05	1400	0.33	19.00
1250	4	56.14	1300	16	5.03	1400	0.5	13.35
1250	7	46.46	1300	20	3.54	1400	1	3.83
1300	0.5	76.09	1350	0.33	48.7	1450	1	1.85
1300	1	51.85	1350	0.5	39.75	1500	1	0

Table 2. Granulometric specification of the initial content

$R\cdot 10^{-4}(\text{cm})$	0-2.2	2.2-5.5	5.5-11	11-16.5	16.5-22	22-27.5
$N(\%)$	18.03	34.35	27.26	11.02	5.47	1.11
$R\cdot 10^{-4}(\text{cm})$	27.5-33	33-38.5	38.5-44	44-49.5	49.5-55	>55
$N(\%)$	0.85	0.77	0.43	0.26	0.17	0.18

tures the process activation is possible because of the additional factors being the process catalysts - mineralizing agents or mechanical tension. An increase in coesite transformation rate under the pressure suggested that the thermodynamic regime was specific, as it provided the coesite keeping - the high rate of decompression, the system low temperature, the fluid confined action.

EXPERIMENTAL STUDY BEARING ON THE PHASE EQUILIBRIA BETWEEN JADEITE AND FORSTERITE, ENSTATITE, PYROPE, DIOPSIDE AT 40 kb

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Na mainly occurs as a jadeite component ($\text{NaAlSi}_2\text{O}_6$) /I/ in pyroxenes of garnet peridotite facies rocks of the Earth's upper mantle. Its content in peridotitic and eclogitic clinopyroxenes reaches 20 and more and 50-70 wt%, respectively. The effect of jadeite component on the liquidus phase relations in the system of garnet lherzolite minerals allows one to estimate the role of jadeite component in generation and differentiation of multicomponent silicate magmatic melts and in petrogenesis of mantle rocks.

The system Fo(forsterite)-En(enstatite)-Di(diopside)-Py(pyrope) is a simplified garnet-peridotitic system. So, we used it for the comparative study as a standard system. Based on the available melting diagrams of binary boundary systems (review in /2/) the liquidus model of the standard system Fo-En-Di-Py was constructed (Fig.1,a) as projected onto the tetrahedron of compositions. The characteristic features of the liquidus are as follows: the five-phase nonvariant point $\text{Fo}, \text{En}_{ss}, \text{Di}_{ss}, \text{Py}_{ss}, \bar{L}$ (minus sign over the phase symbol indicates that phase abundance decreases within the given equilibrium reaction; ss - solid solutions; L - melt); two four-phase peritectic univariant curves $\text{Fo}, \text{En}_{ss}, \text{Di}_{ss}, \bar{L}$ and $\text{En}_{ss}, \text{Di}_{ss}, \text{Py}_{ss}, \bar{L}$; two four-phase cotectic univariant curves $\text{Fo}, \text{En}_{ss}, \text{Py}_{ss}, \bar{L}$ and $\text{Fo}, \text{Di}_{ss}, \text{Py}_{ss}, \bar{L}$; the temperature of the latter decreases with moving away from the nonvariant point.

The present paper is also aimed at the construction of the liquidus model of the system Fo-En-Jd-Py. By comparing this model with the liquidus of the standard system one can estimate physico-chemical role of jadeite component.

The melting diagrams of the boundary binary systems Jd-Py, Jd-En, Jd-Fo were studied experimentally at 40 kbar. They were used along with the available diagrams of the eutectic systems Fo-En, Fo-Di, and Fo-Py /2/ to construct a liquidus model of the system Fo-En-Jd-Py. Experiments were performed in the anvil-with-hole apparatus /3/. Microcrystalline starting material was charged into the sealed Pt or $\text{Pt}_{60}\text{Rh}_{40}$ capsules.

Note that the system Jd-Py (Fig.2,a) is a binary one with simple eutectic without solid solutions whereas the standard

pseudobinary system Di-Py is an internal polythermal joint within the system En-Wol(wollastonite)-Cor(corundum).

The melting diagram of the system Jd-Di belongs to the I Roseboom's type, i.e. it is featured by continuous solid solutions for liquid and solid state. That is why the system Jd-Di-Py may be suggested to compare the relative effect of Jd and Di components on the liquidus phase relations. The joint $\text{Jd}_{50}\text{Di}_{50}\text{-Py}$ (Fig.2,b) of this system was studied experimentally at 40 kbar. The study proved the Jd-component to have greater effect on the liquidus phase relations than the Di one. This evidences the prevalent role of the Jd component in eclogitic liquidus equilibria.

The system Jd-En was studied at 40 kbar. It belongs to the IV Roseboom's type (Fig.2,c) with limited solid solutions. This implies that the system Jd-En is identical with the standard system Di-En with relation to topology and is characterized by the reaction $\text{En}_{ss} + \bar{L} = \text{Di}_{ss}$. The mentioned reaction is responsible both for the peritectic equilibrium $\text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$ in the binary system Jd-En and for the equilibria $\text{En}_{ss}, \text{Jd}_{ss}, \text{Py}, \bar{L}$; $\text{Fo}, \text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$; $\text{Fo}, \text{En}_{ss}, \text{Di}_{ss}, \text{Py}, \bar{L}$ in the ternary systems En-Jd-Py, Fo-Jd-Py and quaternary system Fo-En-Jd-Py, respectively. The temperature of the liquidus curve $\text{Jd}_{ss}, \bar{L}$ in the system Jd-En decreases with moving away from the peritectic point $\text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$. The same decrease in temperature was observed at the cotectics $\text{Py}, \text{Jd}_{ss}, \bar{L}$ and $\text{Fo}, \text{Jd}_{ss}, \text{Py}, \bar{L}$ of the systems En-Jd-Py and Fo-En-Jd-Py, respectively.

The system Jd-Fo (Fig.2,d) by contrast to the standard eutectic system Di-Fo is pseudobinary. This to say, En_{ss} appears as a complementary liquidus phase. The analysis of the basic system Fo-Ne(nepheline)- SiO_2 showed that the system Jd-Fo was its internal polythermal joint. So, it contains information on the nonvariant point $\text{Fo}, \text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$ and univariant curves $\text{Fo}, \text{En}_{ss}, \bar{L}$; $\text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$ and $\text{Fo}, \text{Jd}_{ss}, \bar{L}$. The topological relations of these elements determined experimentally evidence the peritectic nature of the considered four-phase equilibrium and show the eutectic curve $\text{Fo}, \text{Jd}_{ss}, \bar{L}$ to descend with decreasing temperature.

The liquidus of the system Fo-En-Jd-Py (Fig.1,b) differs essentially from that of the standard system Fo-En-Di-Py (Fig.1,a). Although the five-phase equilibrium $\text{Fo}, \text{En}_{ss}, \text{Jd}_{ss}, \text{Py}, \bar{L}$ remains peritectic, the four-phase peritectic curve $\text{Fo}, \text{En}_{ss}, \text{Jd}_{ss}, \bar{L}$ re-orientates itself relative to analogous curve $\text{Fo}, \text{En}_{ss}, \text{Di}_{ss}, \bar{L}$ within the tetrahedron of compositions. This accounts for the

shift of En_{ss} , L primary crystallization volume towards the boundary system Fo-Jd-Py.

The effect of Na component is also observed in the multi-component system $Ol(Fo_{86}Fa_{14})-Opx(En_{84.5}Fs_{10.5}Di_{3}Jd_2)-Cpx(Di,Hed)_{46}(Jd,Akm)_{51}(En,Fs)_3-Gr(Py_{32.2}Grs_{16.4}Akm_{51.4})$ whose clinopyroxene and garnet compositions reproduce those of natural mineral eclogites within the six-component system $Na_2O-CaO-MgO-FeO-Al_2O_3-SiO_2$.

Na jadeite component is thus the most important factor which gives rise to a new course in the evolution of mantle magmatic melts (producing also a considerable decrease in magmatic temperatures).

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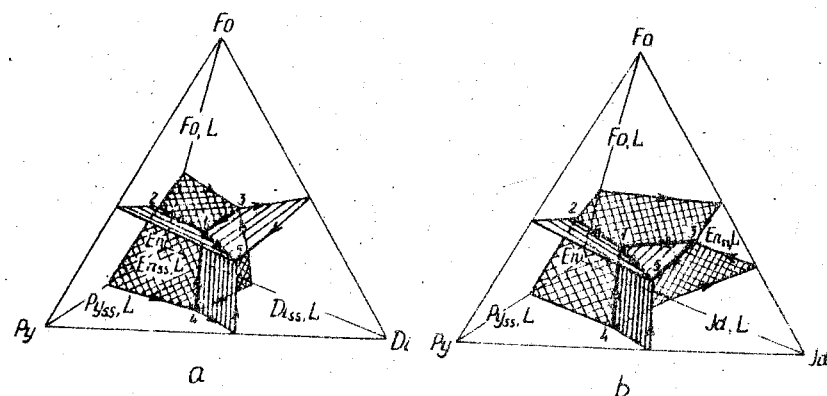


Fig.1. Liquidus models (at 40 kbar) of the systems:
a-Fo-En-Di-Py (1-Fo, En_{ss} , Di_{ss} , Py_{ss} , L; 2-Fo, En_{ss} , Py_{ss} , L; 3-Fo, En_{ss} , Di_{ss} , L; 4- En_{ss} , Di_{ss} , Py_{ss} , L; 5-Fo, Di_{ss} , Py_{ss} , L);
b-Fo-En-Jd-Py (1-Fo, En_{ss} , Jd_{ss} , Py_{ss} , L; 2-Fo, En_{ss} , Py_{ss} , L; 3-Fo, En_{ss} , Jd_{ss} , L; 4- En_{ss} , Jd_{ss} , Py_{ss} , L; 5-Fo, Jd_{ss} , Py_{ss} , L).

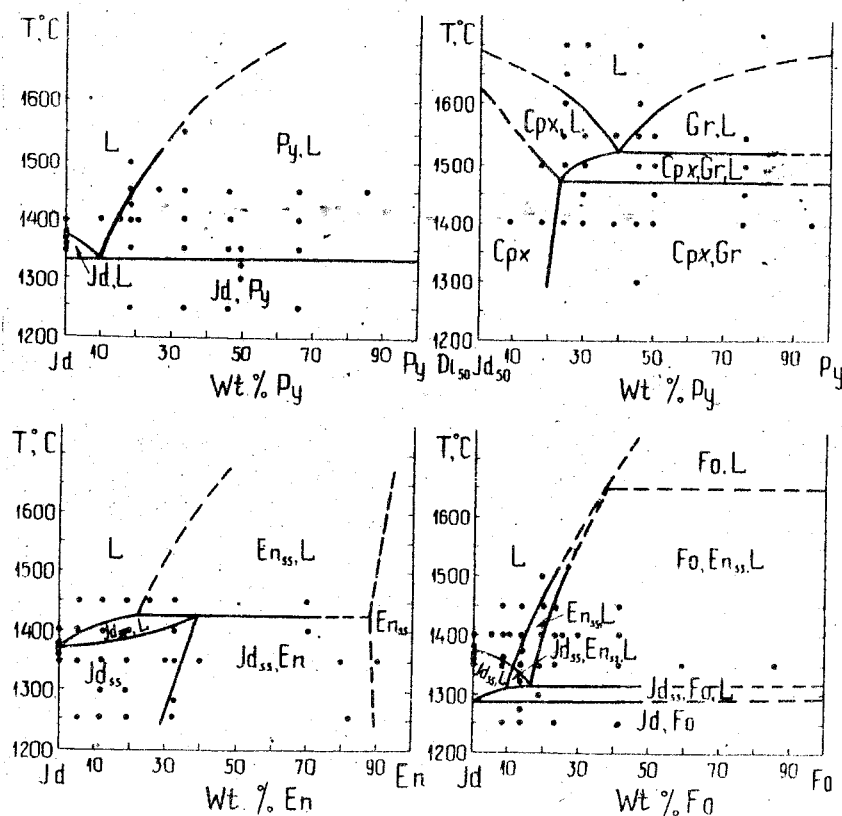


Fig.2. Melting diagrams at 40 kbar of the systems:
Jd-Py; $Jd_{50}Di_{50}$ -Py; Jd-En; Jd-Fo. Experimental points are shown.

NEW RESULTS OF THERMOBARIC STUDIES OF SOME BASIC
PETROPHYSICAL CHARACTERISTICS

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In recent years we have obtained new thermobaric data on elastic, magnetic, thermal and electric parameters of the mineral matter. Some interesting aspects of their geologic-geophysical application are proposed. A few of them are briefly characterized below.

1. Peculiarities of elastic and plastic PT-changes of rocks effected by high thermobaric regimes and a complex stress state have been revealed. The individual character of these changes appears to be created by genesis and the subsequent evolution of minerals in respective thermodynamic situations of the interior.

The study of the rocks of different geologic provinces under the effect of P and by model PT programs has revealed a close relation of the peculiarities of elastic characteristic distribution of some minerals with their geostructural position. It is shown that the elastic parameters of rocks may serve as diagnostic indicators of definite block-fractured structures with which significant stress and thermal field inhomogeneities are associated.

An analysis of geologic-geophysical information, particularly the results of PT-studies of elastic properties of rocks along a DSS-profile serves as the basis of the method of setting up

velocity cross-sections for the upper lithosphere which supplement the seismic constructions /1, 2 et al./.

2. The experiments show /3 et al./ that the changes in rock magnetization at uniaxial pressure are more intensive than in hydrostatics. The main role play the irreversible processes, the effect of the reversible ones being highly restricted. Of great importance is the ferromagnetic dominating the rock. The character of P dependence of the magnetization is also due to the crystal form of the ferromagnetic effecting the domain structure anisotropy in each concrete case. The conditions of the formation of magnetization are created by the total external effect exerted on the rock during its entire evolution. Particularly significant are grain size and structural features of magnetic mineral grains much affecting the coercive force. The latter is closely related with internal stress caused by imperfectness of the crystal lattice of the ferromagnetic, its temperature phase changes at respective temperature, anisotropy of mechanical properties of the grains of minerals (including the rock-forming ones), changes on their boundaries, fragmentation and block formations by deformation. The degree of the influence of these factors on the rock magnetization generally depends on the character and types of the dislocations and domain particles, state and composition of the non-magnetic matrix etc. According to the experiments /3 et al./ the pressure effect on demagnetization is rather appreciable to the 300°C isotherm depth. Below it, the changes of the magnetic properties of rocks are mainly due to temperature.

3. One of the important parameters defining the state of the mineral matter of the interior is its heat conductivity coefficient (λ). P and T differently effect the λ change / 3 et al./.

T increase to 350-400°C results in total lowering of the heat conductivity of rocks, most of them increasing it slightly 25-150°C. Contrarily, the hydrostatic pressure increase to 1,0 GPa notably elevates heat conductivity.

The simultaneous P and T increase changes the heat conductivity in a rather complicate manner. The gradients of its increase to 0,5 GPa and 350°C (the depth of the order of 15-20 km) are different. The uppermost lithosphere seems to be dominated by P effect compacting the rocks and improving the thermal contacts between the mineral grains. Below 5 km the pressure effect is partly compensated by pressure, which brakes the total heat conductivity increase. It has been found that under deep thermobaric conditions of some regions P and T effect and associated differences in gradients of λ changes with depth /3 et al./ may prevail.

4. The distribution of the electric properties of rocks at great depths is due to temperature, pressure, water-saturation, peculiarities of mineral and chemical composition etc. The effect of all these factors also depends on concrete geologic situation of the interior. In the crust the crucial effect is that of differently mineralized fluids and high electric conductivity layers. The degree of the water-saturation is defined by water-saturation and permeability of rocks. In the upper mantle and deeper, the electric conductivity is more notably effected by temperature, chemical composition and partial melting of the mineral matter. A set of our programmed thermobaric experiments has been made on some dry and water-saturated rock samples /3, 4 et al./. For dry samples of the continental crust (e. g. those taken from the shields) the experiments were able to imitate the depths to 60 km. The electric resistance (ρ) of dry rocks has been shown to

decrease more intensively to a depths of 30 km than within the depth range 30-60 km. In the former interval the actinolites, serpentinites, basalts and granites decrease their (ρ) by 3,5, 2,5, 4,0 and 4,5 orders respectively. The latter range shows the mean decrease of their (ρ) by only 0,7, 0,3, 1,4 and 1,3 orders respectively. The ρ scattering is more significant at small depths, then it becomes notably less. The gradients of the ρ changes with depth increase with transition from ultrabasic to acid rocks /3/. The water-saturated rocks exhibit a slightly intensive decrease of electric resistance with depth due largely to their temperature dependence /4/.

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CHANGES IN ELECTRIC RESISTANCE OF ROCKS IN DIFFERENT MEDIA AT HIGH PT-PARAMETERS

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Under the real deep conditions of the Earth's interior oxidation and reduction processes occur and mineral matter is differently water-saturated. Therefore the complex effect of air, inert and water medium on the electric properties of rocks and minerals appears to be very interesting and promising.

The granitoids of Ukraine and Slovakia (ČSSR) exemplify the effect of these media on the character of the thermobaric changes of the electric properties of rocks illustrated by experiments using equipments of the Institute of Geophysics, Ac.Sci.Ukr.SSR (Kiev) and Geophysical Institute of the Czechoslovak Ac.Sci.(Prague)/I, 2 etc./.

An analysis of thermal ($<1000^{\circ}\text{C}$) experiments made in air and inert media for same samples of Slovakia granitoids shows a rather good agreement of the heating curves to $400-600^{\circ}\text{C}$ differing only by 0,7 orders. This evidences similarity of the character of the temperature dependence of the electric resistance (ρ) of rocks in these conditions. Besides of the effect of the charge carrier number increase with elevating temperature, the effect of removing fluid inclusions from the rocks is also expected. These

physico-chemical transformations occur in the inert and air medium. Within the $400-900^{\circ}\text{C}$ range a rather significant air and inert medium $\rho = f(T)$ curve disagreement is observed. The former exhibits intensive iron mineral oxidation which may be only due to inner oxygen potential in argon. At higher temperature the characters of these dependences tend to become similar.

A comparative analysis of the effect of air and water medium on the character of thermobaric changes of the electric resistance of rocks has been made on the experimental data obtained at hydrostatic pressure (P_h) to 1,5 GPa and at simultaneous effect of quasi-hydrostatic pressure (P_q) to 2,5 GPa and temperature to 650°C . High hydrostatic pressure causes differences in changes of ρ depending on its initial value and moisture content. The air-dry samples contain less than 0,1 % moisture. Their porosity varies from 0,1 to 3,6 %. The incomplete water-saturation lowers pore pressure nearly to zero. The baric dependence of ρ of humid and dry basic and ultrabasic rocks is associated with its growth. However, the degree of the electric resistance increase is much higher for humid than for dry samples. Four and two ρ intervals with different ρ gradients of respective humid and dry samples have been established. For humid samples ranging from 0 to 0,2 and from 0,4 to 0,7-1,1 GPa the $d\rho/dP$ ratio increases compared to those in two other pressure intervals. These pressure ranges are due to two prominent porosity types: crack porosity with respective crack fluid conductivity and pore porosity with fluid conductivity. For solutions with low salt concentration surface conductivity is of great importance. The crack pores are closed at pressure to 0,2 GPa. The more intensive ρ increase in the initial P interval is explained by crack pore closure. The

pore porosity is closed at higher pressure. In our experiments the pore porosity closure may be associated with pressures between 0,4-0,7-1,1 GPa. For the not completely water-saturated rocks there is no clear-cut relation between porosity and ρ . The P dependence of ρ for dry rocks is characterized by two P intervals with different gradients of its increase and is explained by effects occurring in the solid rock skeleton. The high hydrostatic pressure lowers the resistance of low resistivity humid and dry samples with $\rho < 10^3$ Ohm m. This is due to pressure effect exerted on semiconductor properties since the electric conductivity of these rocks is defined by ore minerals.

In quasi-hydrostatic a quite different picture exists. The $\rho(P_q)$ curves of air-dry and dry granitoid samples are characterized by low gradients. To 1,0 GPa, ρ is slightly decreased or constant. At $P < 2,25$ GPa the resistance remains almost unchanged or is somewhat increased. For less resistant basic and ultrabasic rocks ρ decreases in the first and second pressure interval. The most intensive resistance decrease with elevating quasi-hydrostatic pressure is observed for the least resistant rocks (serpentinites). Their ρ decreases with P elevation to 2,0 GPa by ca. one order. The difference in P changes of ρ in hydrostatics and quasi-hydrostatics is due to non-hydrostatic component effect on the value and energy of binding of crystal lattice defects.

The effect of the water medium on the character of isothermic and isobaric dependence of resistance was studied in a closed system enabling us to avoid sample dewatering at high temperature. The quasi-hydrostatic pressure increase to 2,0 GPa diminishes the water-saturated granitoid samples like dry ones. The changes

mentioned are observed at temperatures 18, 100 and 200°C. Thus, water does not affect the ρ dependence of granitoids significantly in quasi-hydrostatics. The difference has been established for dry and water-saturated basalt samples of the oceanic floor. The dry samples of these rocks decrease ρ to 2,0 GPa, while the water-saturated ones lower it with increasing pressure to 0,5-0,7 GPa, then decreasing it at higher P_q but the absolute value of these changes is significantly lower than that of thermal ones whose activation energy is by many times lower for water-saturated than for dry rocks.

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CHANGE OF PHYSICAL PROPERTIES OF ROCKS IN THE PROCESS
OF DEFORMATION UNDER HIGH PRESSURES

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Study of processes of rocks deformation, taking place at various depths, are closely connected with such problems as oil and gas prospects at great depths, prediction of earthquakes, etc.

This paper shows the change of velocity and amplitude of elastic waves, electric resistance in the process of rock deformation, having various liquid pore pressures in complicated stress field.

Institute of Geology and Exploitation of Combustible Fuels has developed the techniques of experiment under the influence of regular pressure and took into account the liquid pore pressure and irregular stress, i.e. single axis compression under a high lateral pressure of compression. The known method of studying deformational characteristics of rocks /1/ has been modified to establish the values of specific electrical resistance or velocity and amplitude of elastic waves at all values of stress with deformation alteration /2,3/.

For deformation measurement the elastic tensometers have been used. Strain gauges for measuring the longitudinal and radial deformation are connected as the Wheatstone bridge. The same instruments record readings of the bridge diagrams for measuring the efforts in the process of test under the irregular compression. In this case the record of stress-deformation diagrams takes place. Modified specially treated electrodes have been used for measuring the electrical resistance. These measurements have been done according to two-electrode circuit. The velocity of elastic waves has been measured by impulse ultra-sound method within frequency 0.8-1 MHz.

Two pairs of piezoelectric transformers have been installed on the faced surface of cylindric samples having diameter of 16 mm and length of 25 mm.

The samples of polymict sandstones, tuffstones, limestones and dolomites have been selected for studies. Before the experiment the above samples were saturated with simulated formation water or kerosene.

Deformations and relative electric resistance grow with increase of regular pressure. The electric resistance ρ is very sensitive to a structure of rock and is defined by winding of current conducting channels, microcracks, etc. Therefore even inconsiderable difference in micropore distribution in two samples of the same rock causes various changes of the relative electric resistance under the influence of effective stress. A low changes of ρ in limestones in comparison with the observed one in sandstones should be mentioned. On the whole the relative alteration of electric resistance is closely related to the rock permeability. In more permeable rocks the growth of electric resistance with pressure increase is the least. Such rocks preserve good filtration properties at great depths under the overall compression.

Zones of anomalous changes of deformation, relative electric resistance, permeability factor are typical for the majority of rocks. It is connected with structural alterations of rocks in thermodynamic conditions, corresponding to the occurrence depth. In some sandstones anomalous changes have not been traced, as there is a relationship with rock formation environment and lithogenesis processes. If there is a predominance of clastic volcanogenic rocks in these sandstone, then at a slight deformation change the rapid increase of electric resistance is observed as a result of current conducting channels alteration under a pressure.

The velocity of longitudinal waves in liquid saturated rocks under the influence of overall compression increases slower and it grows much more slower under the rise of pore pressure.

When testing the samples under the irregular compression the obtained graphs of the relative electric resistance - stress considerably complete the deformation graphs. When deformation linearly changes with stress the electric resistance increases or maintains almost constant. The above fact can be traced in the elastic zone. While transmitting into the nonelastic zones the electric resistance begins dropping. The strength is reliably defined according to both graphs. Both the strength and the flow limit increase with effective stress growth.

The electric resistance - stress can be defined according to diagram. Such rocks are predisposed to shattering and discompaction under the irregular compression. In limestones the elec-

tric resistance so intensively decreases in non-elastic zone that at a stress corresponding to the strength it appeared to be less than the initial value, i.e. the values at atmosphere pressure. It means, that the number of current conducting channels increased. The electric resistance in sandstones slightly changes, i.e. maintains rather high even by the moment of destruction. Permeability does not increase under a complicated stress state or it is considerably low.

In the zone of elastic deformation the velocity of longitudinal waves rises and stops rising at that then it drops the formation of principal fracture. At primary development of breaking fractures, velocity of elastic waves begins dropping.

By the alteration of complex physical characteristics in the process of rocks deformation up to their destruction three zones have been distinguished: in the zone of elastic deformation the velocity and amplitude of longitudinal waves rise, the electric resistance slightly grows and the deformation lineary change. With the development of dilatation and with the formation of breaking fractures the values of velocity and amplitude of longitudinal waves are stabilizing, the electric resistance starts decreasing. Before the distribution the velocity of longitudinal waves and electric resistance sharply decrease and, as a rule, the bulk deformation increases (discompaction).

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INVESTIGATION OF ELASTIC PROPERTIES AND SOLIDITY OF VARIOUS GRANITIDS UNDER HIGH-PRESSURES IN UZBEKISTAN

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The following laboratory investigations have been held:

(a) of elastic properties of the rocks in the solid-state device of the cylinder-piston type under quasihydrostatic pressures up to 1.5 HPa; (b) of solidity of the rocks in complex-strained conditions under pressures up to 1.0 HPa. The velocity of P-wave have been measured by an ultrasound impulse apparatus at the 1.0 MHz frequency /1,2/. The density, porosity and velocity of P-wave in atmospheric conditions were preliminary determined. The linear dependence of the velocity increase (V_p) and density (ρ) on the porosity of granitoids has been established in the pressure range from atmospheric up to 0.1 HPa.

The results of experiments let to receive empirical equations describing the dependence between the density and velocity of investigated rocks. The correlation of the velocity and density for these rocks are maximal in the pressure range 0.4-0.6 HPa. It slightly decreases whereas the pressure to be higher, that is probably explained the fracturing in rocks accompanied with the velocity decrease. The established dependency is caused by the mineral and chemical composition of rocks /3,4/. These

can be most clearly looked for the dependence of the rock density on the total content of the biotite and amphibole. The correlation coefficient r equals to 0.87 in this case. It is less for the dependence of density from the total content in rocks of quartz and potassium feldspar ($r = -0.51$), and it's more less for the dependence from the content of the quartz only ($r = -0.35$). Statistical processing yielded the dependence of the density and P-wave velocity in granitoids from the rock-forming minerals content under various pressures. Regression equations describing the dependence of density from the mineral composition and the values of the correlation coefficient have been obtained for the rocks of the granite-diorite series in Uzbekistan:

$$\rho = 0.0058 \cdot \theta_{dc} + 2.63; \quad r = 0.87$$

$$\rho = -0.0016 \cdot \theta_{q,PFS} + 2.75; \quad r = -0.51$$

$$\rho = -0.0007 \cdot \theta_q + 2.68; \quad r = -0.35$$

where θ_{dc} , $\theta_{q,PFS}$ - contents of dark-coloured minerals and total content of the quartz and potassium feldspar in rocks.

Considered combination of the minerals also determines elastic properties of the rocks. Regression equations describing the dependence of the velocity from the content of some minerals and the correlation coefficient in this case look as:

$$V_p = 5.492 + 0.0027 \cdot Q; \quad r = 0.93$$

$$V_p = 6.172 - 0.0042 \cdot PFS; \quad r = -0.46$$

$$V_p = 5.812 + 0.0525 \cdot Bi; \quad r = 0.73$$

$$V_p = 5.844 + 0.0007 \cdot Pl; \quad r = 0.66$$

where Q - quartz, PFS - potassium feldspar, Bi - biotite, Pl - plagioclase.

It has been established that the dependence between the velocity of P-waves and the chemical composition to be most distinct

for the silica (SiO_2), ferroxide (Fe_2O_3 , FeO), magnesium (MnO), sodium (Na_2O). As for other components of chemical composition the correlation coefficient does not exceed 0.6.

It is known that numerical characteristics of the solidity of rocks play an important role in the discrimination of seismic risk within different seismic zones. It has been established some increase of the solidity threshold with quasihydrostatic pressure for all kinds of rocks from the Fergana seismic region. The rate of the solidity increase are different for the rocks from various zones of the Talas-Fergana fault (TFF). Such difference of the solidity characteristics of rocks from the Fergana zone under equal hydrostatic pressure can be explained by secondary changes of the rocks near TFF after that these rocks are fractured in greater power.

As the comparison of experimental results has shown the granodiorites from the Tashkent seismic zone are characterized by the values of the solidity threshold almost twice larger than analogous rocks from the Kizilkum zone. Although their solidity thresholds are approximately same at atmospheric pressure. And the densities of studied rocks are rather different. Thus an average values of the density of granodiorites from the Tashkent and Kizilkum zones are 2.75 g/cm^3 and 2.60 g/cm^3 respectively. Such differences are caused by the greater rate of fracturing of the rocks from Kizilkum zone in comparison with rocks from other regions. It is to be note that the linear decrease of the solidity threshold when the loading slow down has been established and the rate of the solidity threshold decrease of rocks from Kizilkum zone is 15-20 % greater than for the rocks from other zones.

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DEEP GEOPHYSICAL ANOMALIES AS A CONSEQUENCE OF THE FORMATION OF SUPERCRITICAL GAS SOLUTIONS UNDER HIGH PRESSURES AND TEMPERATURES

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Modern physico-chemical views on substance permit us to consider the entire Earth as the system of solutions. A solution is understood as a multi-component system characterized by non-stoichiometric composition and chemical interactions of components accompanied by volumetric and heat effects. Depending on the state, such a system is defined as solid, liquid and gas solutions. By a melt we mean "liquid which under given conditions changes into a crystalline phase with the identical composition" /1/. Therefore, the product of partial melting of rocks at depth must be regarded as a liquid high-temperature solution, but not as a melt. Recent works on petrochemistry make the existence of basaltic melting zones on the global or even on the regional scale doubtful. According to the leading foreign experimentalists /3/ "only occasionally the magma generation in the mantle is a simple process of partial melting in the closed system" /2/. Open systems imply mass and heat exchange with the environment, and volatile components may be their main carriers.

Equations of state of most gases under ordinary conditions show (Fig.1) that the area of their supercritical state corresponds to P, T conditions of deep petrogenesis. For example, in Fig.2 there are shown the equations of state for water in P-T coordinates which correspond to the interior of the Earth. In physics gas is defined as such state of a substance when the kinetic energy of heat flow of its particles significantly exceeds the potential energy of interactions between them. As a result, the particles freely move occupying the whole volume while there are no external fields. From our point of view, the final circumstance is of great importance because it presupposes that the dynamic characteristics of mass and heat transfer qualitatively differ from the liquid ones.

But this definition is too general, so we introduce limitations - the physical constants: critical temperature T_{cr} and cri-

tical pressure P_{cr} . All substances with $T_{cr} \leq T_{cr}$ of water and $P_{cr} \leq P_{cr}$ of water are considered gases. It follows from Table that if all the conditions are satisfied, almost all gases of the Earth are involved, water included. Comparing Table and Fig.2 we see that all gases in the interior of the Earth must be in supercritical state.

The critical parameters for some gases

Substance	$T_{cr}, ^\circ C$	P_{cr}, B
He	- 267.9	2.26
H ₂	- 239	12.8
N ₂	- 147.1	33.9
O ₂	- 118.6	50.4
CH ₄	- 82.5	47.3
CO ₂	31.1	74.0
HCl	51.4	81.5
H ₂ S	100.4	90.1
NH ₃	132.4	113.0
SO ₂	157.2	78.7
HF	197.7	64.9
SO ₃	218.0	84.7
H ₂ O	374.15	218.3

In the "gasosphere" /4/ gases exist at least in six forms. They are: free gas, gas dissolved in liquid and solid bodies, volatiles in chemical compounds, adsorbed gas in cavities and pores of solid bodies, gas solutions and gas plasma. The interchange between them depends on the temperature and pressure.

Let us examine the experimental data allowing us to suppose, for example, their significant role for generating anomalies of electrical conduction in the crust and upper mantle. Density of supercritical vapour at $T=1000-1200K$ and $P=1.5$ GPa equals $800-900 \text{ kg/m}^3$, and its viscosity is less than that of water under standard conditions /5/. Dielectric constant remains high enough (about 20) and vapour retains the ability to cause dissociation of the substances dissolved within it. Ionic product of supercritical vapour then equals 10^{-7} mole/l, i.e. 7 orders higher than ionic product of water under standard conditions. This promotes the reactions of hydrolysis in a gas solution and association of the mo-

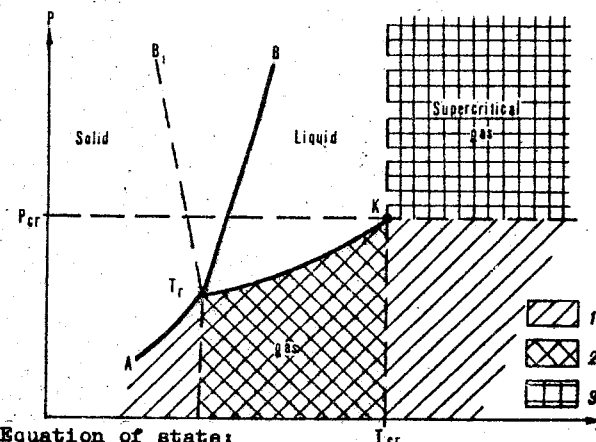


Fig.1. Equation of state: Tr - triple point; A-Tr - sublimation curve; Tr-K - evaporation curve; Tr-B ($Tr-B_1$) - melting curve; K - critical point. 1 - gas area; 2 - vapour area; 3 - supercritical gas area.

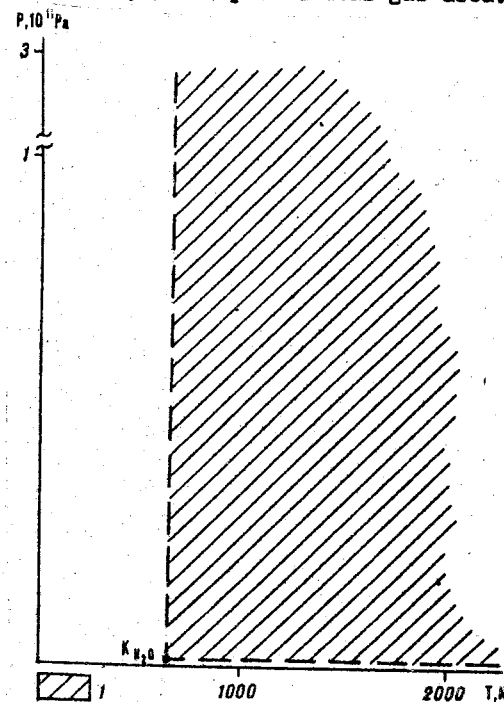


Fig.2. Equation of state of water in P-T Earth's coordinates: K_{H_2O} - critical point of water ($T_{cr} = 647.3K$, $P_{cr} = 2 \cdot 10^7 \text{ Pa}$). 1 - area of supercritical state of water.

lecules and ions of water with the dissolved ions and complexes of other substances which, in its turn, will result in the increase of the electrical conduction of solutions.

Let us show the dissolving power of supercritical vapour at 1000-1100K and 1.5-2 GPa. The ionic compounds (their elements Cl, F, Al, Na, K, Ca, Mg have been found in magmatic gases) will be examined as dissolved components. It has been experimentally determined that the solubility of NaCl in supercritical vapours grows with the increase of pressure and temperature, and at T=1000-1500K it jumps 1-2 orders. NaCl and KCl are electrically conductive in supercritical vapour, which speaks of dissociation of salts. The electrical conduction of a gas solution greatly depends on its density. The salts dissociation abruptly grows when the density of a solution is 500-600 kg/m³ which leads to a sufficient increase of its electrical conduction /5/. This explains the appearance of the upper boundaries of the electrical conduction anomalies in the crust and upper mantle.

With the pressure and temperature growth the processes decreasing the specific electrical conduction of gas solutions begin to play a perceptible role; it is, for example, dissolution of SiO₂. NaCl and KCl present in gas solutions enlarge the solubility of SiO₂ while a degree of the salts dissociation does not exceed 10% under any conditions. Besides, the further density growth of gas solutions results in the decrease of their electrical conduction due to lessening the ions mobility /5/. Perhaps these processes are responsible for the existence of the lower boundary of zones of the electrical conduction anomalies.

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SUPERHARD MATERIALS ARE THE PROMISING PRODUCT OF HIGH PRESSURE TECHNOLOGY

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The increased production of superhard materials (SHM) i.e. synthetic diamonds, cubic boron nitride and others conforms to the most important trends of progress in technology. More than one hundred materials synthesized and sintered at pressures above 4GPa during the last 30 years are classified as superhard. These are materials with microhardness higher than $2.0 \cdot 10^{10}$ N/m² (2000 kg/mm²). According to Mohs scale known from 1811 only diamond crystals among natural materials surpass them in hardness. The class of SHM is enlarged mainly due to high pressure and high temperature technology. SHM are synthesized or sintered at pressures of 5 GPa and higher with heating the reaction mixture above 1500 K up to 2000-2500 K. SHM products are obtained using the processes of mechanochemical machining, concentration, grading, classification and the methods of nondestructive test /1/.

A special complex of physicochemical properties of diamond and diamond-like SHM is determined by the directional covalent bond of atoms in the crystal lattice. Chemical stability is explained by sp³-configuration of valence electrons in the carbon atom and the maximum density of their packing. More poor localization of valence electrons as compared with diamond and less strong interatomic ionic-covalent bond are typical for superhard carbides, borides and nitrides of transition metals.

No physical explanation common to different materials has been found for the superhard state. But one may point out the proportionality of hardness of superhard materials having correlation ratio of 0.8 to the ratio of the product of interatomic bond energy E_0 and the bond covalency index a_0 to the square of interatomic space d (Fig.1) /2/. Crystals of SHM are brittle, their microplasticity is recorded at exceptionally high pressure. The yield strength of diamond and CBN as well as of other brittle materials is not physically identified.

Superhard materials are obtained by crystallization at high static pressures and in shock wave (diamond and CBN crystals); by hot isostatic pressure, by sintering at high temperatures and by

phase transformation in plasma flows, under laser action (polycrystals, films). Through changes in the reaction medium and technological parameters of pressure and heating one can vary in a wide range the physicomachanical properties, the size and the shape of the crystals, the structure of polycrystals, the density and structure of composites.

Consider the different aspects of such influence upon the physical properties of diamond single crystals promising in their use for tool-making and electronics.

Effect of carbon concentration. Excluding the phase of nucleation from consideration we'll discuss the mechanism of diamond crystals growth from carbon solution of different concentration in metal melts. The diamond crystals growth is realized by consecutive addition of single carbon atoms and their complexes dissolved in the metals melt. This occurs both with low (in Ni-Mn-C system /3/) and high (Mg-based system /4/) concentrations of carbon. This mechanism of growth is confirmed by diamond crystals micrographs "in situ" /Fig.2/. The crystals of carbides being present in the "metal shell" of diamond are oriented so, that they cannot provide carbon for the growth of the near face of the diamond crystal.

Perfect diamond crystals grow mainly by laminar mechanism. They are notable for their well-defined habitus and smooth bright faces. The depth of the growth layers is so small that their steps can be detected only using phase contrast, decoration or other very sensitive methods.

Diamond crystal faces are generally formed by polynuclear laminar mechanism. This is testified by the simultaneous formation of several macrolayers on the face. In the case of low carbon concentration the lines of growth layers are rounded, curvilinear or toothed in their form. The well-defined straight lines of growth layers are typical for the faces of diamond crystals grown in the systems with high carbon concentration (Fig.3).

The dislocations-induced spiral-laminar mechanism of diamond crystal growth is rather rare and occurs on {100} faces.

Type, number and position of the growth layers nucleation depend upon the degree of solution-melt supersaturation with carbon. With low degree of supersaturation the structural defects outcoming on the surface of cubic and octahedral faces become the nuclei, layer initiation occurs only at several points of the face. With higher degree of supersaturation the layer nuclei originated at the crystal apices and edges are numerous.

*The Figures are given at the end of the book

The linear growth rate of {111} and {100} faces varies with the supersaturation degree. At any stage of crystallization the change in the supersaturation degree results in overgrowing of some faces and in the origination and intensive growth of faces having been absent in the crystals before. In general case the relative growth rate of {111} faces increases with the degree of supersaturation.

Carbon supply to the growing crystal is found to be the limiting link in the process of diamond crystallization at high static pressures and temperatures. Temperature gradient is one of the factors influencing the carbon transfer in the melt. We have found that with the gradient of the order of 10 to 15 K/mm (which is characteristic for a number of systems presently used for tooling the reaction cell) the quantity of carbon being transferred is about 10^{-4} g/cm².

Increase in the rate of diamond crystals growth can be obtained using high pressure apparatus which provides the stable temperature of 1900-2100 K and higher. This problem is successfully solved methodically. A number of special materials is investigated, and the diamond crystals of good quality sized about 4 mm are obtained in the Mg-based systems. The rate of their growth is from 2 to 3 μ m/s.

Effect of metallic components of the reaction mixture. The growing diamond crystal selectively adsorbs the structural impurities by the faces of different simple shapes. Octahedron faces are more active in adsorbing the metal solvents and alloying elements than the cube faces /5/. Thus, the local X-ray spectrum analysis shows that the mass fraction of nickel impurities in <111> growth pyramids attains 0.08, while in <100> growth pyramids it does not exceed 0.007. Similar mechanism is observed for iron, the mass fraction of which in <111> growth pyramids attains 0.06. Electroactive boron inclusions are mostly accumulated in growth pyramids of octahedron faces.

Selective adsorption of impurities by different faces of the growing crystal results in typical sectorial-zonal structure of the diamonds being synthesized. Homogeneous crystals which poorly exhibit sectorial-zonal structure can be grown only in the case when a definite combination of P-T parameters is strictly kept during crystallization.

Denote two principal mechanisms for the formation of inclusions in diamond crystals /6/: entrapment of inclusions by apices (in the case of uniform supersaturation) and by edges (in the

case of nonuniform supersaturation along the edge length) and overgrowing of carbon-depleted melt at places where expanding layers meet and in the entrance angles of the toothed growth layers.

The crystal habitus, the morphological diversity of growth pyramids for habitus and secondary faces, nonuniformity of their properties and the pattern of metal inclusions distribution within the crystals synthesized are an indication of laminar and spiral-laminar mechanisms of growth (Fig.4*).

Using the principles of diamond growth one can reasonably take the physical conditions for synthesizing diamond crystals with required properties for modelling the synthesis process.

Mathematical model of diamond synthesis. Our paper submitted to the Xth AIRAPT International Conference contained mathematical model which describes time variations of electropotential, temperature and pressure fields that modify diamond crystallization zone in the reaction volume of HPA /7/, and takes no account of graphite-to-diamond phase transformation.

The present work gives results for diamond synthesis modelling taking account of interference of electropotential, temperature and pressure fields and diamond concentration. The reaction mixture is considered to be the mechanical mixture of the three components including graphite, diamond and metal solvent. Efficient physicomechanical properties of the mixture (thermoelastic, thermo- and electrophysical constants) are determined according to the mass concentration and properties of the components.

The complete system of calculations includes 20 equations describing the state of the model in the flow theory of plasticity with isotropic strengthening during high elasto-plastic deformations /8/, equation of nonstationary heat conductivity, equation of electric conductivity, kinetic equation for the rate of changes in the concentration of diamonds being formed (in the region where diamonds are stable and metal is melted) as a function of temperature, pressure and time, as well as seven equations describing efficient properties of the mixture as a function of components properties and concentration. Graphite-to-diamond transformation is described with allowance for changes in graphite and diamond concentrations made in equations for efficient properties. Allowance is also made for a sudden change in the reaction volume during phase transformations.

The first problem to be solved in proceeding with the calculation is that of the reaction cell cold compression during signi-

*The Figure is given at the end of the book

ficant deformation of the container by elastic dies. Subsequent is the solution of nonstationary related problem of electric and thermal conductivity and thermoplasticity with allowance for phase transition in the reaction cell. Consider the recent results of the calculation /9/. Determining the fields of temperature, pressure and density of heat sources one can predict the concentration of diamond crystals in the reaction volume at different moments of synthesis. Fig.5 shows the variation of temperature, pressure and diamond concentration with time at the three points of the reaction cell taken along its symmetry axis. The crystallization of diamonds initiates at the centre of the cell and then the region of their possible crystallization extends. Subsequent to crystallization initiation the two competitive phenomena develop: pressure increase due to the increase in temperature and elastic constants of the product being synthesized and pressure drop in the reaction cell due to the reduction of the space during graphite-to-diamond transformation. The first process prevails at the beginning of crystallization, while starting from a definite concentration the second one becomes predominant, this is shown pictorially in Fig.5.

Thus, choosing a mixture for the reaction cell and optimizing the operating P, T-conditions one can directionally carry out the crystallization of diamonds and other materials in process high pressure apparatus.

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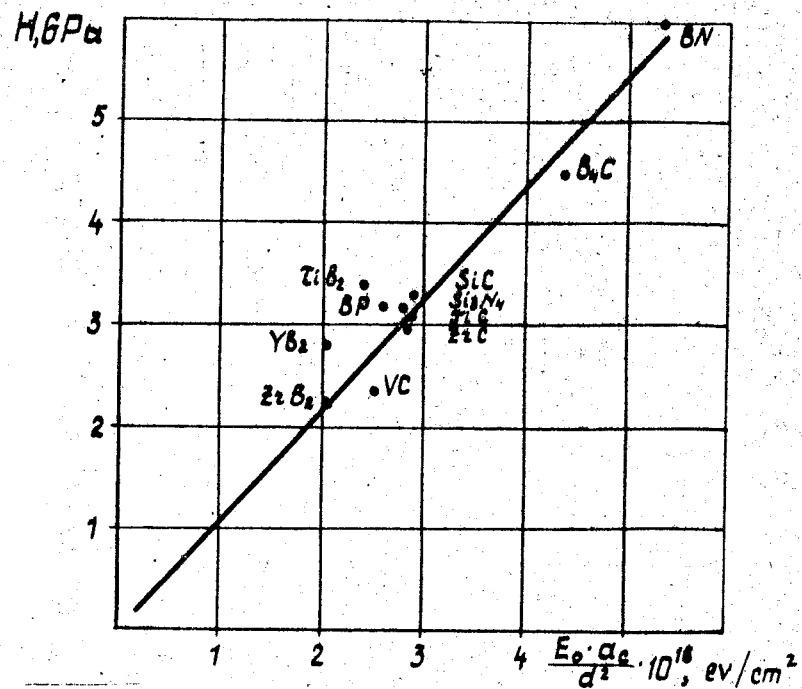


Fig. 1.
Microhardness of matters as a function of a rigidity parameter.

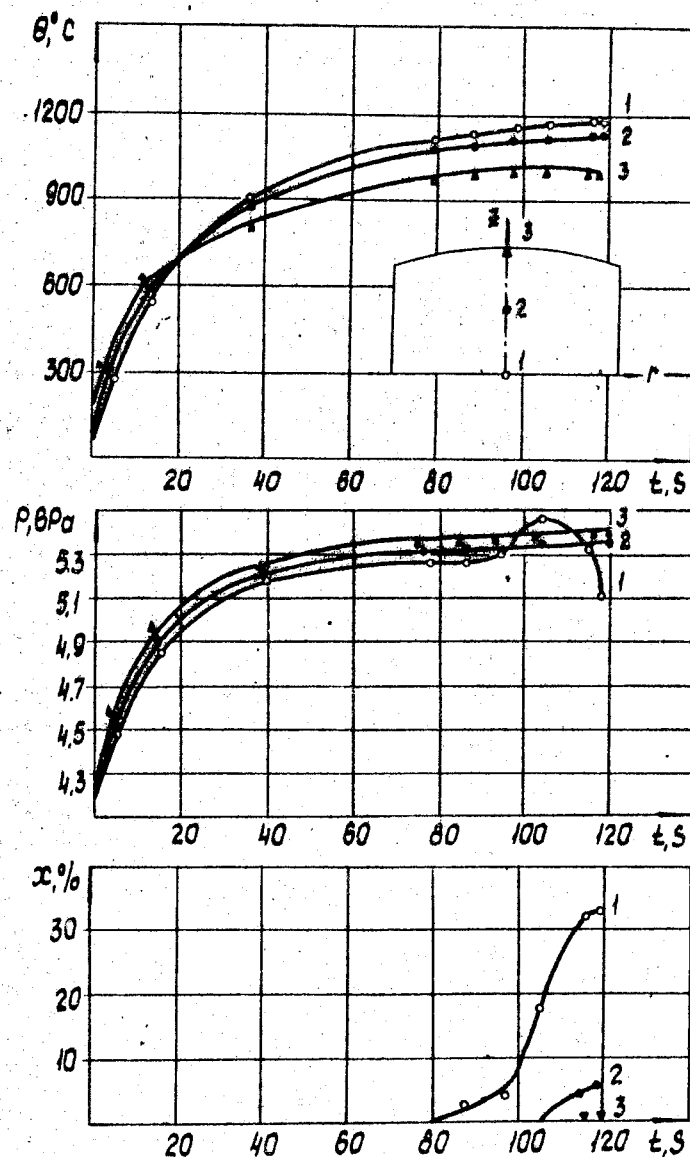


Fig. 5.
Variation of temperature Θ , pressure P and diamond concentration x with time of the synthesis t in different points of the reaction cell (1,2,3).

PRECISE DIAMOND MICROPOWDERS OF ASM-V, ASN-V TYPES

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In the development of up-to-date technique main importance is attached to materials reliable in extreme conditions. Diamond occupies a peculiar position among other superhard materials for tool production due to high Young's modulus and fracture ductility factor insuring longer preservation of tops and cutting edges parameters during working process.

Developed surface topography of crystals also plays a great part.

In spite of its undoubted advantages the traditionally produced diamond micropowders (d. m/p) have some essential defects reducing their unique properties. They are: needle and plate shaped grains in powders of finest classes, pointed crystals (Fig.1*), insufficient isometricity of crystals, inhomogeneity as to grain size, morphological and strength properties, sintering of fine classes, etc.

The above-mentioned defects reduce to a marked degree the effect of using diamond in finishing operations because deep notches appearing on workpieces surface are not acceptable for most applications. The notches are caused during fine finishing operations by pointed crystals, sinters and larger grains rising above the rest of crystals. The above-mentioned defects of m/p are due to the property of diamond to be crushed along cleavage planes forming elongated pointed grains. In traditional technology they are partially removed by prolonged form correction in ovalizers. At any operating conditions up to 2 % needle shaped crystals usually remain in the powder. The understanding of d. m/p defects nature and the fulfilled investigations have allowed to develop principally new technology of producing precise m/p of ASM-V, ASN-V types based on peculiar synthesis conditions of raw materials, crush treatment, m/p classification by closer standards, etc.

The method of treatment ensures intercrystalline separation along intergranular layers and transcrystalline fracture of defected crystals with stress concentrators.

*The Figure is given at the end of the book

In comparison with industrial marks, m/p ASM-V, ASN-V have neither needle and plate shaped grains nor grains with sharp tops with top angles less than 40°. Being more isometric (Fig.2) they ensure I-4 categories improvement of workpiece quality. Besides they are homogeneous by morphological and strength values. The developed ideas about the nature of crystal defectiveness allow to understand the problem of their wear in exploitation. Crystals having high initial strength are destroyed and have greater wear-resistance in comparison with less strong ones. While analyzing the character of reducing of the m/p abrasive properties it was found that most of the grain fractured in the first minutes of their using. These are defective grains with stress concentrators.

The serviceability of diamond grain during grinding is known not exceed 0.5-1.5 sec of continuous cutting in free state*. In the mass of grains diamond serviceability increases up to some minutes. Nevertheless, weak crystals grow fractured in first moments of operating but strong ones rise above causing notches on the surface. That's why the more homogeneous the crystals geometrical relief and strength are the better effectiveness of grinding and polishing operations can be achieved. The experimental studies have shown the corundum removal of 3 mg in the first minute made by traditional ASN-10/7 as compared with 7 mg made by ASN-V; besides the latter doesn't make notches and preserves its cutting properties for longer time. It is vitally important in lapping operations going on for minutes.

The experimental studies have been proved by profilograms of hard alloy TI5K6 surface after finishing with m/p of ASM 3/2 and ASN-V 3/2 types. The profilograms show higher quality and absence of notches for patterns being finished with precise ASM-V m/p.

The developed ideas about crystal defectiveness nature help to understand more clearly the physical essence of m/p's abrasive abilities. Owing to selective fracture of crystals with stress concentrators during crushing treatment the preserved crystals are the most strong and homogeneous in physico-mechanical properties.

The obtained experimental data convincingly prove the necessity of excluding the conditions of d. m/p defects appearance at the

*The Figure is given at the end of the book.

**Bond F.S. Crushing laws. In: Works of European Conference in Crushing. - M.: Technika. - 1966. - 325 p.

very beginning of producing process rather than elimination during their producing.

Wide industrial tests of precise diamond m/p ASM-V, ASN-V in finishing operations of materials with increased demands to surface quality (semiconducting materials, ceramics, jewelries, optical articles and others) have revealed the improvement of surface quality in I-4 categories, the 2-4 times increase of process efficiency the reducing of specific volume of diamond expenditure, the improvement of articles optical qualities, etc. e.g. when finishing jewelries with m/p ASN-V 7/5 they have revealed the cutting properties like to m/p ASN-20/I4, and surface quality was similar to that obtained by ASM 3/2 finishing.

When using precise m/p in cutting, grinding and polishing of semiconducting materials they are superior to traditional m/p in: serviceability by 2.7 times, surface quality in I+4 categories, efficiency by 1.5-2 times, etc.

Taking into account the above mentioned properties of precise ASM-V and ASN-V m/p proved by wide tests in industry, they can be recommended for finishing operations of workpieces with increased demands to surface quality both in the USSR and abroad.

THE DEFORMATION OF THE DIAMOND LATTICE UNDER PRESSURE

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Fields of residual lattice deformations present in a vast majority of crystals of natural and synthetic diamond and their changes observed in 50 crystals under [100] directed uniaxial compression up to 3 GPa have been studied in this work. Results obtained on some of the crystals are given in Tables 1 to 3.

Measurement of the lattice plane spacings $d_{\{113\}}$ ($\Delta d = \pm 1.10^{-6}$ nm) and $d_{\{220\}}$ ($\Delta d = \pm 3.10^{-6}$ nm) was made by the Kossel method when X-raying crystals in Fe K_{α} - and Co K_{α} - radiation. The tensor components of deformations ε_{ij} ($\Delta \varepsilon < 3.10^{-4}\%$) [1] were defined from the $d_{[hkl]}$ values measured in eight crystallographic directions. The value of the accumulated plastic energy of displacement W_p and that of distortion D were defined using the expressions given in [2].

Table 1. The lattice deformation in diamond crystals after the synthesis cycle

Cry- stal index	Growth system	Region of inte- rest	Deforma- tion ra- te $\sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2}$ %	Direction cosines of maximal defor- mation n_i	Angle bet- ween n_{max} and [111]
8A	Ni-Mn-C	whole crys- tal	0.152	-0.48 ; 0.87 ; -0.14	30.64
9	Fe-Co-C	same	0.068	0.46 ; 0.89 ; -0.03	37.51
32	Ni-Mn-C+ +B	<111> <100>	0.141 0.131	-0.80 ; 0.60 ; -0.02 -0.72 ; 0.69 ; -0.04	34.80 32.77

The analysis of the results obtained makes it possible to draw the following conclusions:

1. The residual deformations in lattices of natural and synthetic diamond crystals can amount to 0.15%, the crystals grown in systems containing alloying elements, the case when the growing faces can selectively absorb impurities, for example, boron, being characterized by different deformation rates in growth pyramids for various simple forms and in various zones of a single crystal.

Table 2. The lattice deformation under load in growth pyramids for various simple forms of 3D crystal (Ni-Mn-C growth system)

External load ΔG , GPa	Growth pyramid <100>			Growth pyramid <111>		
	principal deformation $\epsilon_1, \%$	principal axes (hkl)	displacement energy $W_g \times 10^5 J \cdot m^{-3}$	principal deformation $\epsilon_1, \%$	principal axes (hkl)	displacement energy $W_g \times 10^5 J \cdot m^{-3}$
before loading	-0.032 0.014 -0.010	010 001 100	0.116	Same as the corresponding values in the <100> growth pyramid within the measurement error		
0.56	-0.118 -0.092 0.055	1 0 0 0 1 0 0 0 9	7.261	-0.091 -0.053 0.040	1 0 0 0 0 2 0 2 9	4.177
1.45	-0.199 0.053 0.028	1 0 0 0 0 9 0 0 9	10.869	-0.171 0.072 0.026	1 0 0 0 0 0 0 0 9	8.196
1.68	-0.253 0.074 0.026	1 0 0 0 0 9 0 0 7	16.328	-0.265 0.076 0.015	1 0 0 0 0 5 0 4 5	16.533
1.91	-0.047 0.012 0.067	9 0 0 0 6 8 0 8 6	0.601	-0.035 0.012 0.006	9 0 2 2 5 6 2 8 6	0.363
2.78	-0.266 0.069 -0.055	9 5 0 0 0 1 5 9 0	4.807	-0.186 0.058 -0.035	9 5 0 0 0 1 5 9 0	4.787
after unloading	-0.064 -0.051 0.031	1 0 0 0 1 0 0 0 1	2.163	Same as the corresponding values in the <100> growth pyramid within the measurement error		

2. The uniaxial loading of diamond at room temperature results in elastic and plastic lattice deformations. The elastic deformations can amount to 0.25%. They can vary in different crystal zones. This is caused both by the nature and the rate of the initial residual deformation and the unequal elastic properties of various face growth pyramids.

3. The relatively slow rise of the deformation and the displacement energy in the diamond lattice with external load acting on crystal can alternate by their sharp decrease. The maximal change of the displacement stresses is observed in the [112]

Table 3. Displacement stresses in the (111) plane under {100} directed uniaxial compression of 8 $\bar{1}$ crystal

Growth pyramid	Displacement stress σ (hkl) under external load, GPa				Displacement direction
	1.55	1.67	1.96	2.38	
<111>	-1.69	0.16	-0.96	-1.51	[110]
<100>	-1.98	0.26	-1.11	-1.22	
<111>	-1.64	-0.06	-0.91	-1.46	[211]
<100>	-1.95	-0.09	-1.10	-1.26	

along (111), which is characteristic for the mechanical microtwinning.

4. The compression within the entire range of loading leads to the change of the crystal distortion. After unloading the crystal distortion can assume values both higher and lower compared to the initial one. However, in all the cases when after the compression the stress relaxation occurs the crystal distortion lowers. The decrease of the differences in the distortion levels of growth pyramids for various simple forms of a single crystal suggesting the lowering of the displacement stresses can be explained by the relaxation of stresses in the diagonal interlayers (the composition planes of {111} and {100} face growth pyramids).

5. The uniaxial compression of crystals at room temperature and pressure above 1.5 GPa leads to the plastic lattice deformation in diamond which can amount to 0.2% at 3 GPa. The external load removed, the crystals reveal residual compressive deformations that differ from the initial residual ones. At that, the change is observed not only in the values of deformations but in their orientation as well.

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WURTZITE-LIKE BORON NITRIDE AS A BASE FOR NEW PROGRESSIVE SUPERHARD MATERIALS

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The use of explosion technology for the production of the wurtzite-like modification of boron nitride [1], allowed to solve not only the problem of mass manufacturing of this important superhard material but also to provide its granulometric composition (grain size less than $1 \mu\text{m}$) and corresponding structural changes and presence of defects (dislocation density about 10^{12} cm^{-2}) which served as a base for creating of superhard polycrystal shock resistant materials for cutting and abrasive tools by means of superhigh pressures technique. The first information of this new in essence ability of the superhard material was published during 1971-1973 in the USSR in some works concerning PTNB (polycrystal hard BN) and Hexanit-R [2,3].

Hexanit-R is double-phase material with wurtzite-like and sphalerite-like nitride structure intended for use in cutting tools and has physical and mechanical properties not worse than that of superhard polycrystal materials based on cubic (sphalerite) boron nitride, and this material even exceeds them with such important characteristic as bending strength (Table, data of authors of developments are given) As a result of special investigations accomplished by IPM [4] it was shown that cracking resistance of superhard materials on the base of wurtzite-like boron nitride (Hexanit-R, PTNB) ranges from 15 to 18 $\text{MPa/m}^{1/2}$, while superhard materials based on cubic boron nitride have had it on the diamond level, i.e. 6 $\text{MPa/m}^{1/2}$.

Fig.1(a,b) shows the wear of cutters of Hexanit-R with different phase composition depending on operation time in continuous (a) and discontinuous (b) cutting (HVG steel with HRC 60-62, groove - 4 mm, $V=80 \text{ m/min}$, $S=0.07 \text{ mm/rev}$, $t=0.2 \text{ mm}$).

The corroboration of high impact resistance of tools based on wurtzite-like boron nitride compared with tools based on its cubic modification is direct comparative test of Hexanit-R and its nearest analogs during treatment of parts of HVG steel with

To the paper: Zharikov V. A., Persikov E. S., Bukhtiyarov P. G., Pol'skoy S. Ph. «Physico-chemical properties of fluid-magmatic systems at high temperature and hydrogen pressures».

Fig. 2. Concentration thermo-capillary convection (Marangoni's effect [3]) in the model melt $\text{Di}_{57}\text{An}_{43}+10 \text{ wt\%}$ of PbO (diffusion experiment, $P_{\text{H}_2} = 20 \text{ MPa}$, $T=1300^\circ\text{C}$, $t=5 \text{ min}$, isobaric quenching): 1 — convectational flows, enriched in reduced Pb; 2 — starting (which has not reacted with H_2) melt.



To the paper: Novikov N. V. «Superhard materials are the promising product of high pressure technology».

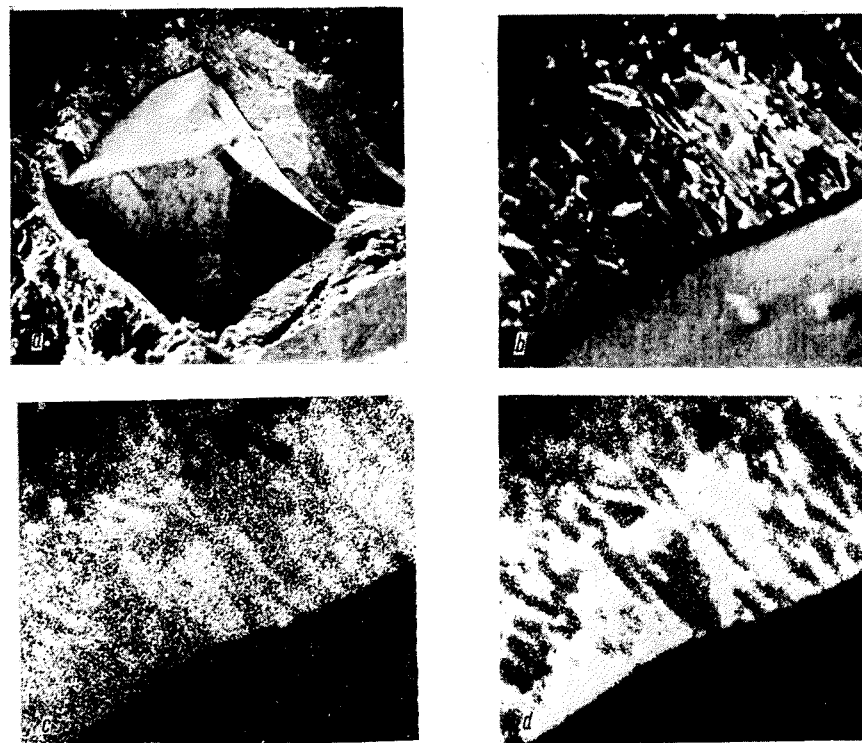


Fig. 2. Diamond crystal «in situ»: (a, b) — reflected electron image ($\times 50$; $\times 250$, respectively); (c, d) — characteristic $\text{MnK}\alpha$ and $\text{NiK}\alpha$ images ($\times 250$).

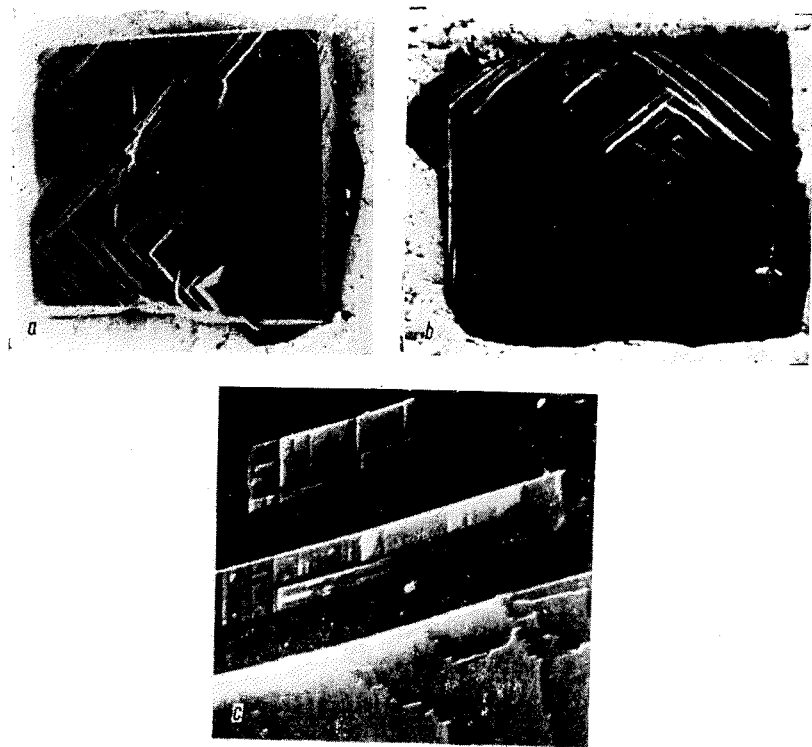


Fig. 3. Surface of synthetic diamond crystal faces, grown in high supersaturation. $\times 180$ (a, b), $\times 1500$ (c).

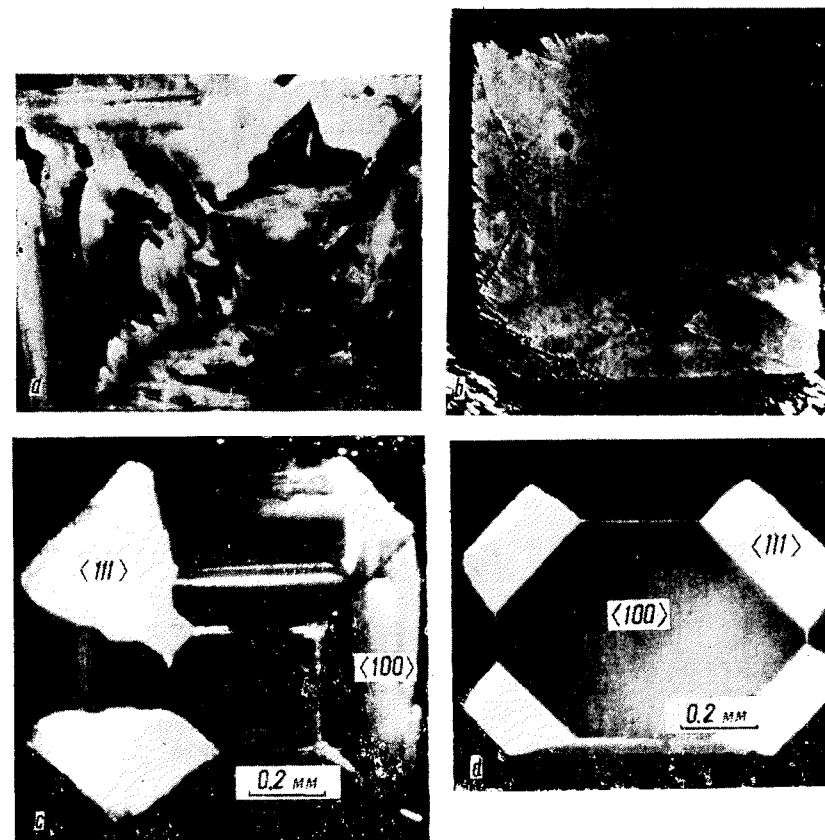


Fig. 4. Location of metallic inclusions in diamond crystals: (a) inside the growth pyramids ($\times 680$); (b) in the diagonal layers ($\times 100$). (c, d) Forms of the growth pyramids of cube and octahedron faces ($\times 75$).

To the paper: Trefilov V. I., Samoilova L. M., Milman Yu. V., Baraban V. P. «Precise diamond micropowders of ASM-V, ASN-V types».



Fig. 1. ASM 10/7 pointed crystal, 5000X1.5.

Fig. 2. ASM-V 10/7 single crystal, 10000X.

To the paper: Kushtalova I. P., Stasyuk L. F., Radić S. M., Ristić M. M. «The influence of high pressures on titanium-carbon reaction».

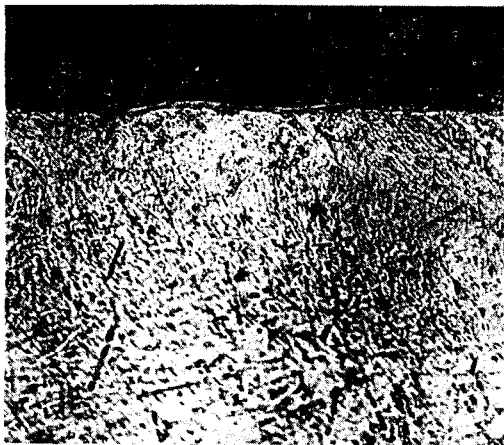
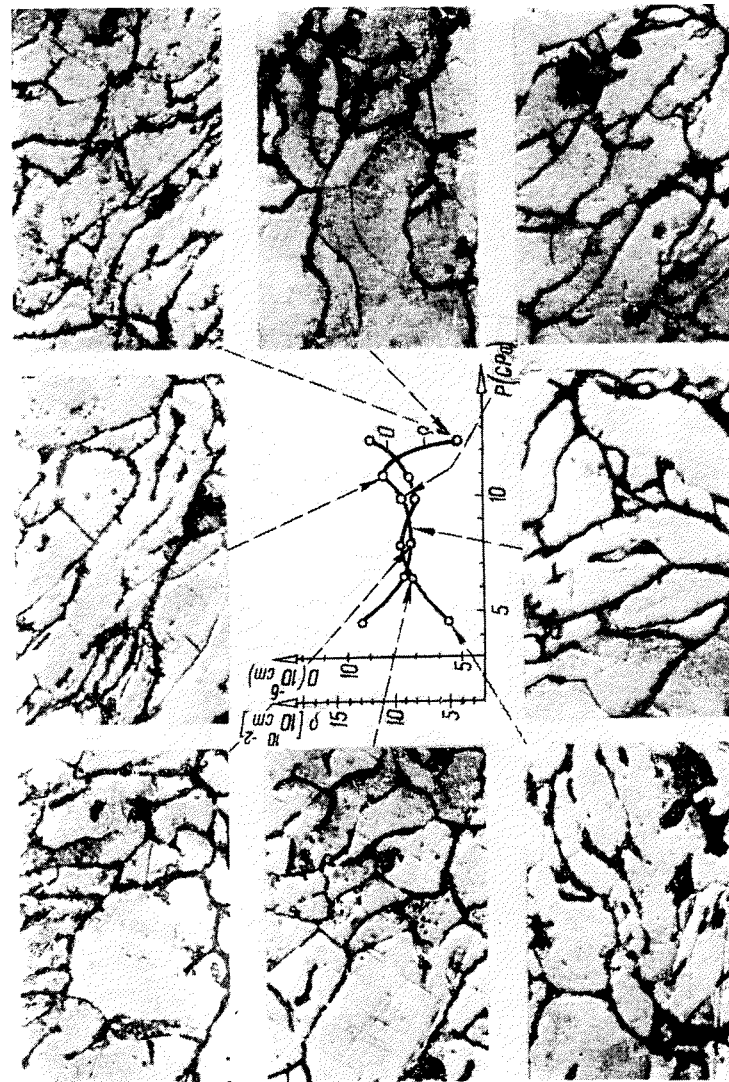


Fig. 1. A structure of graphite-titanium border under pressure of 1.0 GPa and at temperature 1673 K (X500).

To the paper: Stefanović D. Č., Djurić M., Petrović V., Dukić Z., Ristić M. M. «The investigation of cold sintering of iron powder».



The microstructure of samples and dependence of dislocation concentration (ρ) and the microcrystalline size (D) on pressure.

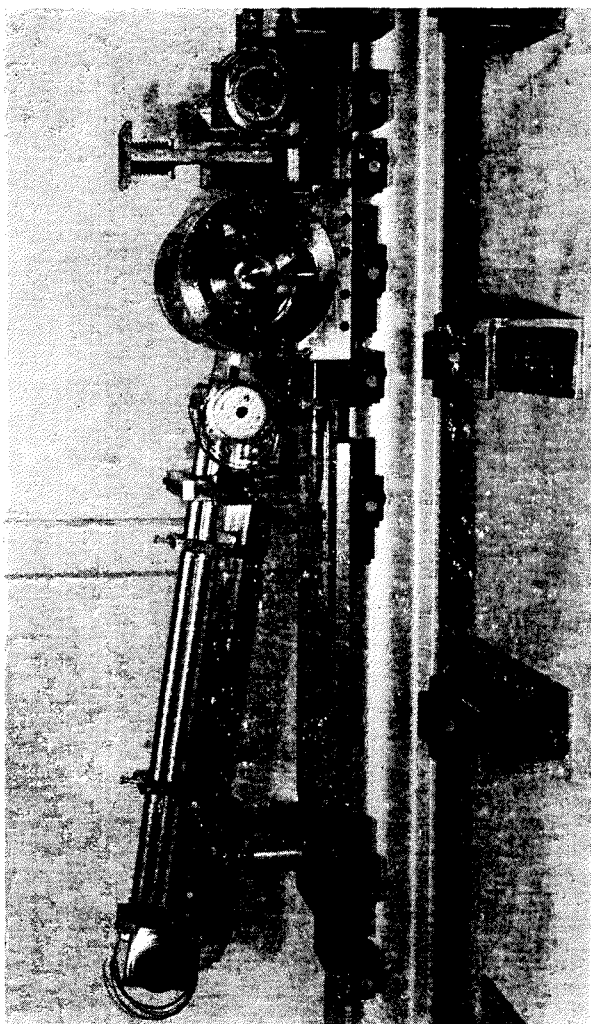
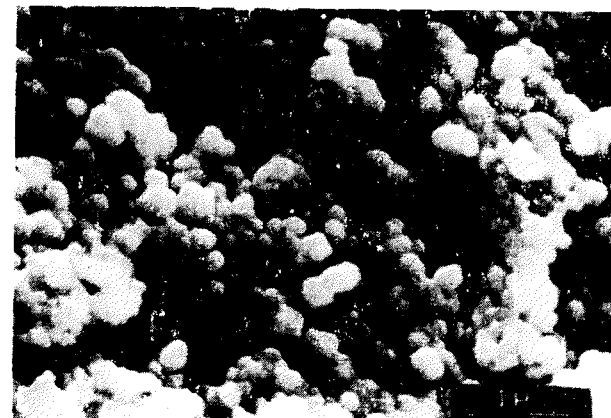


Fig. 1. The diffractometer and the high pressure cell. The diffractometer is designed to operate at a fixed scattering angle 2θ between 6° and 10° . Two tungsten carbide slits located on the right-hand side of the 15 cm diameter steel jacket limit the horizontal and vertical divergences of the incident beam. The cell itself is in position inside the jacket with one of its anvils removed and displayed in the foreground. The vertical divergence of the diffracted beam is controlled by two 50 cm long molybdenum parallels which can be seen on the left of the cell assembly between another pair of tungsten carbide slits. The pair located furthest from the cell limits the horizontal divergence and the other acts as an anti-scatter slit. All slits are motorised for remote control.

To the paper: Gorobtsov V. G., Krot O. I., Sanko Yu. P. «Effect of the consolidation process of powder bodies under extreme conditions on their structure and properties».



Surface fracture of TiN specimen, produced under high-rate loading conditions.

To the paper: Dobromyslov A. V., Dolgikh G. V., Talutz G. G. «The influence of pressure on the crystallography of fracture of molybdenum single crystals of high purity».

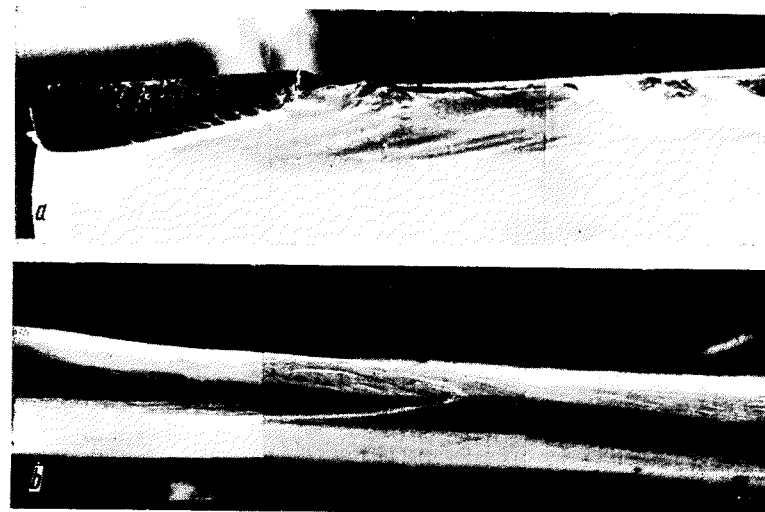


Fig. 4. Macroscopic fracture surfaces of the single crystals, tested at $P=800$ MPa: a — $\zeta=18^\circ$; b — $\zeta=52^\circ$ ($\times 130$).

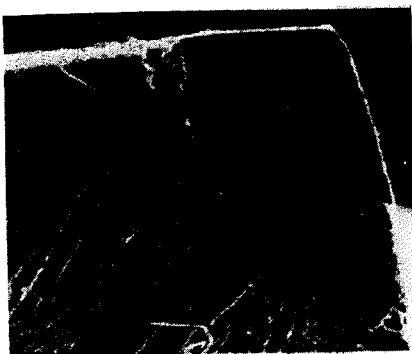


Fig. 5. Example of slow crack initiation sites in specimen, tested at $P=800$ MPa ($\times 500$).

To the paper: Teplov V. A., Taluts G. G., Tupitza D. I. «Phase transformations in iron alloys under pressure».

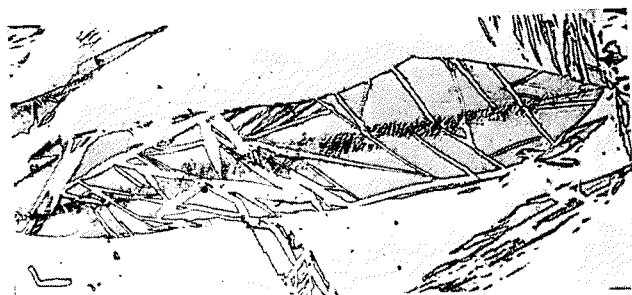


Fig. 2. Martensite crystals with austenite plates of bcc-fcc transformation induced by static pressure of 8 GPa at 20°C ($\times 500$).



Fig. 3. Martensite crystals with austenite plates of bcc-fcc transformation induced by dynamic pressure of 13 GPa ($\times 500$).

HRC 60-62, groove - 4 mm ($V=80$ m/min, $S=0.07$ mm/rev, $t=0.2$ mm).

Tools of Hexanit-R (cutters, milling cutters) have been introduced into production and are produced by series. The main field of their application is treatment of hardened steels and cast iron with hardness HRC 40-65 both in discontinuous and continuous cutting regimes.

Physical and mechanical properties of superhard materials

Material	Density, g/cm ³	Knoop microhardness, GPa	Elastic modulus, GPa	Compression strength, GPa	Bending strength, GPa
Diamond	3.515	68-94	1160	8.7	0.29
BN cube	3.45-3.47	47	720	5.0	-
Elbor-R	3.31-3.39	34	665-885	1.9-2.1	-
Hexanit-R	3.41-3.44	47	720-820	3.0-4.0	1.2
Amborite	-	40.5	680	-	0.57
Sumiboron	4.2	30-33 (Vickers)	-	-	-

The abrasive version of Hexanit-R characterized by stable predominance of sphalerite constitute have been given the commercial name of Hexanit-A and intended mainly to production of grinding wheels.

Hexanit-A is manufactured mainly in the form of powder with graininess 1000/800-50/40 μm and is characterized by high strength of grains. In addition, Hexanit-A proves to be the only superhard material based on boron nitride able to take itself to perform not only sharpening but also coarse grinding and roughing operations with possible minimal surface roughness.

Abrasive wheels of Hexanit-A with BST organic binder and WVIK metallic binder developed by IPM are introduced into production and manufactured by series.

The sharpening of high speed steel tools by means of Hexanit-A wheels ensures high productivity and good quality of treated surface. Compared with Elbor and synthetic corundum wheels the efficiency of Hexanit-A wheels increases from 1.5 to 2 times and service life of sharpened tools increases from 1.5 to 2.5 times.

Thus, superhard materials based on wurtzite-like boron nitride does not practically yield to superhard materials based on cubic boron nitride and even exceed them in such important pro-

property as impact strength which allows to hope for further widening of application field of superhard materials based on boron nitride.

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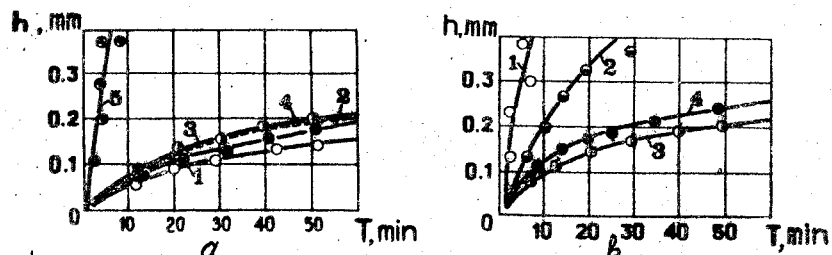


Fig.1. Wear of cutters of PSTM type Hexanit-R (diameter 9 mm) with different phase composition depending on operation time: a - continuous cutting (1 - 98, 2 - 80, 3 - 60, 4 - 40, 5 - 20 weight per cent of BN_{sph}); b - discontinuous cutting (1 - 98, 2 - 80, 3 - 60, 4 - 40 weight per cent of BN_{sph} , 5 - fracture during fixing PSTM).

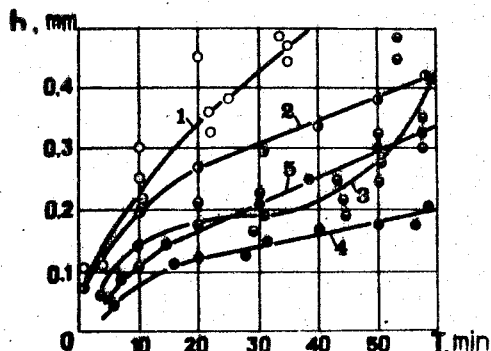


Fig.2. Results of comparative tests of Niborit (1), Kiborit (2), Sumiboron (3), Hexanit-R (4) and Amborite (5) in discontinuous cutting condition.

CBN SYNTHESIS IN THE TERNARY SYSTEM B-N-Mg

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$\text{hBN} \rightarrow \text{cBN}$ conversion has been studied using Mg_3N_2 , Mg and MgB_2 as catalysts and two kinds of hBN powder with different amounts of B_2O_3 : type A (0.7%) and type B (4%). By means of X-ray diffraction the main phases formed in the sample and the impurity phases in the cBN crystals have been identified. The emission spectrometry has been used in measuring the amount of Mg in the crystals. From the experimental data, the probable reactions occurring in the BN-catalyst- B_2O_3 systems are discussed. The impurity level in the cBN crystals appears to be related to the B_2O_3 amount in the hBN starting material.

Studying $\text{hBN} \rightarrow \text{cBN}$ conversion in the BN-Mg system, Endo et al./1/ revealed the formation of the ternary compound $\text{Mg}_3\text{B}_2\text{N}_4$ and presumed that cBN crystals precipitated from the liquid-phase solution $\text{BN-Mg}_3\text{B}_2\text{N}_4$. Eliutin et al. /2/ also found $\text{Mg}_3\text{B}_2\text{N}_4$ in the BN- Mg_3N_2 system and furthermore they revealed two phases of this compound - α and β - which decompose releasing cBN.

MgB_2 has been also used as catalyst in the cBN synthesis /3/, but the reaction mechanism has not been explained. At normal pressure MgB_2 is known to be unstable over 800 °C, forming MgB_4 and releasing Mg. Therefore, the cBN synthesis mechanism in the BN- MgB_2 system might be considered to start with the Mg release. In this paper, it is shown that this hypothesis is not valid because the thermal stability of MgB_2 markedly rises at high pressures.

According to Endo et al./4/, the activity of the catalyst-solvent $\text{Mg}_3\text{B}_2\text{N}_4$ is reduced by the presence of oxygen in the hBN starting material. Sato et al./5/ noticed a decrease of the cBN yield as well as typical features in the crystal morphology and surface because of MgO precipitation. The present authors have found that the B_2O_3 amount in hBN determines the impurity level of the cBN crystals.

The samples were prepared from a mixture of hBN and catalyst powder. Using three catalysts (Mg_3N_2 , Mg and MgB_2) and two kinds of hBN (type A with 0.7 % B_2O_3 and type B with 4 % B_2O_3), six types of reaction systems were obtained.

The synthesis experiments were performed at pressures between 3.7 and 5.2 GPa and temperatures between 1300 and 1600 °C. The samples were kept under preestablished pressure-temperature conditions for 20 minutes.

In order to identify the phases, X-ray diffraction analyses were made both on the samples and on the cBN crystals. A plasma emission spectrometer was used to measure the Mg amount in the crystals. With this purpose, crystals of the same size, synthesized under the same pressure-temperature conditions were selected.

Results and discussions

a) The ternary compound $\text{Mg}_3\text{B}_2\text{N}_4$ is the main phase formed in the BN- Mg_3N_2 reaction system, in a large quantity which rises with the temperature by the reaction:



In the X-ray diffraction patterns, both at 1300 °C and 1600 °C, the lines of the α phase reported by Eliutin /2/ were predominant.

b) In the BN-Mg system the main reaction product is MgB_2 . The lines of α - $\text{Mg}_3\text{B}_2\text{N}_4$ were also identified. The probable reaction occurring in this system is:



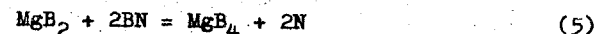
c) In the reaction system BN- MgB_2 , the ternary compound $\text{Mg}_3\text{B}_2\text{N}_4$ was not found. In the X-ray diffraction patterns, the lines of MgB_4 appeared together with the lines of the starting MgB_2 which are strong even at a ratio $\text{MgB}_2/\text{hBN} = 1/9$. The following reaction may virtually occur with a very small rate:



If reaction (3) takes place, it results that the same mechanism

controls cBN formation in all the three systems: BN- Mg_3N_2 , BN-Mg and BN- MgB_2 .

The formation of MgB_4 may also be explained by the reactions:



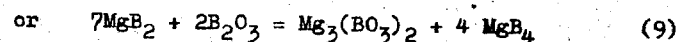
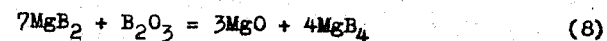
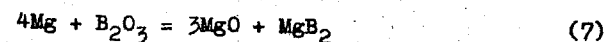
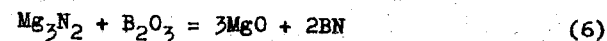
Our X-ray diffraction analyses made on MgB_2 samples processed at 4.7 GPa and 1600 °C for 20 minutes revealed that less than 10 % of MgB_2 decomposes under such conditions. The quantity of Mg released from the reaction (4) is too small to account for a shift toward BN-Mg system. The possibility of cBN synthesis using MgB_2 is not related to the pyrolysis reaction (4).

Due to the weak reactivity of MgB_2 with BN, experimentally observed, it follows that reaction (5) is more probable than (3), which requires a greater amount of MgB_2 . If reaction (5) is a reversible one, it appears as a possible mechanism for cBN synthesis in the BN- MgB_2 system. Further investigations are required to clarify this problem.

d) MgO was formed in all the reaction systems, but in a larger quantity when hBN type B was used as starting material. In the hBN type B - MgB_2 system, MgO was formed together with $\text{Mg}_3(\text{BO}_3)_2$.

X-ray diffraction on the cBN crystals has proved that MgO is the only impurity phase when Mg_3N_2 is used as catalyst. MgB_2 and MgB_4 appear as impurities in the crystals obtained in the BN-Mg and BN- MgB_2 systems.

The following reactions for catalyst oxidation take place:



Due to its crystal structure, similar to that of cBN, MgO can be entrapped in the cBN lattice, and the other products MgB_2 and MgB_4 are brought with it. It results that the impurity level

in the cBN crystals is related to the B_2O_3 amount of the hBN starting material. This is proved by the values of Mg content in the cBN crystals. This values are given in Table.

Impurity phases and Mg content in cBN crystals obtained at 5.2 GPa and 1600 °C

hBN	Starting materials	Crystal colour	Impurity phases	Mg content (%)
A	Mg ₃ N ₂	white	MgO	0.4
A	Mg	brown-grey	MgO, MgB ₄ (weak)	0.8
A	MgB ₂	dark-brown	MgO, MgB ₂ (weak)	1.0
B	Mg ₃ N ₂	white-yellowish	MgO (strong)	2.2
B	Mg	brown	MgO (strong), MgB ₂ (weak)	4.1
B	MgB ₂	black	MgO (strong), MgB ₄ (very weak)	3.0

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THE STRUCTURAL TRANSFORMATIONS OF DIFFERENT FORMS OF BORON NITRIDE AT THE PRESSURES UP TO 10 GPa AND TEMPERATURES

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It was investigated the behaviour of two different types of starting graphitic boron nitride: a random-layer lattice form (BN_t) and an ordered-layer lattice form (BN_{ord}) in the pressure range 5 - 9 GPa and temperatures 500 - 2500K.

The diffraction pattern of BN_t has two diffuse maxima corresponding to (002) with $d_{002}=0,356$ nm and (10). The data for BN_{ord} are: $d_{002}=0,3336$ nm, G.I.=1,2, where G.I. is the "Graphitization Index" showing the degree of three-dimensional ordering of the structure, $G.I.=\frac{I_{100}+I_{101}}{I_{102}}$ [1]. The impurities (Mg, Ca, Si and C) did not exceed 0,03 wt.%(each) in BN_t and 0,1 wt.%(each) in BN_{ord} (by spectroscopic analysis). After the treatment (5 GPa, 1550K, 15 min) the content of the impurities was increased to 0,6 wt.%(each). BN_t contained water not more than 3 wt.%. The average size of the grains of BN_t was 10 nm, and that of BN_{ord} was 5 μ m. Details of the experiments are described elsewhere [2]. X-ray powder diffraction (DRON-2) was used for the examination of the products after P-T treatment.

Fig.1 shows the P-T conditions (at 15 min) for the formation of cubic phase (BN_c) starting from BN_t and BN_{ord} . The initial pressure of direct transformation to BN_c is 6 GPa for two types of the material. The initial temperature differs depending on the starting material: 1200K is from BN_t and 1800K is from BN_{ord} . In the case of starting from BN_t the wurtzite form (BN_w) is absent in the products. The BN_{ord} transforms to BN_w within the temperature range 500-1800K

According to data of electron microscopy (N.F. Borovikov, IFVD) the BN_c crystals from the starting BN_t have very small size about 5 nm (at initial P-T conditions) and tetrahedral habitus. The activation energy (E_a) of BN_c formation from BN_t is about 50 kkal/mole. It was determined from the kinetic curves of equal yield (25 wt.%) of BN_c as a function of different times (variation in time were from 15 s to 90 s, across 15 s, and 120 s, 300 s, 900 s) at temperatures of 230K, 1350K and 1500K at the pressure of 6,5 GPa. According to [4] the E_a of the direct transformation to BN_c from BN_{ord} (or BN_w) was about 200 kkal/mole at 6,5 GPa. This is very large value which corresponds to the energy of vaporization.

The structural changes of BN_t precede the BN_c formation both on temperature and pressure. It is observed a discontinuous reduction of d_{002} from 0,356 nm to 0,329 nm (d_{002} for BN_{ord} is 0,3336 nm), Fig.2. The kinetic curves of the d_{002} changes have minimums. Value and position of the minimums depend on the temperature. The comparison of Fig.2 and Fig.3 shows that two identical values of d_{002} correspond to different the G.I. values at the same temperature. It means that for BN_t only the reduction of d_{002} isn't a measure of structural perfection. The process of a three-dimensional ordering commences at 50K (900 s) and with increasing temperature the process is accelerated, Fig.3. The E_a of the ordering process is about 35 kkal/mole.

After analyzing all the data the following conclusions emerge. In the case of starting BN_t the activation energy of the direct transformation to BN_c is four times less than from BN_{ord} . The ordering process of BN_t takes place in P-T conditions preceded to BN_c formation, however, the BN_w phase is absent in products. It is possible that in the case the starting BN_t the formation of BN_c begins from intermediate structural state (between BN_t and BN_{ord}).

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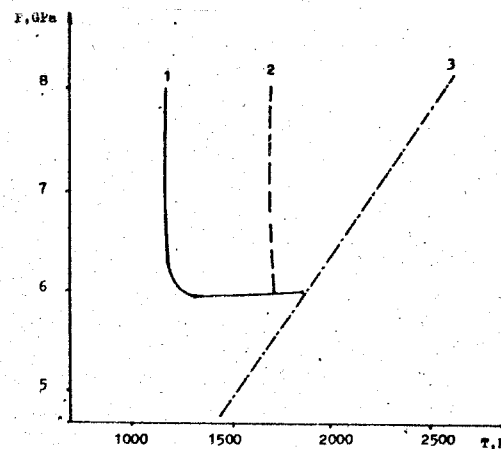


Fig. 1.
The P-T conditions for initial formation of cubic BN (25 wt.%) from the starting turbostratic BN (line 1) and from the starting three-dimensional ordered BN (line 2); line 3 - an equilibrium line [3].

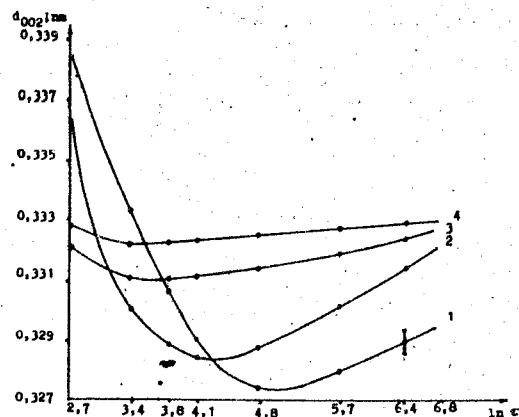


Fig. 2.
Dependence of interlayer spacing (d_{002}) of the starting turbostratic BN on $\ln$ of the time (time in seconds) for four temperatures: 950K (1), 1150K (2), 1500K (3), 1700K (4) at 5 GPa.

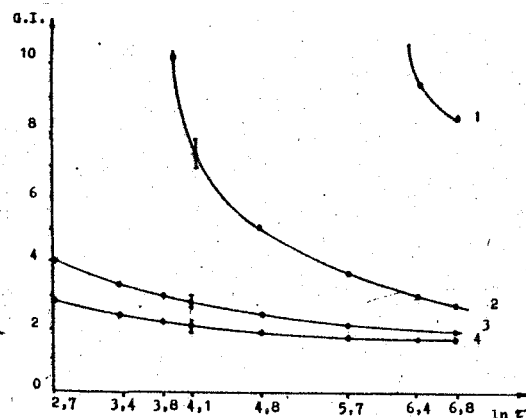


Fig. 3.
Dependence of the "Graphitization Index" (G.I. value) of the starting turbostratic BN on $\ln$ of the time (time in seconds) for four temperatures: 950K (1), 1150K (2), 1500K (3), 1700K (4) at 5 GPa.

THE STRUCTURE FAULTS OF GRAPHITE-LIKE BORON NITRIDE AND PHASE TRANSFORMATIONS

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The investigation of the structure changes of HBN having different degree of ideal structure under high pressure and high temperature conditions was made in this study.

Experiments were made in the high pressure apparatus (HPA) "toroid" type. The sample temperature was determined by means of calibrated curve. The pressure was fixed in each test. The time of thermotreatment is one minute. The starting HBN tablet was placed into molybdenum container for the diffusion of container material into the sample to be excluded.

The boron nitride with the structure from high crystal to turbostratic was used as a starting material (Table I). The impurity of boron oxide in the samples was absent, the common oxygen content being less than 1.3 wt.%.

Table I. X-ray structure characteristics of starting HBN samples

Sample number	"C", nm	GI	γ , %	10^3 rad.		D, nm		
				(101)	(102)	(100)	(110)	(002)
1	0.6667	2.0	3.0	0.7	0.8	25.2	26.9	19.6
2	0.6673	6.6	3.4	1.4	1.0	28.4	29.2	22.6
3	0.6683	9.7	4.4	5.4	1.1	28.0	28.4	19.3
4	0.6698	20.1	7.9	7.5	3.5	25.8	27.4	16.2
5	0.70	∞	-	-	-	14.9	16.4	5.0

It was determined in this work that the concentration of the turbostratic stacking faults increase in the course of increasing of the treatment temperature and pressure under the high pressure conditions (Fig.1). It was established that the breadth of (101) and (102) reflections, connected with stacking faults - β_{101} and β_{102} has the same tendency as one of γ when the change of pressure and temperature take place. It was discovered that the concentration of the turbostratic stacking faults for the sample No 2 has the least changes (Fig.2), the least values of β_{101} and

β_{102} are characteristic for this sample. The comparison of the ratio β_{101}/β_{102} values for the samples with the equal concentration of the turbostratic stacking faults showed that the concentration of the polytype stacking faults, seems also to increase when the treatment temperature and pressure increase.

The sizes of CDR along normals to (100) and (110) do not practically change when D_{002} has the same decreases when the treatment temperature increases.

The GI change did not allow the simple regularity of the samples behaviour under the influence of pressure and temperature to be found.

The "C"-parameter does not change in practice with the treatment temperature increasing under the pressure 4.2 GPa. The increasing of "C"-parameter is observed when the temperature increases under the pressure 5.0 GPa and 6.8 GPa.

The investigation of the starting point of CBN formation from the samples of HBN having different degree of ideal structure showed that this dependence had an extremal character with the maximum at starting sample "C"-parameter is 0.6673 nm. Such result together with the data concerning the character of β_{101} , β_{102} , γ changes gives us an opportunity to draw the conclusion that the "intermediate" structure of the sample No 2 has the greatest stability under high pressure conditions.

The change of the turbostratic boron nitride structure was studied (Table 2). It was stated that "graphitization" temperature of the turbostratic boron nitride containing the admixture of B_2O_3 coincides with the melting-point of boron oxide.

Table 2. Change of turbostratic boron nitride GI

No	Experimental conditions		Impurity content, wt. %		GI
	P, GPa	T, K	B_2O_3	$[O_2]_{com.}$	
1	4.2	1770	-	5.0	20.6
2	5.0	1770	-	5.0	4.0
3	6.8	1770	-	5.0	1.9
4	5.0	1070	5.0	8.5	∞
5	5.0	1270	5.0	8.5	2.6
6	5.0	1770	5.0	8.5	1.8
7	4.2	1770	-	less than I	∞

It was determined in this work that the disorder of the starting HBN structure for any kind of starting material occurred in the thermotreatment process taking place under high pres-

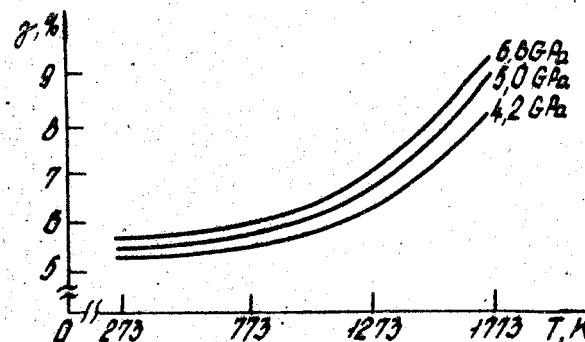


Fig. 1. Dependence of the turbostratic stacking faults concentration on the temperature of the treatment for sample No 1 at different pressures.

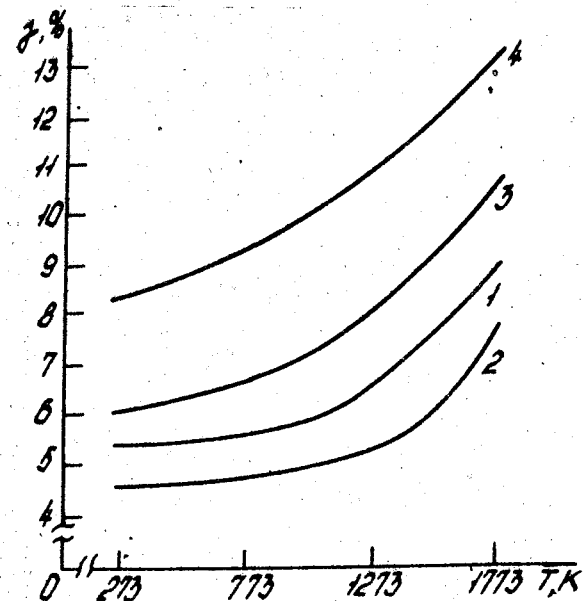


Fig. 2. Dependence of the turbostratic stacking faults concentration on the temperature for different starting HBN samples at the thermotreatment at 5.0 GPa.

sure. It was shown that "graphitization" of turbostratic boron nitride depends on the presence of oxygen impurity in the sample and its connected with the appearance of boron oxide fluid phase. It was confirmed that the HBN with "C" = 0.6673 nm has the greatest temperature of beginning formation of CBN. It was supposed that this structure has maximum stability under high pressure and temperature conditions. The data obtained suppose the possibility of the transformation of high crystal boron nitride into wurtzite-like boron nitride by martensit way, while lower crystal structure reconstructs into CBN.

SPECIAL THERMOPHYSICAL FEATURES OF DIAMOND AND CUBIC BORON NITRIDE AND THEIR APPLICATION IN SCIENCE AND TECHNOLOGY

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Recent progress in technology substantially extended the scope of superhard materials application. Ever more frequent in many cases is the essential part performed by thermophysical properties. This is primarily true of diamonds and cubic boron nitride (CBN). The data given promote our knowledge of these properties as obtained on separate single crystals.

Thermal conductivity (λ) was measured by the method of heat flow constriction /1/. Listed in Table 1 are representative values of λ for type II a natural diamonds in the range of 300 to 700 K and extrapolation to 1000 K from experimental data /2/ completed with other measurements on single crystals of this type. λ for type Ia diamonds is greatly influenced by nitrogen impurity. Many single crystals showed a correlation between λ at 300-320 K and IR-absorption index at 1175 cm^{-1} thoroughly investigated in /3/. This correlation was not observed in synthetic diamonds. The interrelation was only traced between the mean values of λ and the mean nitrogen concentrations within the limited range of concentrations for the groups of synthetic single crystals obtained in the Institute.

Specific heat C_p for IIa, Ia and Ib types of natural and for synthetic diamond single crystals was measured in the range of 300-700 K using DSC-III differential scanning calorimeter (Setaram) /4/. Temperature dependence of C_p reveals no special features and diamonds of different types showed no differences outside the limits of C_p error (2 to 5%) (see Table 2). The Debye temperature (θ) was evaluated from C_p data (setting $C_p \approx C_v$). Different types of single crystals show slight difference in θ values, so one may assume $\theta = (1900 \pm 25) \text{ K}$.

λ for separate single crystals of kibur-type CBN was measured for the first time /5/. The maximum size of specimens attained 500 μm , their depth being 100-200 μm . The data for nine sin-

gle crystals of CBN are listed in Table 3. Difference in λ can be specified by both morphological features and different concentration of centers modifying sectorial colouring of single crystals.

C_p in the range of 300-900 K /6/ was determined for kibar powder with the grit size of 125/100 that comprises specially selected identical single crystals, see Table 4. From these data the Debye temperature for kibar has been evaluated, $\theta = (1680 \pm 70)$ K.

Experimental values of λ and C_p for the same specimens are known to give their thermal diffusivity, so essential thermophysical characteristics were found for diamond and CBN single crystals.

Thermal conductivities at 300-320 K were measured on home and imported polycrystals of diamond and CBN /7/ (see Table 5).

Natural diamonds are used in different branches of science and technology, the most frequently they are used as heat sinks for solid-state electronics, rare and expensive type IIA natural diamonds are the best heat sinks. Recently developed synthetic diamonds with $\lambda = 1800-2000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at 300 K /8-9/ seem to be competitive with type IIA naturals, they are used as heat sinks not only for microelectronics, but also for other devices requiring efficient heat removal.

High-thermally conductive polycrystalline diamond and CBN are also promising in various heat removing substrates.

Table 1. Thermal conductivities of type IIA natural diamonds

T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
300	2020	450	1200	600	800	800	485
350	1665	500	1035	650	700	900	365
400	1400	550	900	700	615	1000	275

Table 2. Specific heat of diamond single crystals

T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
300	515	450	980	600	1285
350	680	500	1090	650	1405
400	845	550	1190	700	1495

Table 3. Thermal conductivity of CBN single crystals

No	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	No	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$	No	T, K	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
1	311	416	4	306	645	7	307	472
2	309	582	5	307	768	8	312	542
3	306	476	6	308	467	9	316	490

Table 4. Specific heat of kibar

T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$	T, K	$C_p, \text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$
300	662	500	1269	700	1530
350	863	550	1332	750	1570
400	1022	600	1416	800	1608
450	1148	650	1475	900	1692

Table 5. Thermal conductivity of polycrystalline diamond and CBN

Specimen	Country	Manufacturer	$\lambda, \text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$
Syndite	Great Britain	De Beers	550
Formset	USA	General Electric	700
DA-150	Japan	Sumimoto Electric	130
Polycrystal-line diamond*	USSR	Institute of High Pressure Physics, the USSR Academy of Sciences	450-580
Polycrystalline diamond	ditto	Institute for Superhard Materials, the UkrSSR Academy of Sciences	250-440
ACB*	ditto	Poltava Plant of synthetic diamonds	330
CKM*	ditto	ditto	250
CBA*	ditto	ditto	235-275
Teplonit (CBN)	ditto	Institute for Superhard Materials, the UkrSSR Academy of Sciences	350

*Electrically conductive specimens

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THE CHEMICAL BOND AND THE PROPERTIES OF NONMETAL HIGH-MELTING-POINT COMPOUNDS

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Nonmetal high-melting-point compounds is a narrow class of matters composed by B, Al, C, Si, N, P, O elements. They have the covalent type of chemical bond (SiC , B_4C) combined with a certain percentage of the ionic one (Al_4C_3 , AlN) and reveal the crystalline structure of tetrahedral atomic pattern. Lately there has been developed a possibility to directly calculate the bond energy and the chemical, physical and mechanical properties in such crystals. This brings forth favourable conditions for the intentional synthesis of new complex compounds of predetermined properties as the above elements can substitute each other in compounds entailing a change in the bond length, its polarization and, consequently, a change of properties.

The bond energy and the properties calculations can be made additionally easier if performed by the simplified LKAO method [1]. The bond energy calculations by this method involve the usage of $-E_s, -E_p$ atomic terms (Table 1).

The total bond energy in covalent high-melting-point compounds consists of the activation energy, E_{act} , the energy of interaction which is associated with the overlapping of the wave functions of the first-nearest neighbours, $V_0(d)$ and the bond formation energy, E_{bond} , which represents a gain in the energy of binding and that of hybridized states, E_h .

$$E_{tot} = -E_{act} - V_0(d) + E_{bond}, \quad (1)$$

where the last two terms are bond length dependent.

Table 1. The values of atomic terms for the elements composing nonmetal high-melting point compounds, eV

Element	Electron configuration	$-\mathcal{E}_S$	$-\mathcal{E}_P$	$\mathcal{E}_h = (\mathcal{E}_S + \mathcal{E}_P)/2$	$V_1 = (\mathcal{E}_S + \mathcal{E}_P)/4$
B	$s^2 p^1$	12.54	6.64	8.12	1.47
C	$s^2 p^2$	17.52	8.97	11.11	2.13
N	$s^2 p^3$	23.04	11.47	14.36	2.88
O	$s^2 p^4$	29.14	14.13	17.88	3.76
Al	$s^2 p^1$	10.11	4.86	6.18	1.33
Si	$s^2 p^2$	13.55	6.52	8.27	1.76
P	$s^2 p^3$	17.10	8.33	10.52	2.19

The activation energy, E_{act} , is the energy that equals to the difference between the hybrid state energy $\mathcal{E}_h$, and the electronic energy of a free atom. It equals to $(\mathcal{E}_p^A + \mathcal{E}_p^B) - (\mathcal{E}_s^A + \mathcal{E}_s^B)$ per one atom, or $V_1^A + V_1^B$ per one bond (see Table 1). The bond energy, E_{bnd} , in covalent crystals equals to the double energy of covalent hybridized orbitals bond [1].

$$E_{bnd} = 2V_2^h = 2 \cdot 4.37 \hbar^2 / md^2 \quad (2)$$

where V_2^h is the energy of covalent hybridized orbitals bond, m is the electron mass, $\hbar = h/2\pi$ is the Planck constant, $\hbar^2/m = 7.62 \text{ eV} \cdot \text{\AA}^2$, d is the atomic spacing.

The energy $V_0(d)$ is very difficult to calculate. But its magnitude can be defined by the virtue of the experimental values obtained for the total bond energy, E_0 ($E_0 = E_{total}$) and the E_{act} and E_{bnd} energies (Table 2).

$$E_0 = \Delta H_{AB} + E_a^A + E_a^B \quad (3)$$

where ΔH_{AB} is the heat of the AB compound formation; E_a^A , E_a^B is the heat of atomization for the A and B elements.

Apart from the components of the total bond energy, the Table 2 contains also the energy of ionic hybridized orbitals bond and the degree of covalence. These values are necessary for the definition of properties.

Table 2. The components of the total bond energy in covalent crystals

Matter	$d, \text{\AA}$	E_{bnd}, eV	E_{act}, eV	$V_0(d), \text{eV}$	E_{tot}, eV	V_3^h, eV	a_c^h
C	1.54	28.08	4.26	20.14	3.68	0	1.0
BN	1.58	26.67	4.35	18.98	3.34	3.12	0.97
AlN	1.89	18.64	4.21	11.54	2.89	4.09	0.92
Si ₃ N ₄	1.72	22.51	4.64	13.50	4.37	3.04	0.96
SiC	1.89	18.64	3.89	11.50	3.25	1.42	0.97
B ₄ C	1.63	25.06	3.60	16.95	4.51	1.49	0.99
B ₄ Si	2.06	15.69	3.23	9.51	2.95	0.08	0.99
BP	1.99	16.81	3.57	10.72	2.52	1.2	0.99
AlP	2.35	11.64	3.52	5.99	2.13	2.17	0.62
SiP	2.27	12.92	3.95	4.74	4.23	1.12	0.65

Most properties of the matter are atomic spacing dependent and it is therefore necessary to know not only the absolute values $V_0(d)$ but the dependence of this energy on the bond length as well. It can be obtained through the force constant, C_0 . Assuming the parabolic law for the energy variation with distance, the energy for

small deviations from the equilibrium state, d_0 , will be:

$$V_0(d) = \frac{1}{2} C_0 \frac{(d-d_0)^2}{d_0^2} \quad (4)$$

when defining mechanical properties of matters, the second constant, C , is very important as well. The latter can be obtained through the covalent bond energy (Table 3) [1].

$$C_1 = 2\lambda V_2^h (a_c^h)^3 / 3 \quad (5)$$

where $\lambda = 0.88$.

Thus, the bond energy in the form of an analytical dependence on the bond length according to (2) and (4) can be expressed by the following equation:

$$E_d = -\frac{1}{2} C_0 \frac{(d-d_0)^2}{d_0^2} + 66,6 \frac{\text{\AA}^2}{d^2} \quad (6)$$

Table 3. The force constants and the volumetric modulus of elasticity for covalent matters

Matter	C_0, eV	C_1, eV	$\partial^2 E_d / \partial d^2, \text{eV/\AA}^2$	$\chi 10^{-11}, \text{Pa}$
C	70.4	8.26	41.36	5.37
BN	69.83	7.14	39.76	5.03
AlN	60.75	4.26	21.46	2.27
Si_3N_4	58.86	5.84	33.12	3.85
SiC	60.75	4.55	18.12	1.98
B_4C	66.37	6.84	34.24	4.20
B_4Si	59.48	4.46	8.17	0.79
BP	62.57	4.78	9.68	0.97
AlP	48.75	0.81	4.27	0.36
SiP	35.99	1.04	8.04	0.71

Using the eqn (6) the second differential coefficient can be found the value of which for the distance d_0 corresponding to the energy minimum is proportional to the volumetric modulus of elasticity (Table 3) [1]:

$$\chi = \frac{1}{8d_0} \cdot \partial^2 E_d / \partial d^2 \quad (7)$$

The elastic constants and the elastic moduli are also calculable from the general law. They are directly related with the chemical bond strength. The elastic modulus, E , the shear modulus, G , and the Poisson's ratio, M , which are applied by the general elasticity theory, can be found from the elastic constants of the stress tensor:

$$E = \frac{(C_{11}-C_{12})(C_{11}+2C_{12})}{(C_{11}+C_{12})} \quad (8)$$

$$G = C_{44} \quad (9)$$

$$M = E/2G - 1 \quad (10)$$

where C_{11} , C_{12} , C_{44} are the elastic constants.

By writing down the variation of electron energy due to the shear strain in the vicinity of the bonding orbitals one can find the elastic constants from the expression [1]:

$$C_{11}-C_{12} = \sqrt{3} \lambda (a_c^h)^3 V_2^h / 3 \quad (11)$$

where $\lambda = 0.88$, V_2^h is the covalent hybridized orbitals energy, a_c^h is the degree of hybridized orbitals covalence. The elastic constant C_{44} can be calculated using the force constants, C_0 and C_1

$$C_{44} = \frac{32}{(2,3d_0)^3} \cdot \frac{C_0 C_1}{C_0 + 8C_1} \quad (12)$$

Table 4. The elastic and the shear moduli

Matter : A		E, GPa		G, GPa		μ	$E_V \cdot 10^5, \text{J/cm}^3$
		Calcul.	Exper.	Calcul.	Exper.		
C	1.05	1171.8	1164.0	492.9	544	0.188	8.82
BN	1.03	953.0	973.4*	395.8	454*	0.203	7.47
AlN	1.04	317.1	480.2*	131.6	202.9*	0.204	2.51
Si ₃ N ₄	0.88	600.1	304.1	213.8	-	0.24	4.07
SiC	1.09	400.3	401.3	175.2	169	0.142	2.64
B ₄ C	1.12	709.4	493.0	320.3	-	0.21	6.20
B ₄ Si	1.22	273.9	-	134.2	-	0.02	1.71
BP	1.11	325.5	-	144.4	-	0.13	2.16
AlP	1.07	52.4	-	23.2	-	0.13	0.46
SiP	1.65	-	-	-	-	-	0.41

* The calculated data from [3].

The elastic constants C_{11} - C_{12} and C_{44} allow to define the anisotropy factor which tends to 1 for the crystals of tetrahedral bonds [3]:

$$A = 2C_{44} / (C_{11} - C_{12}) \quad (13)$$

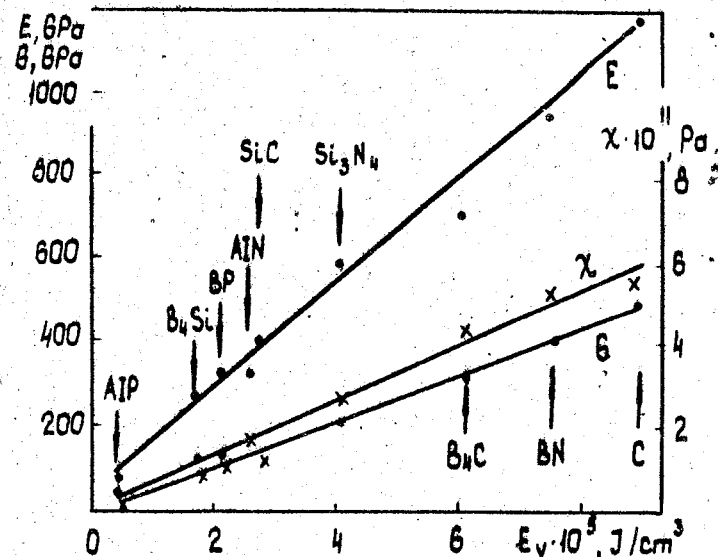
In this case the following interrelation can be established between the elastic constants:

$$C_{12} = C_{44} \quad (14)$$

$$C_{11} = 3C_{44} \quad (15)$$

The elastic, E , and shear, G , moduli usually applied in the general elasticity theory, can be found using the above interrelations (Table 4).

The value, E_V , revealing the dimension of bonds in a unit volume and being equal to $V_0(d)a_c^h / d_0^3$, is also given in the Table 4. The elastic moduli and many other matters' properties have the linear dependence on the value, E_V (see Figure).



The dependence of the elastic moduli on the stiffness, E_V

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ACTIVATION OF SINTERING OF DIFFICULT-TO-SINTER COMPOSITE MATERIALS BY HIGH PRESSURE

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Consolidation of samples by sintering in TiB₂-AlN(15%), Al₂O₃-TiC(30%) and Al₂O₃-TiN(20%) systems cold pressed under high pressures (P ≤ 6.8 GPa) is investigated. Pressing and sintering of the latter composite material were investigated most thoroughly in view of the components thermodynamic compatibility under higher temperatures (up to ~2200 K /3/). Alumina powder of TMMK type with S ≈ 2.5 m²/g (after comminution) and two types of TiN powder: TiN_{0.98} of furnace synthesis with S=2.0-2.5 m²/g (TiN(I)) and plasma-chemical TiN_{0.96} with S=20 m²/g were used. TiB₂ powder with S=2.0 m²/g, plasma-chemical AlN (S=12-18 m²/g) and synthesized by solution method SiC with S=1.5-1.7 m²/g were used for the rest of the investigated composite materials.

Consolidation of composite materials with TiN(II) is more difficult than with TiN(I), and equal density (θ > 0.6) in the first materials is obtained under higher pressures. It is explained by difficulty of ultrafine particle deformation /6/, "seizure" effects, and probably with collapse of air in pores, and the probability of their formation rises when ultrafine powders are used.

Quasi-hydrostatic reduction under high pressures results in substantial substructural changes in TiN particles /7/, whereas corundum particles, probably, show less deformability /8/. The estimation of substructural changes in particles of powders components in composite materials after pressing under high pressure (5 GPa) and short-term firing was realized by analysis of (III), (222), (200) and (400) TiN and (102), (204) α-Al₂O₃ diffraction maximums.

The data obtained (Table I) show that quasi-hydrostatic reduction of individual powders causes increase of the lattice microplastic distortion and decrease of the coherent scattering area (blocks or particles). This decreasing effect is characteristic of macroscopic brittle substances with a covalent chemical bond. Co-

undum particles, both individual and as components of a composite material, show more rigidity and less deformability of the lattice in comparison with TiN. The latter behaves originally being as a component of a composite material - microdeformations in it are accumulated to a considerably less degree and coherent scattering area grows smaller more intensive than in TiN(I) individual powder. The latter is obviously explained by higher hardness of corundum, the particles of which indent the particles of less hard TiN. Furthermore, the size of the coherent scattering area in TiN(I) after reduction can be compared with the similar size in TiN(II). In this connection one can expect the similarity increase as to behaviour when sintering composite materials under limiting pressures.

Table I. Parameters of fine structure for phase components of α-Al₂O₃-TiN composite materials in different processing states

Material state	TiN(I)		α-Al ₂ O ₃		TiN(I)		α-Al ₂ O ₃	
	individual		individual		in comp.mat.		in comp.	
	ε · 10 ³	D, nm	ε · 10 ³	D, nm	ε · 10 ³	D, nm	ε · 10 ³	D, nm
Powder after comminution, 30 h	1.6	70	-	-	-	-	-	-
Pressing in high pressure apparatus under 5 GPa (293 K) 10 s	3.6	44	1.9	44	1.9	27	1.5	44
Firing-sintering in high pressure apparatus under 5 GPa (1770 K) 240 s	2.1	52	-	-	0.5	>10 ³	Full deformation pick-up	>10 ³

Sintering of samples was carried out in a pure nitrogen atmosphere in a resistance furnace equipped with a special dilatometric attachment allowing to fix shrinkage under heating rates from 0.04 to 0.67 degree/s up to 2270 K. After the desirable temperature was reached, an isothermic lag was carried out with a given rate in every cycle up to a full shrinkage and to a sample structure formation (see Figure). The shrinkage curves include three typical sections: a sloping section without an evident shrinkage, a "rapid" shrinkage area and a section of shrinkage moderation under high temperatures. The shrinkage nature depends on pressure and structural state of a component. Thus, in a composite material

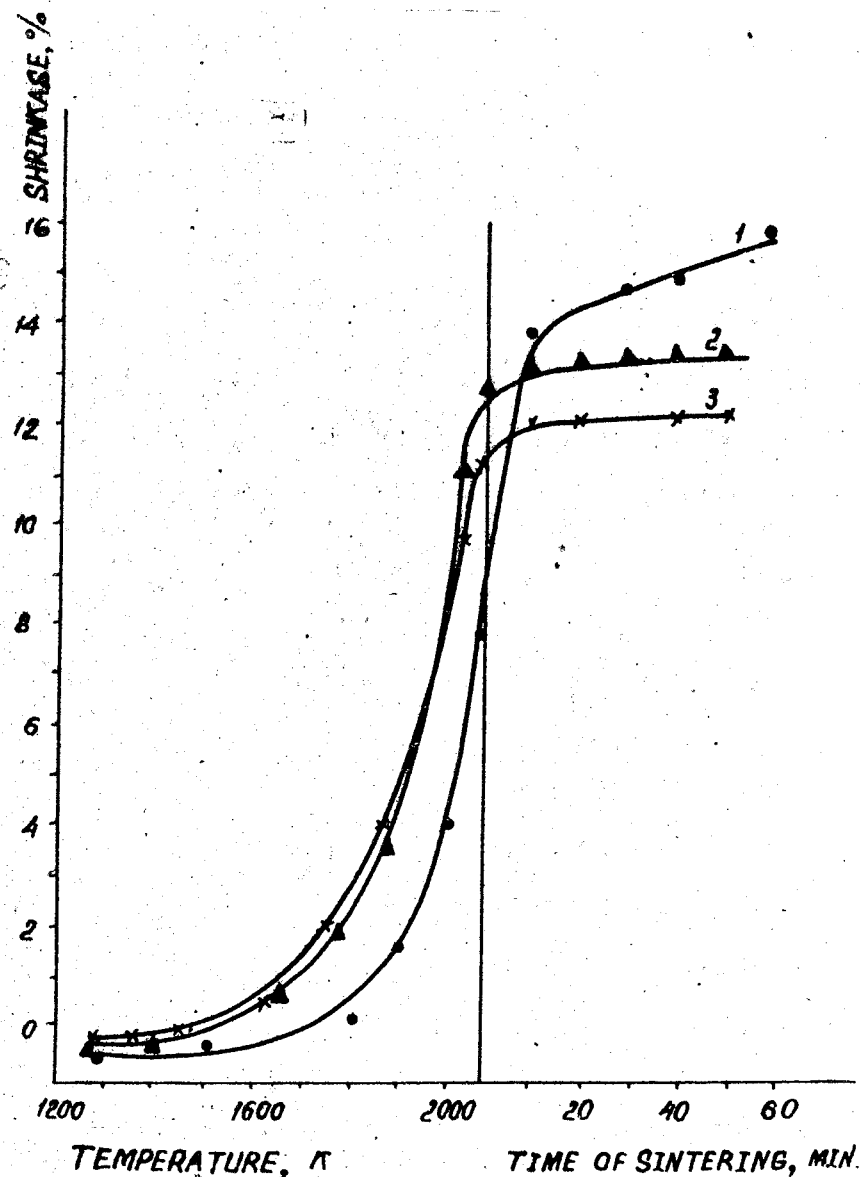
with TiN(I) shrinkage is not practically realized up to 1550 K, and when pressure decreases the temperature of shrinkage initiation increases up to 1800 K. Consequently, pressure activates sintering owing to microdeformation of particles of TiN phase, "leading" in composite materials sintering process. On the contrary, in composite materials with TiN(II) the temperature of an active shrinkage initiation decreases when pressure falls. It may be associated with formation of a more perfect matrix from the "leading" phase and with greater freedom of slipping of TiN(II) ultrafine particles relative to corundum particles. When pressure increases the total composite materials shrinkage falls due to contraction of pressing free volume.

Shrinkages registered by experiment approximate to theoretical when pressure increases, the difference between investigated composite materials is levelled.

Heating rate rise from 0.17 to 0.5 deg./sec when nonisothermal sintering exposes the tendency to compression activation in low temperatures area, but final shrinkage with that decreases. It may be explained by gas phase effect in closed pores, and probability of their formation increases. Higher pressure decreases contribution to shrinkage in isothermal phase of "resintering". In TiN(II) composite materials this contribution is always lower and under $P > 3$ GPa there isn't any at all. Perhaps it is associated with "seizure" effects as well as with exhaustion of possibility for further rearrangement of particles and pore structure. Therefore (Table 2), the final density of TiN(II) composite materials is lower as compared with TiN(I) but porosity is higher accordingly.

Table 2. Density and open porosity of Al_2O_3 -TiN composite materials samples after sintering in nitrogen atmosphere under 2070 K during 1 h

Nitride type	Pressure, GPa	Open porosity, %	Density, 10^{-3} kg/m^3	Relative density, %
TiN(I)	1	0.2	4.26	99.5
	3	0	4.28	100
	5	0.1	4.28	100
TiN(II)	1	0.7	4.21	98.6
	3	1.3	4.11	96.3
	5	0.5	4.17	97.3



Shrinkage curves for Cortinit (80% Al_2O_3 + 20% TiN(I)) samples pressed under high pressure in nitrogen atmosphere at 2070 K: 1-pressure 1 GPa; 2-pressure 3 GPa; 3-pressure 5 GPa.

TiB₂-TiN, TiB₂-AlN composite materials (0.6-1.5 % porosity, not higher) are analogous by sintering. It should be added only that components of the considered systems are consistent in the investigated temperature range. When an attempt was made to activate sintering of Al₂O₃-TiC components composition ("black" mineral ceramics) marked difference lying in impossibility of obtaining dense articles in similar sintering conditions (in nitrogen) even after pressing under P=5 GPa was determined. The reason of such different behaviour for Al₂O₃-TiN and Al₂O₃-TiC compositions is a lower temperature limit for co-existence of components in the latter system. Under higher temperature interaction is accompanied by gas emission preventing sintering (minimum residual porosity is 20% while in Al₂O₃-TiN composite materials - 0.5-2.0% and in TiB₂-AlN - 0.4-1.6%).

Properties of composite materials sintered after compression under high pressure are identical to properties of hot-pressed composite material. Thus, stresses intensity coefficient K_{IC} for sintered composite materials with TiN(II) and TiN(I) is 4.9 and 4.5 MN/m^{2/3} accordingly with H_v 7.9 GPa (K_{IC}=4.8 MN/m^{2/3} for hot-pressed Cortinit). Wear resistance of sintered cutting inserts under similar specific conditions for cutting raw 45 steel did not yield to that of hot-pressed Cortinit - flank wear h_{FW}=0.2 mm during 20 min. (v=260 m/min, s=0.025 mm/rev., t=0.5 mm). In that way, use of high quasi-hydrostatic pressure for composite materials pressing allows to obtain after sintering high-density, strong products provided temperature threshold for thermodynamic compatibility of composite materials components is high enough.

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DIFFUSION IN METALS AND SEMICONDUCTORS UNDER HIGH PRESSURE

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1. Introduction

Diffusion processes like other thermally activated processes in solids are governed by an Arrhenius-Boltzmann type of equation. Within the framework of the so-called transition state theory of diffusion, the diffusivity can be written as:

$$D = g a^2 f v_0 \exp[-AG/kT] \quad (1)$$

In (1) AG is the isothermal, isobaric work (increment of Gibbs free energy) required to create defects and surmount the diffusion barrier. g is a geometric factor characteristic of the lattice geometry, a the lattice parameter, f the so-called correlation factor which accounts for the spatial correlation between successive diffusion jumps and v₀ the attempt frequency of the order of the Debye frequency. k denotes Boltzmann's constant and T absolute temperature.

As usual the Gibbs free energy can be decomposed into these terms according to

$$\Delta G = \Delta E + p\Delta V - T\Delta S, \quad (2)$$

where ΔE, ΔV and ΔS denote activation energy, activation volume and activation entropy and p the hydrostatic pressure.

Using (2) the temperature dependence of the diffusivity has the well-known form

$$D = D_0 \exp(-\Delta H/kT) \quad (3)$$

where the pre-exponential factor is given by D₀ = g a² f v₀ exp(ΔS/k) and the activation enthalpy is simply ΔH = ΔE + pΔV.

The pressure dependence of the diffusivity is given by

$$D = D_0 \exp(-\Delta E/kT) \exp(-p\Delta V/kT). \quad (4)$$

The activation volume is the isothermal change in volume of a real, finite crystal associated with a diffusive jump. Diffusion in solids usually involves thermally generated defects. The activation quantities and in particular the activation volume are then composed of terms which concern defect formation (superscript F) and defect migration (superscript M) according to

$$\Delta V = V^F + V^M \quad (5)$$

The microscopic significance of the formation volume V^F is clear: the formation of a defect in an otherwise 'rigid' crystal would change the volume by $z \Omega$ (Ω = atomic volume), where $z = +1$ for a vacancy, $z = +2$ for a divacancy and $z = -1$ for a self-interstitial. Since the real, finite crystal relaxes one must add the relaxation volume around the defect, V_{rel} , corrected by the Eshelby factor, f_{Esh} , which is due to the presence of the external surface:

$$V^F = z \Omega + f_{Esh} V_{rel} \quad (6)$$

Typical values of f_{Esh} lie between 1.3 and 1.6 depending on the Poisson's ratio of the material (see e.g. [1]). For vacancy-type defects V_{rel} is negative and for self-interstitials V_{rel} is positive. The significance of the migration volume V^M is less clear. Experiments and estimates show that V^M is small and positive. The present paper briefly reviews measurements of the activation volumes of self-diffusion on the noble metals Au and Ag and on the semiconductor Ge which have been performed in the recent years in the author's group. Detailed descriptions and discussions have been published elsewhere [2-4,6,7].

2. Experimental Procedures

^{199}Au , ^{110}Ag and ^{71}Ge were used as radioactive trace elements in combination with monocrystalline samples (purity better than 99.999 %) to eliminate effects of grain-boundary diffusion. The radioisotope was deposited on a polished surface of the samples providing a thin-film diffusion source. Diffusion anneals were performed in a pressure vessel using inside an internal heater (see [2]). The pressure vessel was filled with high-purity Ar as pressure transmitting medium using

a two-stage gas pressure system. Afterwards the sample was heated to the desired temperature. Temperature and pressure were continuously recorded. For temperature measurements and control a chromel-alumel thermocouple was used. The pressure dependence of the thermoelectric power was taken into account. After the diffusion anneals, the samples were sectioned in an ion-beam sputtering device. Counting of the section radioactivity was performed by standard methods.

3. Experimental Results and Discussion

For the boundary conditions of the present experiments the distribution of the specific activity of the radioactive trace element is given by the thin-film solution of Fick's second law

$$C = \frac{C_0}{(\pi Dt)^{1/2}} \exp[-x^2/4Dt] \quad (7)$$

where x is the penetration distance, t is the time of the diffusion anneal and C_0 a constant. Fig.1 shows as an example penetration curves of ^{71}Ge in Ge crystals for different pressures at a given temperature. The variation of the self-diffusion coefficients for Au and Ge as functions of pressure for various temperatures are plotted in Fig.2.

The activation volumes for Au are shown in Fig.3 together with data from other groups [8,9]. The almost temperature independent value of the activation volume is consistent with a monovacancy mechanism of diffusion over the temperature range investigated. Fig.4 indicates that for Ag the activation volume increases with increasing temperature [2,10]. This gradual increase is consistent with the picture that at lower temperatures monovacancies are the dominating vehicle of diffusion and that with increasing temperature an increasing amount of divacancies contributes to the transport of matter. The activation volume of a divacancy (ΔV_{2V}) is larger than that of a monovacancy (ΔV_{1V}). Therefore, the measured activation volume which is a weighted average of the activation volumes of the two defects should increase with temperature. The solid line in Fig.4 has been calculated for the values $\Delta V_{1V} = 0.67 \Omega$ and $\Delta V_{2V} = 1.11 \Omega$. For details see [2].

Fig.5 shows that the activation volumes found in Ge are considerably smaller than

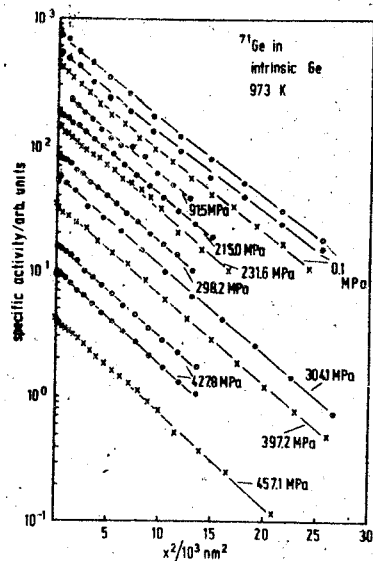


Fig.1. Penetration curves for diffusion of ^{71}Ge in Ge at 973 K and at various pressures.

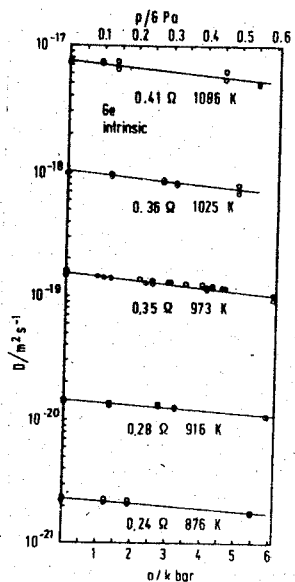
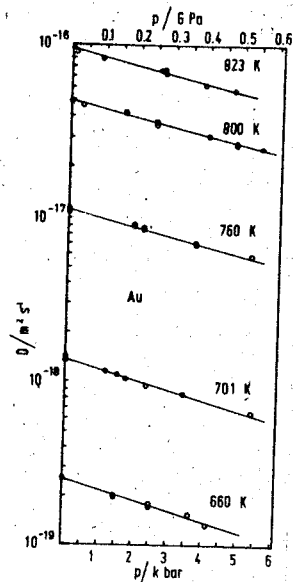


Fig.2a. Pressure variation of the self-diffusion coefficient at various temperatures for Au (left) and for Ge (right).

Fig.2b. Pressure activation of the self-diffusion coefficient for Ge.

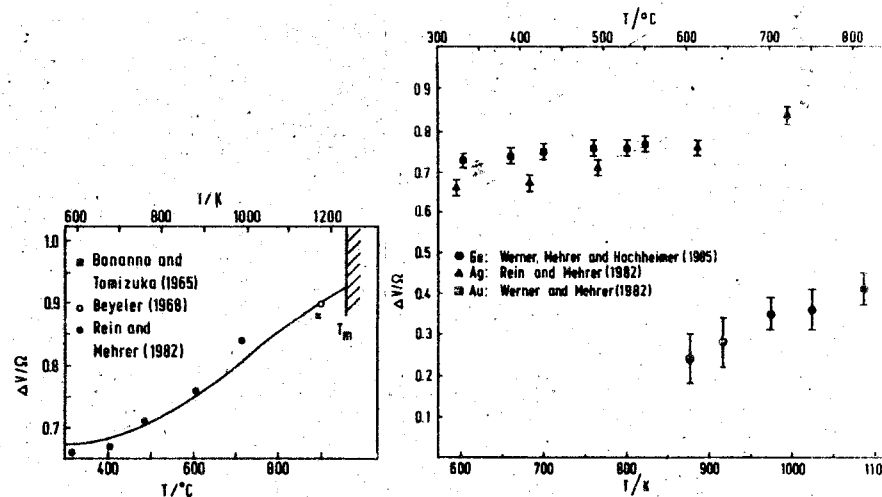


Fig.3. Activation volume of self-diffusion in Au according to [3].

Fig.4. Activation volume of self-diffusion in Ag according to [2].

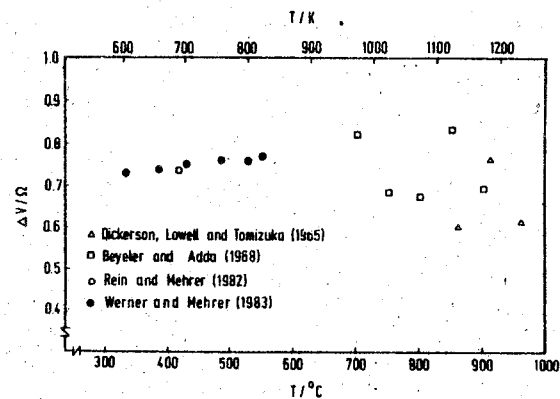


Fig.5. Activation volume of self-diffusion in Ge according to [4].

those for the noble metals. This indicates that the relaxation volume of vacancy-type defects in Ge according to (6) is strongly negative. It was also observed that the activation volume in p-doped Ge is larger than in n-doped material [3]. This has been interpreted as evidence for two different charge states of the Ge vacancy. The neutral vacancy is the dominating diffusion vehicle in p-doped material with an activation volume of 0.56 Ω . In n-doped material the mass transport is dominated by negatively charged vacancies with an activation volume of 0.28 Ω . The variation of the observed activation volume with temperature in Fig. 5 reflects an increasing contribution of neutral vacancies with increasing temperature.

4. Conclusion

Measurements of the effect of hydrostatic pressure on diffusion are very useful in characterizing and identifying atomic defects responsible for diffusion.

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THE INFLUENCE OF HIGH PRESSURES ON TITANIUM-CARBON REACTION

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The study of titanium-carbon reaction was performed at titanium-carbon sandwich-like samples. The samples were heated at temperature ranging from 1773-1973 K in a high pressure chamber type of "Thoroid" where the pressure was from 1-7 GPa. The heating time was 240 sec. Having been exposed to constant pressure the samples were, after heating, cooled by quenching at room temperature in order to retain the obtained structure.

The samples were then prepared for metallographic investigation by usual procedures. A reaction zone of TiC phase began to appear at 1673 K and under the pressure of 1 GPa. A titanium carbide layer resembles a dense and polished crust between layers of graphite and titanium (Fig.1). At that temperature but under higher pressure a layer of titanium carbide proved not to be discovered by a metallographic method. The rise of temperature caused the growth of thickness of a titanium carbide layer when the pressure of 1 GPa maintained constant. At the same time, the increment in pressure at constant temperature caused reduction of a layer thickness of the formed carbide (Fig.2).

Microstructural investigations proved that a transition zone consists of two layers, the first of which represents a solid solution of carbon in titanium and the second one is titanium carbide.

Using experimental data we determine the coefficients of a reaction diffusion by equation with the aim to define quantitatively a mass transport during reaction between titanium and carbon /1/:

$$D = \frac{x^2}{4t} \quad (1)$$

where x is the reaction layer thickness, t is the time. The results obtained are given in Table 1. In comparison there also are given the data under atmosphere pressure /2/.

*The Figure is given at the end of the book

Table 1. Coefficients of a reaction diffusion of carbon through TiC reaction layer (m²/s)

T (K)	Pressure (GPa)				Author /2/	
	1.00	2.55	4.23	7.00	Latysheva	Zhunkovskii
1773	8.0x10 ⁻¹²	4.4x10 ⁻¹²	2.4x10 ⁻¹²	-	3.55x10 ⁻¹¹	7.8x10 ⁻¹¹
1873	10.5x10 ⁻¹²	7.3x10 ⁻¹²	4.0x10 ⁻¹²	2.0x10 ⁻¹²	4.27x10 ⁻¹¹	31.2x10 ⁻¹¹
1973	22.2x10 ⁻¹²	14.9x10 ⁻¹²	9.3x10 ⁻¹²	4.5x10 ⁻¹²	-	-

It is obvious that the pressure has a considerable influence on deceleration of a diffusion process. The same conclusion can be made when considering the influence of pressures on activation energy of diffusion (Table 2) that was calculated by the Arrhenius equation.

Table 2. The influence of pressures on activation energy of carbon diffusion in TiC (kJ/mol)

/3/	Pressure (GPa)		
	1.0	2.55	4.23
236	295	354	393

S.A.Rice and N.N.Nachtrieb /4/ having studied the influence of high pressures on diffusion showed that this dependence can be presented by the following equation:

$$D_p = D_{op} \exp \left(- \frac{bp}{RT} \right) \quad (2)$$

where b-a specific function of a normal frequency and of a vacancies formation volume, p-pressure, R- a gas constant and T-temperature.

It follows from equation (2) that:

$$\left(\frac{\partial \ln D}{\partial p} \right)_T = - \frac{b}{RT} \quad (3)$$

On the other hand a diffusion process is characterized by the activation volume /5/ that follows the definition:

$$\Delta V = \left(- \frac{\partial \Delta G}{\partial p} \right)_T \quad (4)$$

where ΔG - change of a free energy.

With this in mind, we can write:

$$\Delta V = -RT \left(\frac{\partial \ln D}{\partial p} \right)_T$$

$$\Delta G = -RT \ln(D/\gamma a^2 \nu) \quad (5)$$

where γ - a geometric factor, a - a constant of a crystal lattice and ν - a vibration frequency of atoms.

When comparing equations (3) and (5) we obtain

$$\Delta V = b \quad (6)$$

The activation volume for diffusion in the investigated system has been estimated using equations (2) and (6) and the results thus obtained are shown in Table 3.

Table 3. Activation volume for diffusion in TiC

T(K)	1773	1873	1973
$\Delta V(\text{m}^3/\text{mol})$	5.49×10^{-6}	4.39×10^{-6}	4.38×10^{-6}

It is interesting to mention here that the activation volume for diffusion at 1873 K and 1973 K is practically the same. That fact defines more closely the state of titanium carbide crystal lattice, too under the mentioned conditions /6/.

It is supposed that /7/ under normal conditions existing in the course of a diffusion process, a carbon atom can transfer to a neighbouring vacancy if one of the closest titanium atoms that prevent its transition, is absent. Therefore, the rearrangement of carbon atoms cannot be performed without simultaneous rearrangement of vacancies in metal sublattice of titanium carbide. That is why we can suppose that a diffusion arrangement both of carbon and titanium atoms does not separately take place in each sublattice but is performed by a mutually connected process when bivalencies, being consisted of carbon and titanium vacancies, were used.

Formation of bivalencies has been obviously aggravated under pressure conditions what made a diffusion difficult, as well. This has been confirmed by obtained scientific results as given in Table 1.

On the basis of calculated values for activation volume (Table 3) it can be expected /8/ that volume ΔV is connected with the concentration of dotted defects that control the processes occurring in investigated system. As its value decreases with temperature, that indicates, at any rate, the fact that the forma-

tion of equilibrium defects is compensated by the action of high pressures what causes retardation of a reaction rate between titanium and carbon with the pressure rise.

The influence of high pressures on reaction in a solid state between titanium and carbon within temperature interval 1773-1973 K has been investigated. It was shown that increment in pressure causes retardation of a diffusion rate in reaction product what points to deceleration of a reaction rate in a solid state, as well. A mass transport mechanism within a reaction field proved to be a diffusion through bivalencies consisting of carbon and titanium vacancies.

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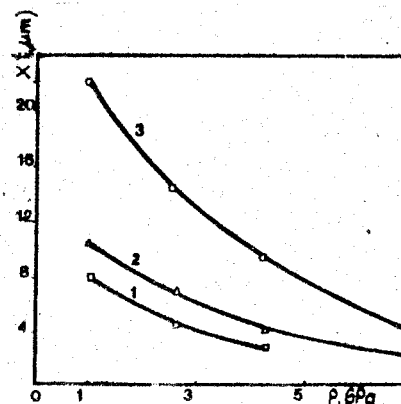


Fig. 2.

The dependence of titanium carbide layer thickness on pressure after reaction of 240 sec (1-1773 K, 2-1873 K, 3-1973 K).

THE INFLUENCE OF HIGH PRESSURES ON STRUCTURE AND PROPERTIES OF SILICON NITRIDE

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Silicon nitride as a material with both small coefficient of thermal expansion and high oxidation resistance attracts fixed attention of specialists in various fields of science and technology [1]. Covalent bonding in this compound is the reason for using of high temperature sintering.

Sintering temperature of covalent matters - boron, silicon, silicon nitride - is in the range of $0.85-0.9 T_{\text{melt}}$ (Fig.1) [2]. Under such conditions dissociation pressure for silicon nitride becomes quite substantial.

In this work we investigate the influence of high pressures (up to 9 GPa) and temperature (up to 1400 °C) upon the change of phase composition and density of various kinds of silicon nitride powders (see the Table).

Characteristics of powders

Batch	% α - Si_3N_4	S, m^2/g	$\bar{d}$, μm
I	3	1.7	1.1
II	9	2.5	0.75
III	45	37.5	0.05
IV	Amorphous powder	109	0.017

Fig.2 yields the change of density with pressure. As we can observe, the difference in compressibility of powders depending on different particle sizes is kept unchangeable in the whole range of considered pressures and the attempts to obtain compact samples turn out unsuccessful (maximum relative density is 0.6), especially in the case of ultrafine powders ($S \geq 20 \text{ m}^2/\text{g}$).

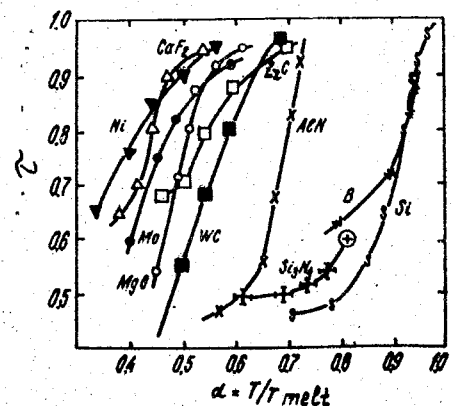


Fig. 1. Densification of powders CaF_2 , Mo, Ni, ZrC, MgO, WS, AlN, B, Si, Si_3N_4 as a function of temperature.

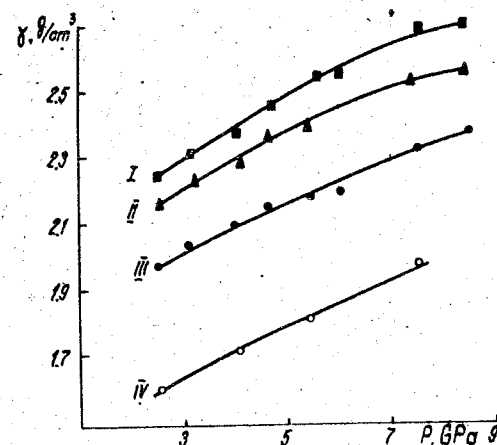


Fig. 2. Influence of pressure upon the density of powders (batch I, II, III, IV).

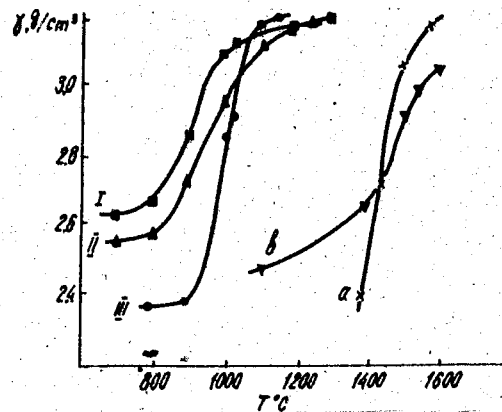


Fig. 3. Temperature dependence of powder densification of batch I-III ($P = 8.5$ GPa, $t = 30$ s) and of powders /4/ with surface area $23.7 \text{ m}^2/\text{g}$ (a) and $4.2 \text{ m}^2/\text{g}$ (b) ($P = 3$ GPa).

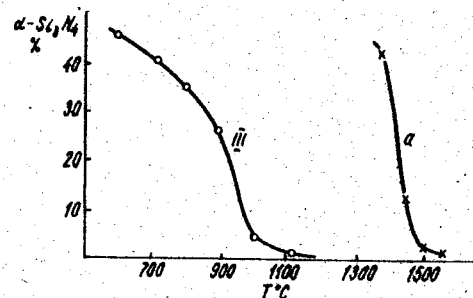


Fig. 4. Influence of pressing temperature upon phase content of powders (batch III and /4/, $S = 23.7 \text{ m}^2/\text{g}$ - curve "a").

The influence of the temperature on the density and α -phase content is shown in Fig.3 and 4 ($P = 8.5$ GPa). There are no differences in the densification at high temperatures ($T \sim 1200^\circ\text{C}$), however at lower temperatures densification of ultrafine powders takes place more rapidly.

Full transformation $\alpha \rightarrow \beta$ takes place at $\sim 1200^\circ\text{C}$ (phase content was investigated according to the methods /1,3/). The similar occurrence of more rapid densification for ultrafine powders under 3 GPa is noted in /4/ (curve "a" in Fig.3).

Amorphous silicon nitride powders were hardly densified as well as in work /4/. Increasing of pressure from 3 GPa to 8.5 GPa in comparison with experiments of /4/ allowed us to decrease the temperature of substantially full consolidation approximately by 400°C ; however approximately the same temperature decreasing was observed for full $\alpha \rightarrow \beta$ -transformation. Properties and mechanism of this monotropic transformation under high pressure conditions ought to become the object of special investigation.

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HIGH PRESSURE SYNTHESIS AND ELECTRICAL PROPERTIES OF SEMIMETALLIC Si III AND SEMICONDUCTING Si IV

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Abstract

Pure cubic (BC8) silicon III which is metastable at ambient has been grown at 17 GPa in the diamond anvil cell, in the form of monocrystalline slabs. The samples transform to hexagonal lonsdaleite Si IV by heating to 500 K at room pressure. This is also stable at ambient.

Ohmic electrical contacts have been developed and transport measurements could be made for the first time.

Low temperature conductivity and Hall effect show Si III to be a hole semimetal with $p \approx 5 \times 10^{20} \text{ cm}^{-3}$. The photoconductivity spectrum of Si IV corresponds to a semiconductor with a gap in the vicinity of $\approx 0.8 \text{ eV}$.

This is compared with existing theoretical predictions and possible applications of these new materials are suggested.

Several forms of silicon are metastable at ambient, in addition to diamond cubic Si I, and a - silicon.

Pressurizing above 10 GPa; at 300 K brings about the Si I $\Rightarrow$ Si II (β -Sn) phase transition which irreversibly /1/ transforms back to the body-centered BC - 8 Si III structure. Calculations have predicted it to be either /2/ a zero gap semiconductor or a semimetal /3/. Heating Si III above 500 K transforms it into Si IV which has the hexagonal diamond (lonsdaleite) structure /4/, and is predicted to be a semiconductor /5/. In this paper, we show that Si III is a hole - conduction semimetal and Si IV a semiconductor with intermediate energy gap.

In all cases, monocrystalline p-type ($p = 3 \times 10^{16} \text{ cm}^{-3}$) material was used. For electrical measurements, standard ohmic con-

tacts were deposited. These were found to remain ohmic, under pressure, and after release of pressure through the phase transitions. Samples, typically 150 x 150 x 20 micrometers in dimension were placed in a diamond anvil cell, with silicone oil as a pressure medium. It vitrifies above 6 to 8 GPa, enclosing the samples in a rigid glass, and thus helps preserve the integrity of the samples and contacts by cold isostatic pressing. Debye-Scherrer diagrams were used to characterize the material, at ambient conditions. Samples subjected to pressures between 12 and 14 GPa showed continuous lines of disordered Si III with discontinuous spots of crystalline Si I. On the contrary, samples subjected to pressures of 17 GPa only showed Si III diffraction patterns /6/. Thus, the sequence Si I $\Rightarrow$ Si II $\Rightarrow$ Si V $\Rightarrow$ Si II $\Rightarrow$ Si III seems to be required in order to obtain pure Si III. Indexation of up to 14 lines confirms the BC 8 structure. Heating the samples to 470 K for 2 hours transforms Si III to Si IV which has the hexagonal (lonsdaleite) diamond structure (2H - 4).

Electrical resistivity down to 1.2 K and Hall effect at ambient by the 4 probe van der Pauw method were used to characterize Si III. Results of Hall effect are given in the table. Scatter in the data, from sample to sample, comes from irreproducibility in the fabrication procedures, and variations in the state of disorder of the crystals. Nevertheless Si III always behaves like a semimetal with hole (p-type) Hall conductivity at ambient and an apparent carrier density of a few 10^{20} cm^{-3} . Apparent electrical resistivity at ambient is between 3 to 10 milliohm x cm. Despite this scatter in absolute value, the variation with temperature (figure) is in all cases characterized by:

- A linear T dependence above 25 K
- A $T^{1/2}$ law between 15 and 1.2 K.

Hall effect on Si III samples at 300 K

Sample number	Maximum pressure, GPa	Resistivity $10^{-3} \Omega \times \text{cm}$	Hole concentration p: 10^{20} cm^{-3}	Apparent mobility: $\text{cm}^2/\text{V}.\text{sec}$
1	I3	3	6	3
2	I4	4	4	4
3	I5	6	5	2
4	I8	4	4	4

Neither dependences can be related to the expected behavior of a semiconductor, semimetal, or metal, and thus must come from the high degree of disorder of the sample.

High resolution electron diffraction photographs indeed show the Si III samples to contain microcrystals as small as 4 nanometers with no observable precipitates at the grain boundaries and statistically random orientation of the atomic planes: no memory remains of the original monocrystalline orientation and no observable trace exists of amorphous regions. The temperature dependence of resistivity is then readily explained along existing theories for disordered conductors: The high-temperature linear region is characteristic of localization [7] with electron - electron scattering. The $T^{1/2}$ low - temperature variation is due [7,8] to electron - electron correlation with repulsive interaction at the Fermi surface. Hall effect measurements should also be corrected for disorder, and the apparent mobilities and carrier densities, are not exactly these of bulk Si III. All that can be said, at the present, using the formulae for mosaic crystals [9], is that the carrier density is of the order of a few 10^{20} cm^{-3} , but that the mobility, which is much more sensitive to disorder may be much larger (one order of magnitude or more) than a few $\text{cm}^2/\text{V}\cdot\text{sec}$.

Silicon IV, when completely transformed by moderate heating has an apparent resistivity which is $\approx 10^4 \text{ ohm} \times \text{cm}$, that is four orders of magnitude larger than the $1 \text{ ohm} \times \text{cm}$ original bulk crystal. Here again, disorder will partly explain this large difference, but it may also be due to the variation of the ionization energy of the boron dopant, in the hexagonal structure of Si IV. This low conductivity precluded Hall effect. We used the photoconductivity response to characterize it. The photoresponse extrapolates to zero at about 0.6 eV. This is only a minimum value for the gap since the disorder in the samples is expected to cause a defect density of states in the gap which may be responsible for band tailing.

Conclusions of this work may be summed up as follows:

a) BC-8 Si III and 2H - 4 Si IV can be grown under high pressure and their transport parameters measured, although their behavior is dominated by structural disorder.

b) Nevertheless, Si III is identified as a semimetal with hole conduction and thus experiment confirms predictions that it is an indirect overlap semimetal [3], rather than a zero bandgap semiconductor [2].

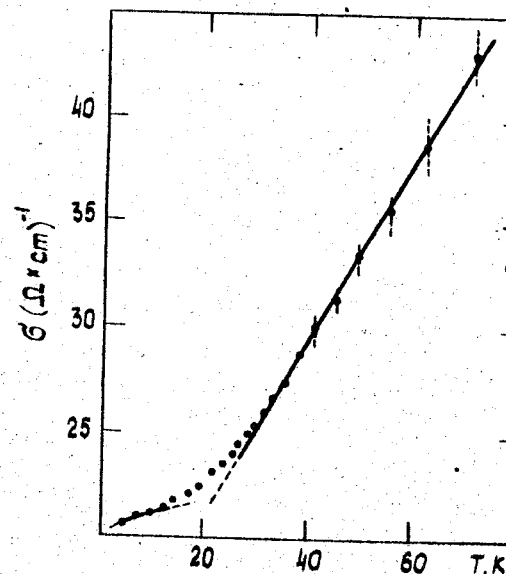
It does not exhibit superconductivity down to 1.2 K.

c) Si IV behaves like a semiconductor with intermediate bandgap, and this tends to confirm existing predictions of a 0.85 eV indirect gap material [5].

d) Complete characterization of those new materials, as well as other metastable forms [10] of silicon will have to await fabrication of macroscopic bulk samples, which may not be impossible in the near future.

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Conductivity vs. temperature of a Si III sample. Below 15 K, $T^{1/2}$ dependence. Above 30 K, T dependence.

ANISOTROPY OF REFRACTORY COMPOUNDS STRUCTURAL CHANGES UNDER HIGH PRESSURES

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A study is made of anisotropic deformation effects in crystal lattice of aluminium and titanium nitrides as well as titanium, zirconium, niobium diborides after treatment in high pressure chambers. The treatment was carried out under pressures up to 7 GPa and temperatures up to 2000 °C /1,2/.

After high pressure and temperature treatment X-ray reflection lines of aluminium nitride are blurring, the process being not identical for reflections from planes /h0l/ with different "l" evenness. Reflection lines from planes /h0l/ with $l=2n$ do not practically blur, and in those from $l=2n+1$ blurring is considerably greater. It indicates stacking faults arising in AlN lattice after treatment. As it was pointed out in /3/ such faults' storage can be a reserve to form multilayered polytypes in aluminium nitride wurtzite structure.

As a result of AlN treatment under different pressures and temperatures an insignificant decrease in crystal lattice periods are observed. Especially clear it is along axis "c".

In aluminium nitride with initial lattice parameters $a_0=3.106$ Å, $c_0=4.992$ Å, $c/a=1.61$ in the X-ray chamber under pressure 8 GPa the lattice periods are changed as follows: $a=3.044$, $c=5.06$ Å, $c/a=1.66$. While this, compressibility coefficients along directions /100/, /002/, /101/ are 2.6, 1.8 and 2.7 respectively. Hence, crystal lattice is compressed anisotropically. As compressibility along hexagonal axis is less than in the basis plane, c/a under pressure is increased hence, wurtzite structure stability can be decreased /4/. As a kind of check for the data above is behaviour of aluminium nitride under low temperatures. Maximum compression while temperature lowering, a crystal lattice suffers along basis plane which also leads to the rise of c/a ratio in the structure of wurtzite aluminium nitride.

In contrast to aluminium nitride, that of titanium possesses cubic lattice of NaCl-type. Under high pressures and temperatures treatment an irreversible decrease in lattice period takes

place. It rises with the increase in temperature and pressure. The change in the lattice period revealed may be due to the nitrogen partial loss under pressure in titanium nitride, homogeneity region.

A study of the samples substructures showed that during treatment under the regime above brittle fracture, microplastic deformation and recrystallization take place. At the temperature rise up to 800 °C under both pressures the values of crystal lattice distortions and dimensions of coherent dissipation region (CDR) increase. At 1000 °C the pressure 7 GPa still provides additional storage of crystal lattice distortions but at 3 GPa the microstresses decrease.

Pressure rise at the room temperature results in CDR splitting under equal residual microstresses. Pressure rise at elevated temperatures shifts recrystallization towards higher temperatures.

In contrast to the isotropic distortions of titanium nitride crystal lattice, changes of fine crystal structures of titanium, niobium and zirconium diborides are anisotropic.

We analysed diffraction lines broadening in two directions - along hexagonal axis "c" (planes (001) and (002)) and along axis "a" (planes (100) and (200)). In titanium diboride at the room temperature and under pressure 1 GPa microdistortions of crystal lattice are not observed, and at 5 GPa microdistortions amount up to $2.8 \cdot 10^{-3}$ and are practically anisotropic ones as it was pointed out in /5,6/. After applying pressures 1 and 5 GPa microdistortions along hexagonal axis at 1000 and 1600 °C are not observed and are revealed only at 2000 °C. Along hexagonal axis at all temperatures CDR splitting takes place. Analysis of X-ray diffraction lines broadening from planes (100) and (200) showed that in this direction at all temperatures (1000, 1600 and 2000 °C) crystal lattice microdistortions are present, their value being increased with the pressure rise. CDR splitting either does not take place at all, or occurs in a less degree than along axis "c". Thus, after combined effect of high pressures and temperatures in titanium diboride, significant anisotropy of crystal lattice residual microdistortions is observed. Crystal lattice along axis "a" suffers considerable plastic deformation and accordingly in this direction higher residual microdistortions are observed. Their absence (or low value) and stronger CDR splitting along axis "c" point to the enhanced brittleness in this direction. Apparently it may be connected with strengthening covalent interaction

tion along axis "c" under high temperature pressure shaping. It agrees well with the results of X-ray studies on compressibility of titanium diboride according to which /7/ this compressibility under 4 GPa along hexagonal axis is twice as big as that in the basis plane, and respective values estimated using single crystals elastic constants differ more than 4 times at rather low anisotropy of thermal expansion coefficient in titanium diboride /8/.

Values of crystal lattice microdistortions in zirconium and niobium diborides are higher than in titanium diboride and are observed under all treatment regimes. As distinguished from titanium diboride here under all treatment regimes microdistortions along axis "c" are present and achieve higher values than along axis "a". CDR splitting in niobium diboride is stronger along axis "a" than along axis "c" under all treatment regimes as well. Such anisotropy character opposite to that of titanium diboride is specially distinct for niobium diboride. We have no data on its compressibility and anisotropy of thermal expansion coefficient is significant and amounts approximately to 1.7 (along axis "c" and "a") /9/ which prevents from atoms convergence along axis "c" under pressure at high temperature and does not lead to the interaction enhancement in this direction.

As a result of the studies the effects of plastic deformation for a number of refractory materials were revealed. For compounds with hexagonal crystal lattice they are essentially anisotropic. This fact reflects chemical bond anisotropy and promotes faults storage in the structure during deformation under quasi-hydrostatic high pressures which results in strengthening difficult to deform materials based on refractory compounds.

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THE INVESTIGATION OF COLD SINTERING OF IRON POWDER

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Cold sintering, that is the consolidation under the action of pressure, of dispersive-porous systems enables synthesis of materials with new, in advance set properties /2/. Our investigations of the pressing process of iron, so far, were limited to pressures lower than 1 GPa /1-3/. The design of our new tool UVP-1 /6/ enables now the investigations at considerably higher pressures. The properties of samples which were obtained on that way depend on the several parameters. On the basis of microstructural investigations, that is on the basis of measurements of electrical properties, we have proposed the theory about pressing process of dispersive-porous materials at low pressures, in our previous papers.

Iron powder NC 100.24, from "Hoegenes" company, which have been used in our investigations of cold sintering was obtained by reduction of magnetite ore. To the aim of classification of powder /4/ by Hall's unit, the powder flow rate and apparent density are determined. The green density, the density of a compact, at pressure which is most frequently used, 412 MPa was also measured. The dispersion analysis, that is the determination of powder particle size distribution, was performed by laser analyzer "Malvern 3600". On the basis of the data which have been obtained the powder index /4/ was determined:

06024655-X12.5(-W+X)7.7W4.1(-T+W)17.5T13S24.6Q13.1+Q7.5

We performed investigation of cold sintering in the tool specially made for high pressures. This tool includes the usage of cylindrical compacts obtained at lower pressures. Those cylindrically shaped compacts of 10 mm in diameter was obtained by using laboratory hydraulic press, of 100 KN maximum force. The basic samples for the investigation of cold sintering process was obtained at 300 MPa pressure and at compression rate of 0.083 mm/s.

The samples obtained in this way was placed in the center of the UVP-1 tool. By using precise hydraulic press of maximum force of 10 MN, at compression rate of 0.016 mm/s, cold sintered samples at different pressures, higher than 4 GPa were formed.

The densities of these samples was determined by hydrostatic method. The results are shown in Table.

The results of measurements of structural parameters of compacts

Pressure /GPa/	Relative density /%/	Hardness /GPa/	Coercitive force /A/m/	TEMP /mV/
4.5	96.3	1.41	563	3.67
5.1	96.4	1.43	597	2.30
6.1	96.6	1.45	625	2.29
6.5	96.8	1.46	611	2.39
7.5	96.9	1.52	524	1.40
8.0			622	2.96
9.0			533	2.55
10.0	97.1		528	2.48
11.5	97.3	1.57	686	2.83
12.5	98.3		465	1.69
20.0			554	2.25

Note: The values not be found in the Table were not measured.

To the aim of characterization of structure of cold sintered samples, in further work we performed measurements of microhardness, coercitive force and thermoelectromotive force of the samples by the method used in our previous investigations /2/. The results obtained from those analyses are shown in Table.

The results of the microscopic and X-ray investigations are shown in Figure*.

It can be seen from the powder index that it is the case of a polydispersive powder. Therefore, we think that the values of structural properties of cold sintered samples have general significance. This was also pointed out by microstructural investigation of the samples (see Figure), that is by microhardness.

Namely, by numerical analysis it could be printed out that microhardness with precision greater than 96% is linear function of pressing pressure: $HC = 10.111 P + 36.556$.

* The Figure is given at the end of the book

The dependence of this kind indicates that energy of interaction of dislocation with structural defects is of the same order of magnitude as own energy of dislocation. In other words, during pressing of powder under high pressure constant generation of dislocations occurs, with concurrent formation of structural defects, which is manifested by changes in the structure of grain boundaries of compact during etching.

The process of particle deformation takes place due to generation of dislocations, for pressures lower than 6.5 GPa; this is verified by the increase of coercitive force, that is the decrease of TEMF (see Table). The range of critical pressure is interesting, which amounts to about 7.5 GPa. This pressure characterized also the logarithmic dependence of relative density on pressure. Similar logarithmic dependence exists at relatively low pressures [3]. That is, we can say now that our earlier conclusion in reference with recrystallization, at pressures higher than 6.5 GPa, for Fe are not correct. Namely, the pressing process proceeds at very high pressures also in steplike changes of the first derivation of logarithmic dependence of relative density on pressure. In other words, it means that critical pressures at which devastation of particle surfaces occurs, because of accumulated defects in them, still exist. That is, the successive fragmentation of particles of basic powder occurs, and at same time the recovery of the structure inside of particles is going on. This recovery of the structure is manifested by increase of TEMF, that is by reduction of coercitive force for pressures higher than the critical one. This occurrence is perceived up to maximum pressing pressure of 20 GPa. If this happens to be true, it would mean that our theoretical considerations based on the model of electronic structure, which results from the theory of Pavle Sadic about behaviour of materials under high pressures, could be extended to very high pressures as well. These analyses are the subject of our further investigations.

By designing special tool we were able to expand our previous analyses of pressing process, to the range of higher pressures (4-20 GPa). By the analysis parameters such as microstructure, microhardness, TEMF and coercitive force, we came to the conclusion that various mechanisms take place at higher pressures too (in the investigated pressure range of about 7.5 GPa). Those mechanisms overlap just at the critical pressure. According to this, earlier considerations about simple recrystallization for pressures

higher than 1 GPa are probably insufficient. Further more, our considerations for low pressures can be extended to high pressures as well. Further investigations of X-ray structure and microstructure of boundary, that is of grain volume, would enable to postulate an exact electronic theory of powder compression under high pressures. In that way, new method for analysis of material properties under high pressures, which has been postulated in our previous investigations [5] could be confirmed.

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HIGH-PRESSURE STUDIES USING ENERGY DISPERSIVE DIFFRACTION OF SYNCHROTRON RADIATION AND A DRICKAMER-TYPE CELL

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ABSTRACT

We have measured the compressibility of TiB_2 up to 130 kbar using the radiation produced by the 5 Tesla Wiggler of the U.K. Synchrotron Radiation Source (SRS), a Drickamer-type high pressure cell and Energy Dispersive X-Ray Diffraction (EDXRD). The bulk modulus of TiB_2 was determined as 4.1 Mbar. The measurements were made at an angle of diffraction of 9° with high energy radiation. These two features and the high intensity of the source produced a resulting accuracy in relative d-spacing measurements of 1 part in 10^4 . Pressures were determined to within 0.5 kbar up to 130 kbar using Cu as internal calibrant.

INTRODUCTION

We are interested in the mechanical properties of very hard low density materials subjected to high stress. Presently we are studying titanium and compounds and alloys containing titanium. The bulk properties of these materials are best studied using large samples and a Drickamer-type cell is best suited to such work. The cell used here allows sample volumes of approximately 1.5 mm^3 and a pressure range of 0 to 200 kbar. As the cell windows limit the beam geometry to a very small angular range, fixed angle EDXRD is the appropriate technique to use. With such a technique, optimum resolution is achieved at very low angles of diffraction with highly collimated radiation [1], and hence high energy radiation is required. The most suitable source of such radiation operating today is the SRS Wiggler which produces intensities typically

10^6 times higher than a conventional generator up to 100 keV and with a natural divergence of 0.25 mrad. In order to take advantage of these features, we have built a low angle diffractometer which matches the geometries of the direct and diffracted beams. This diffractometer is shown in Figure 1.*

EXPERIMENTAL TECHNIQUE

A diagram of the Drickamer-type cell is shown in Figure 2. In such a cell pressure is applied by tungsten carbide anvils to a mixture of sample and pressure calibrant surrounded by several millimeters of pressure transmitting material. This also requires the use of high energy X-rays as the absorption of the mixture of LiF and epoxy packing used here is high enough to stop almost totally dipole radiation and makes the Wiggler the only suitable source of radiation. As the cell allows the use of large samples, the diffracting volume is determined solely by the geometry of the collimation. This also produces a simple geometry in which sample positioning is not critical [2]. Further, the high energy radiation and small angles of diffraction not only increase the resolution, but also the sensitivity to changes in lattice parameters. All these features, when combined with the high intensity of the source, produced high signal-to-noise ratios and a resulting accuracy in relative d-spacing measurements of 1 part in 10^4 . Correspondingly, pressures were determined to within 0.5 kbar up to 130 kbar using copper and aluminium as internal calibrants. Furthermore, as the spectra consist of reflections from the sample and calibrant, the wide dynamic range of energies produced by the Wiggler is an extremely important feature of the technique.

RESULTS AND DISCUSSION

The samples consisted of thin discs, approximately 1.5 mm in diameter, which had been machined using diamond-coated tools as TiB_2 is a very hard material. The pressure calibrant was copper and the packing a mixture of 50% epoxy, 50% LiF. The thicknesses of the copper foils were either 50 or 100 μm and those of the slices of TiB_2 varied between 110 and 140 μm . Most of the measurements were made using a 450 μm thick sample assembly. The maximum pressure of 130 kbar was obtained after a reduction of the thickness to 290 μm . Two spectra are shown in Figure 3. Both the signal-to-noise ratio and the resolution are very good. In addition,

*The Figure is given at the end of the book

the combination of the high energy radiation from the Wiggler with a low Bragg angle of 4.5° ensure that useful intensities are available up to 80 keV.

TiB₂ has an hexagonal structure with space group P6₃/mmm (Kiessling, 1950). At most pressures 8 peaks were used to determine the change in the lattice parameters a and c . The first five reflections of the copper spectrum were used to determine the pressures up to 130 kbar. The accuracy achieved in the pressure calibration was approximately 0.5%. Table 1 below contains the results of our measurements which are illustrated in Figure 4 (a), (b) and (c). With a volume change of -3% at 120 kbar (Figure 4 (c)), TiB₂ is nearly as incompressible as diamond which has a bulk modulus K_0 of 4.42 Mbar [3]. The bulk modulus of TiB₂ was determined from the slope of the linear least squares fit to the V/V_0 versus pressure data. Its value was calculated as 4.1 ± 0.25 Mbar.

With a solid pressure transmitting medium, hydrostatic conditions cannot be fully achieved, but only approached. Non-hydrostatic strains lead to an inhomogeneous stress distribution within the sample and thus to line broadening. As the pressure is maximum at the centre of the cell and decreases as the radius increases, a pressure gradient exists within the long diffraction volume and causes line broadening. During the work reported here, we have measured the magnitude of this effect and found it to vary between 5% and 25% of the peak width at zero pressure. These values correspond to pressure variations of approximately ± 1 and ± 5 kbar at 100 kbar. The large uniaxial load causes plastic flow within the sample which tends to equalise the stresses in all directions. However, as the sample has a finite shear strength, this equalisation cannot be complete. The exact description of the resulting distribution of stresses and strains is complex, but can be reasonably approximated by the superposition of an uniaxial component, in the direction of the applied load, and a hydrostatic component. According to the analysis given by Singh and Kennedy [4] for a sample with a cubic structure, the uniaxial component may be detected and even measured, in the most favourable conditions, by plotting the strain in the direction hkl as a function of the parameter $\Gamma(hkl)$ where

$$\Gamma(hkl) = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2}.$$

If a relationship exists between $\Gamma(hkl)$ and the strain, Singh and Kennedy showed that it indicates the presence of an uniaxial component. Further, if the relationship is linear, then its magnitude

can be estimated from the gradient of the straight line obtained. It also indicates that a state of stress continuity prevails between the crystallites in the sample. This technique has been used by Syassen and Holzapfel [5] and more recently by Vailya, Grosshans and Holzapfel [6]. In both cases the effect just described was reported. We have performed such an analysis on data obtained from copper at 108 kbar. We found no relationship between the strain and $\Gamma(hkl)$, but a scatter which corresponded in magnitude to the errors associated with the calculated pressures (Table).

CONCLUSION

We have successfully combined the wide dynamic range of penetrating radiation produced by the United Kingdom SRS Wiggler with a Drickamer-type high pressure cell for high pressure studies using the EDXRD technique. The brightness of the source and the high collimation of the radiation have enabled us to work with a geometry guaranteeing a high signal-to-noise-ratio and spectra free of contamination from the packing and anvils. With a relative accuracy of 2×10^{-4} in measurements of changes in d -spacing, we have obtained state-of-the-art accuracy in compressibility measurements up to 130 kbar. During more recent work we have increased the intensity of the diffracted beam by a factor of 10 by optimising the collimation further. We have also investigated the errors introduced by physical and geometrical aberrations in EDXRD [7]. These effects have not been discussed in the literature so far. Our findings will be published elsewhere. The technique developed here promises very good results in intensity measurements as the diffracting volume is independent of pressure. The few relative intensity measurements made so far have shown maximum variations of a few percent over the range 0 to 130 kbar. This shows that little or no preferred orientation was present within the samples and indicates a very nearly hydrostatic pressure distribution which is very promising for future measurements.

ACKNOWLEDGEMENTS

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Measured compressibility data of TiB_2 up to 130 kbar

P(kbar)	$\pm$	a/a_0	c/c_0	V/V_0	$\pm$
11.6	0.3	0.9987	0.9989	0.9963	0.0011
25.2	0.3	0.9985	0.9976	0.9946	0.0007
47.2	0.3	0.9968	0.9957	0.9893	0.0010
71.1	0.4	0.9961	0.9947	0.9869	0.0017
84.0	0.4	0.9930	0.9917	0.9778	0.0014
98.8	0.5	0.9944	0.9922	0.9811	0.0013
116.3	0.5	0.9927	0.9909	0.9764	0.0017
123.5	0.5	0.9913	0.9887	0.9716	0.0021
130.4	0.4	0.9886	0.9875	0.9651	0.0011
130.5	0.5	0.9884	0.9875	0.9648	0.0011
$a_0=3.0274 \pm 0.0008 (\text{\AA})$					
$c_0=3.2282 \pm 0.0009 (\text{\AA})$					
$V_0=25.623 \pm 0.012 (\text{\AA}^3)$					

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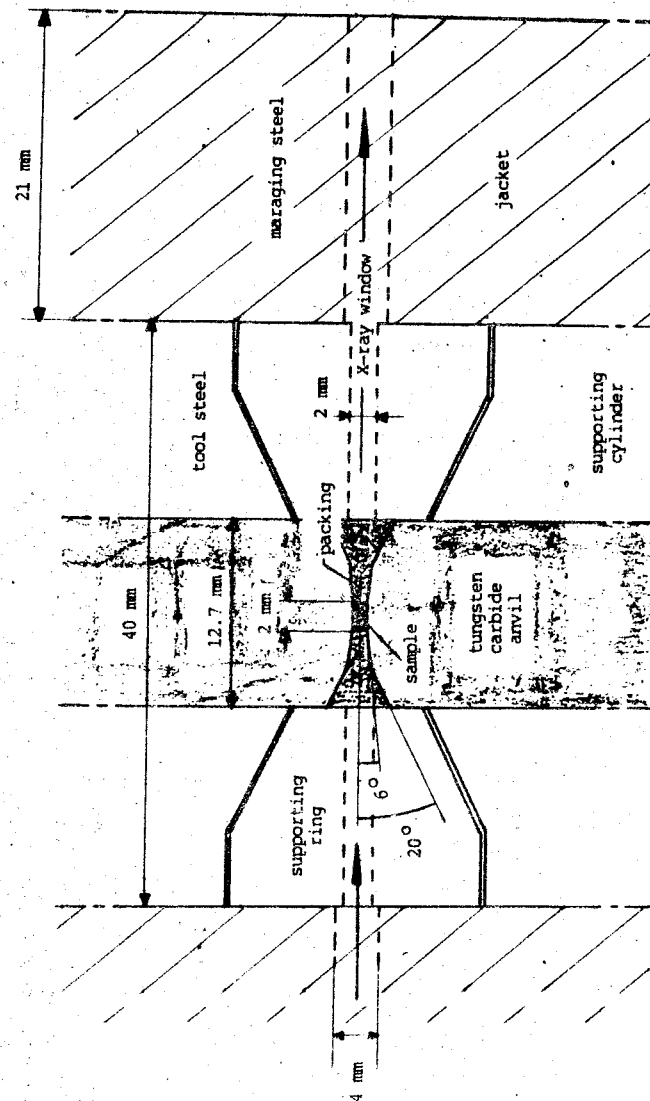


Fig. 2. Diagram of our Drickamer-type high pressure cell. The section is through the axis of the cell. The windows are offset by 8° with respect to one another in the plane perpendicular to that of the diagram. The packing consist of a mixture of LiF with epoxy resin. The sample is mixed with a pressure calibrant such as Cu, Al or NaCl.

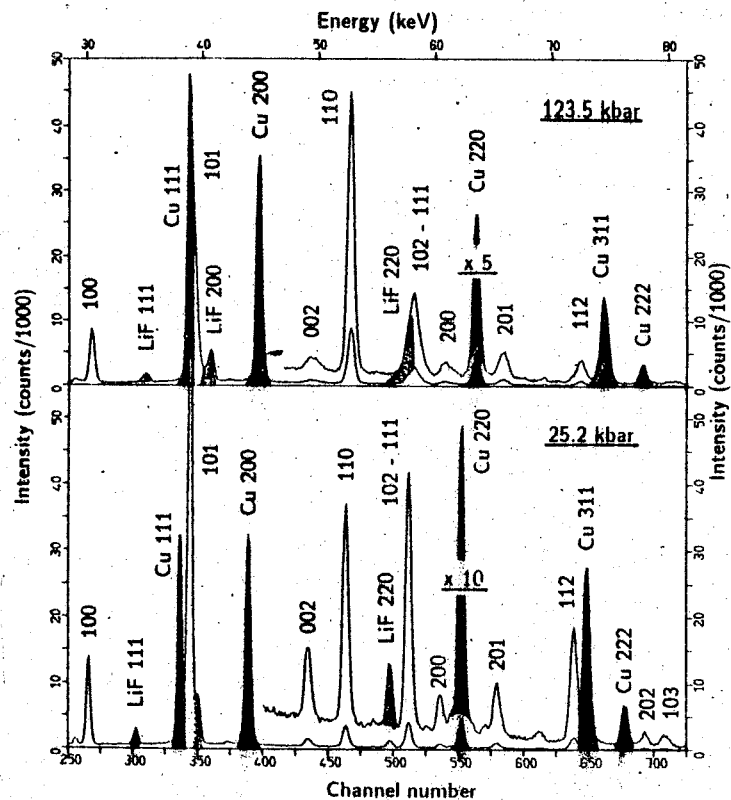


Fig. 3. Energy dispersive spectra of TiB_2 obtained with Wiggler radiation at $2\theta \approx 9^\circ$. The spectrum at 25.2 kbar was collected in 25 minutes, that at 123.5 kbar in 45 minutes. The SRS was operating at 2 GeV and a current varying from 300 to 100 mA. The pressures were determined from the copper reflections (shown in black) and the peaks only labelled 'hkl' are those of TiB_2 . The low intensity reflections from LiF are small contributions from the packing.

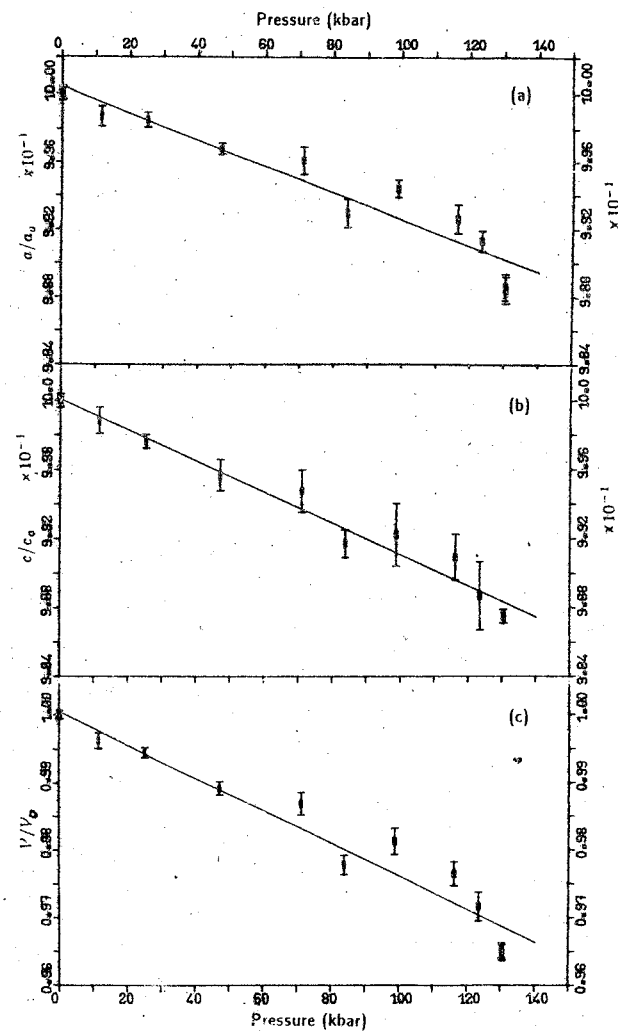


Fig. 4. Reduced lattice parameters and volume as a function of pressure for TiB_2 . The straight lines are the results of least square fits and the error bars represent standard deviations. The data plotted are: (a), a/a_0 ; (b), c/c_0 ; (c), V/V_0 . The measured changes in a/a_0 and c/c_0 are equal to within the accuracy achieved in these measurements.

THE INFLUENCE OF PRESSURE ON THE STRUCTURE OF AlN AFTER
SINTERING IN HOT ISOSTATIC PRESS AND HIGH PRESSURE
APPARATUS OF THE "TOROID"-TYPE

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Aluminium Nitride and ceramics on its base is of great perspective for electronics as a thermal conducting material with high isolating qualities. However, the production of compact, pore-free products from AlN is rendered more difficult, because this compound disposes of strong covalent bonds. It has been found, that addition of some oxides, which are able to form a liquid phase, promote an intensive condensation of AlN /1/. Formerly we established /2/, that the application of ultradisperse powders causes a decrease of the sintering temperature of about 200-300 °C.

In the present work the influence of the pressure of Nitrogen and high pressure on the kinetics of densification and the formation of structure of ceramics from ultradisperse AlN powders (UD) and relatively coarse technical AlN powders (T) were examined. The chemical composition and specific surface of these powders are given in the Table.

AlN	Chemical composition, mass %					Specific surface m ² /g
	Al _{tot.}	N ₂	Al _{free}	O ₂	Fe	
UD	65.4	33.7	0.16	1.5	not est.	19.5
T	65.0	33.2	0.80	0.6	0.6	1.8

Sintering was carried out in the laboratory gasostat under Nitrogen pressure of 0.1; 10 and 100 MPa and in the high pressure apparatus of the "Toroid"-type at pressures of 4 to 9 GPa in a temperature of 1300 to 2000 °C. The shrinking and the mass lost of the sintered samples are shown in Figure.

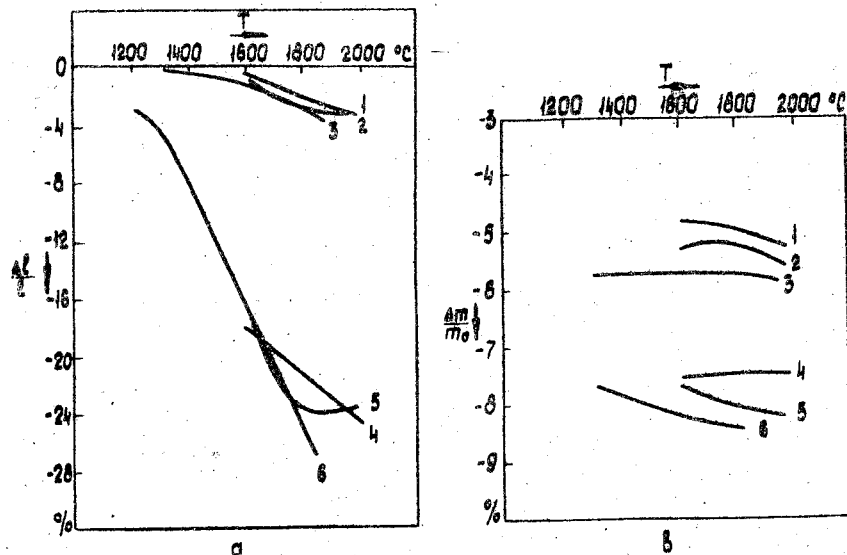
As the diagrams show, the samples from coarse powder sinter badly and the increase of the Nitrogen pressure up to 100 MPa shows practically no influence on the velocity of the densification of the sintered material. The sintering of samples from UD-powder under Nitrogen pressure of 0.1 MPa occurs actively in the temperature range from 1300 to 1850 °C, where shrinking reaches 28%, and after sintering the density approaches the theoretical value.

With increasing Nitrogen pressure to 100 MPa the shrinking is somewhat smaller (24-26%), the density also does not approach the theoretical value but reaches 2.95 g/cm³. The mass lost of the samples is the smaller, the higher the Nitrogen pressure is.

Electron microscopic investigations of the microstructure permit to explain the following morphological and structural transformations. In AlN-UD samples the Oxygen adsorbed on the surface of the particles forms an Oxynitride phase at temperatures above 1200 °C, which is localized at the triangular boundaries of the particles /3/. At temperatures above 1600 °C a quick densification of the starting particles takes place forming aggregates, in which monocrystalline particles originate afterwards. The Oxynitride layer dissolves in the particles of the main phase by forming a solid solution of Oxygen in Aluminium Nitride. At a temperature above 1700 °C there takes place a growth of the particles, while packing defects in the (0001) - plane appear, and monolayering polytypes arise at 1800-1900 °C from which particles of a plate type are formed. The increase of the Nitrogen pressure causes the retardation of the processes described above and the slowing down of the recrystallization. At the particle boundaries there appear pores between the grains, which are probably filled with gas and are preserved up to the highest temperatures. The recrystallization growth of the particles retards even more in those samples, which were sintered in the high pressure chamber. There are no polymorph transformations in the structure, the particles of an octahedral form grow larger in their dimension.

Conclusions:

The application of high pressures permit the regulation of structural changes and recrystallization processes, which take place in the process of sintering ultradisperse Aluminium Nitride powders and thus affect the physical and mechanical properties of Nitride ceramics.



Temperature dependences of the shrinkage, $\Delta l/l$ (a) and the mass lost, $\Delta m/m$ (b) at the sintering of AlN-T (1-3) and AlN-UD (4-6) under nitrogen pressure 0.1 MPa (3, 6), 10 MPa (2, 5), 100 MPa (1, 4); time of reaction - 60 min

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INFLUENCE OF PRESSURE ON THE STRUCTURE AND PHASE COMPOSITION OF Al-Ni MONOLITHS

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The problem of obtaining products from composite dispersive materials in which each particle consists of a core of one material and an ultradispersive shell of another material is quite topical.

Composite Al-Ni powder was obtained in an autoclave by the hydrogen reduction of nickel under pressure from the aqueous saline solution on the surface of Al powder particles [1]. In the original material nickel and aluminium are mainly in a free state. The radiographic studies showed some amount of Al_2O_3 in the original material. Before applying high pressure the original dispersive material was compactified under a pressure of approximately ~2-3 kbar. In the experiments the application of hydrostatic pressure and heating of the treated material were carried out simultaneously.

Under a pressure of 2.5 GPa nickel and aluminium are present both in a free state and in compounds Al_2O_3 , $NiAl_3$ and $NiAl_3+Al$. NiO is present in a very small amount. Traces of plastic deformation are not observed in the structure; the original material gets compactified and conditions are created for obtaining a chemical compound of the definite composition, $NiAl_3$, where aluminium content is 57.97%. On the one hand, the $NiAl_3$ compound can be obtained by the penetration of ultradispersive nickel particles from the surface of the composite Al powder but, on the other hand, the matrix may contain free Al particles and the reaction between nickel and aluminium may take place after the application of load. The absence of plastic deformation traces can be explained if we assume the process of dispersive material treatment to be a set of successive actions.

In the first place the enlargement of particles takes place because free spaces in the original material disappear. Besides, under the action of external load, the outer shell of the composite powder deforms. Some part of the shell material penetrates in-

side a grain, while some part is pressed out into free spaces adjoining the particles. Finally, the compactification and enlargement of particles result in the formation of a monolithic state due to the filling up of free spaces existing in the original dispersive material.

At a pressure of 2.5 GPa the process of formation of monolithic state is not realized completely. The aluminium core seems to consist of separate particles oriented in the definite way with respect to the external load. The factor promoting the formation of the monolithic state is the creation of a strong chemical bond between the initial components of the composite material.

At this pressure value the energetic conditions for obtaining the NiAl compound are realized. The formation of the chemical compound is the second stage in the loading process connected with mass transfer. The energetic balance of the composite Al-Ni powder loading creates conditions for two stages: the enlargement of particles and mutual mass transfer.

When pressure is raised up to 5 GPa the process becomes more intensive and the phase composition changes. The NiAl₃ compound becomes a structural component of Ni₂Al₃ in which the nickel content increases from 42.03% to 59.19%. The formation of Ni₂Al₃ compound corresponds to a higher energetic level since it requires more mass transfer.

After the Ni₂Al₃ compound is obtained, the system still has a sufficient energy for the plastic deformation of that formed compound. The formation of the compound completes at pressures below 5 GPa and therefore, the third stage, i.e. the plastic deformation of the obtained structure becomes possible. Traces of the plastic deformation are clearly seen in structure.

At a pressure of 2.5 GPa the original structure does not change after heating. There occurs only a pointwise nickel penetration into the aluminium core.

While at pressure of 5 GPa the joint mass transfer of the shell material develops. Ultradispersive nickel, overcoming the resistance of the part of aluminium, penetrates inside the composite particle and produces fragmentation of the original aluminium grain into a fine particles, of approximately 3 μm in size. In this case nickel plays the role of a boundary between the aluminium grains. The increase of nickel penetration into aluminium leads to the growth of volume occupied by aluminium which, consequently,

leads to the convergence of aluminium cores. Therefore, the volume fraction of the aluminium accumulations increases.

The fragmentized part of the sample has traces of the plastic deformation. Inside the grain the plastic deformation takes place by twinning, while at the grain boundaries - by sliding.

The question as to whether aluminium can melt in these loading conditions is of principal importance.

It is well-known that in the case of heating up to 1273 K Ni-Al beads compactified at a pressure of 0.7 GPa, the interaction of nickel and aluminium with the formation of the alloy begins already at a temperature of 736 K [2]. The aluminium melting temperature is 933 K. The nickel-aluminium alloys and the Al₂O₃ compound melt at temperatures exceeding the aluminium melting point. For a number of melts the heat conductivity decreases as pressure grows. Nickel belongs to this category. The effect of heat conductivity decrease is 12.0%.

If we take into account that during experiments pressure and temperature increase simultaneously, then we can conclude that no fusion of aluminium should take place under loading. The structure formation occurs in a solid state.

This statement can be justified by other considerations. There is a certain resemblance between the influence of pressure and temperature on a substance state; namely, the increase of pressure causes changes similar to those taking place under cooling, i.e., conversion of the gaseous state to the liquid state and that of the liquid state to the solid one are accompanied by the growth of density and of the ordering degree. On the other hand, high pressures and temperatures contribute to the increase of the rate of many reactions.

The joint influence of temperature and pressure is usually stronger than the sum of the same influences apart.

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EFFECT OF THE CONSOLIDATION PROCESS OF POWDER BODIES UNDER EXTREME CONDITIONS ON THEIR STRUCTURE AND PROPERTIES

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A number of experimental investigations show that reducing of powder particle sizes greatly influences on structure and properties of the produced materials [1-3]. Firstly, it refers to the materials, produced from ultradisersion powder with particle size from 0.01 to 0.1 μm . Up to now the problem of consolidation of these powders remains to be restricting new materials development.

Ultimate particle size, considerable amount of adsorbed gases and the powder tendency to agglomeration, resulting in chain, globular and other spatial structures formation during powder production, enable one to classify ultradisersion powders as a special group of materials worth studying.

The investigation of consolidation of spatial specimens from ultradisersion powders in a sealed container by liquid pressure enabled to state the dependence between powder body structure and the rate of loading.

Reduction of particle size and loading rate can lead to formation of non-homogeneous structures and unstable properties of the produced specimens, thus increasing with density and size of the latter. At loading rates, less than sound rate in a powder body, the consolidation of the specimen external layers in the initial stages is accompanied with sequential gases release from the porous space of the densified layers into the central specimen area. Maximal particle movement and consolidation of the porous body occurs in the external specimen layer, agglomerates mainly deform in the plane, normal to loading direction. Beginning with some density value, the external layer of the porous body suffers more external loading, thus preventing deformation of inner layers. Further consolidation of the inner layers is possible only in case of failure or deformation of the external layer. That occurs when strain exceeds the critical strain value:

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$$\sigma_k = k \cdot E(\rho) \frac{\Delta}{R}$$

where k, Δ = coefficients of resistance and external layer thickness, respectively;
 E = elasticity module, depending upon the obtained density ρ of the external layer;
 R = external radius of the consolidated specimen

In the initial stage of consolidation when loading rates exceed the sound rate in a powder body, a significant role belongs to intensive compression of the gas enclosed in the porous space. Consolidation of agglomerates, their deformation and formation of new bonds between particles both inside agglomerates and between agglomerates take place. Further consolidation results in formation of strong space carcass and its volume deformation, leading to intensive particles warm up in the contact zone and the adsorbed gases release, thus creating additional pressure in the porous space.

Theoretical calculations and experimental testing show that gas pressure in the porous space of consolidated material can approach the value capable to destroy the specimen in the final stage of structure formation and further during unloading.

The investigations were carried out with titanium nitride powders, the mean particle size being 0.06 μm and specific surface 32000 m^2/kg . Loading pressure was up to 350 MPa under quasi-static (0.001 m/s) and high-rate conditions (100m/s).

The specimens with the initial powder charge porosity not exceeding 76-80%, produced under high-rate conditions have not revealed failure and cracks. The obtained globular-type structure (Fig. 1) has open porosity with pore effective diameter from 0.03 to 0.08 μm and more strong interparticle bonds inside the globules than between the globules. With initial porosity more than 94% total deformation of the specimens to separate conglomerates took place.

At quasi-static loading the powders reveal the increase of the relative density in the 5-6 mm thickness external layer up to 10% and formation of specific texture in it.

The extreme condition of the ultradisersion powders consolidation under high-rate loading is due to the fact that with par-

The Figure is given at the end of the book

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particle size decreasing the residual pressure increases in the porous space, which finally defines the structure, porosity and strength of the powder materials.

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INVESTIGATION OF CADMIUM OXIDE CONSOLIDATION UNDER HIGH PRESSURE

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A consolidation process of cadmium powder oxide depending on the pressing has been investigated. It was proved that during this process an increment in nonstoichiometric structure of this oxide occurred. The X-ray study established the changes in a crystal structure taking place during this process.

Introduction

The application of the pressure as unique operation for obtaining dense material from dispersed powders known as cold sintering, is used presently in the metallurgy of powder /1/. Compaction gives a product density that strongly depends on the pressure applied.

In this paper, the behaviour of finely divided CdO powder is investigated in the pressure range from 0.2-2 GPa primarily from the structural aspect.

Experimental

The powder of cadmium oxide, particle size below 0.5 μm , was pressed under the pressure of 0.2-2 GPa and mechanically stable specimens with ϕ 10x5 mm were obtained. The density of the samples were measured and the results obtained are given in Fig.1.

All the specimens were chemically analyzed and this have revealed a non-stoichiometry (Fig.2), which is in accordance with the results obtained by A. Vereshchagin /2/.

The unit cell dimensions of the samples were measured on a PHILIPS X-ray powder diffractometer using Ni-filtered Cu-K α (λ = 1.54178 $\text{\AA}$. 154178 nm), 40 KV 20 mA, slit system 1 $^\circ$, 0.1 $^\circ$, 1 $^\circ$, scan rate 1/8 $^\circ$ 2 θ per minute. The positions of diffraction lines were measured at the half width of each peak. Also the positions were determined by scanning of reflection at intervals of 0.02 $^\circ$ 2 θ .

Prior and after the measurement the stability of the instrument was tested with Si standard. The unit cell dimensions were determined by two procedures. In the first the refinement of cell constants was performed by standard leastsquare procedure using GA 16/440 computer. In second the values of a_0 were determined with the best straight line drawn through points at $\cot^2 \theta = 0$. From these results we have estimated that our standard deviation is 0.00004 nm.

Results and discussion

Establishment of a dependence between the pressing pressure and the properties of the obtained pellets is one of the most important problems existing in both the theory and technology of pressing powder systems. The process of densification took place due to particles gliding, deformation of particles contact areas, as well as volume distortion. Having this in mind, the very establishment of laws of pressing requires complex investigation of the interdependence of physical parameters that characterize the investigated system.

The change of CdO pellet density as a function of the pressing pressure is shown in Fig.1. It is obvious that the pressing process of the investigated powder took place in three different stages while the boundary between the first and second stage is at 0.5 GPa and between the second and third stage is at 0.8 GPa, approximately.

In Fig.2. the line representing the change in a_0 as a function of applied pressure is shown. First in a series of samples is one subjected to pressure of 0.2 GPa; obtained a_0 value of 0.46945 nm is close to the value given in ASTM index for CdO of 0.46953 nm. From the trend of our curve it can be estimated that a value for our specimens at normal pressure would be close to 0.46950 nm, cubish compares well with ASTM value. It can be seen that at low pressures the lattice reacts rapidly and at 0.2 GPa, a_0 reaches the lowest value recorded in our measurements ($a_0 = 0.46921$ nm). Further increase in pressure is accompanied by distinct increase in cell volume up to 0.8 GPa where a_0 the value of 0.46974 nm. The change from a_0 value at 0.2 GPa is 13 standard deviations will the further increase in pressure expansion of the unit cell is less pronounced and at 2 GPa $a_0 = 0.47000$ nm.

In Fig.3 the relation between dislocation densities and applied pressure is shown. The measurements were made on the metal-

lographic planes 111. The density of dislocations increases shortly up to the pressure of 0.8 GPa, where it approximately reaches the maximum after which it asymptotically approaches the value of 10^{11} (cm⁻²).

The analysis of the results which are presented in Figs.2 and 3 following behaviour of CdO lattice will the applied pressure the effects recorded are those which remain frozen after the applied pressure.

Having analysed the microstructure of a pellet fracture [3] it could be noticed that in the first stage of consolidation the pellet density increased due to rearrangement and better packing of the powder particles, but, to a lesser degree due to of their contact surface. The second and third stage of consolidation is characterized by more intense growth of the contact surface owing to particles deformation.

At the pressure of about 800 MPa there is a point from which further the unit cell volume as well as the number of dislocations do not change appreciably. This is also the region from which, with the increase of pressure a non-stoichiometry begin to appear.

Therefore we have here Cd_{1-x}O phase and shape of the curves on the diagrams may be the net result of the applied pressure and non-stoichiometry.

Conclusion

The behaviour of finally divided cadmium oxide powder subjected to the pressures between 25 and 200 MPa is investigated by X-ray diffraction and by chemical analysis. It is shown that, over 800 MPa the Cd content increases with the applied pressure. Precise measurements of unit cell dimensions and of the number of dislocation revealed then dependence on pressure. Interdependence between these three dimensions is assumed.

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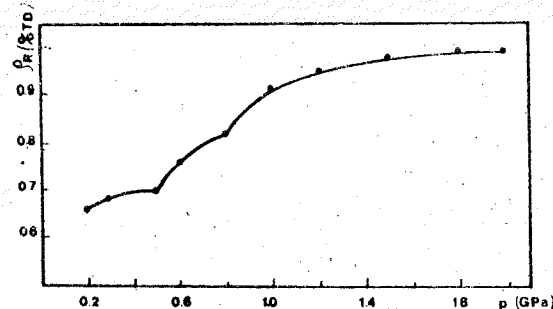


Fig. 1. The change of CdO specimens density in the function of the pressure.

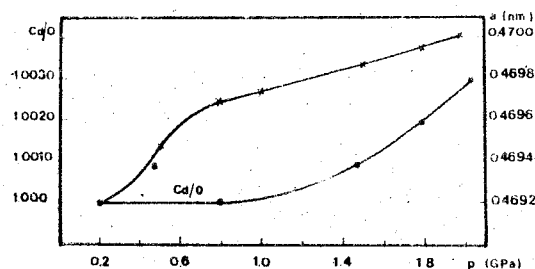


Fig. 2. The change of unit cell dimensions (a) and non-stoichiometry of CdO as a function of applied pressure.

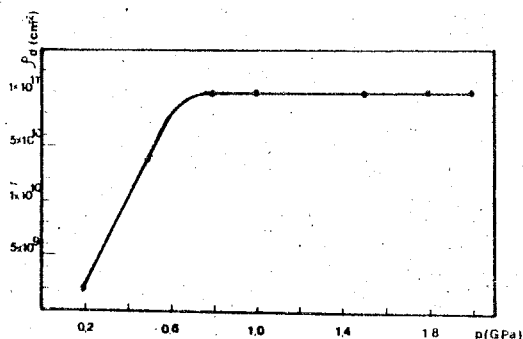


Fig. 3. The dependence between dislocation densities in CdO and applied pressure.

THE INFLUENCE OF PRESSURE ON THE CRYSTALLOGRAPHY OF FRACTURE OF MOLYBDENUM SINGLE CRYSTALS OF HIGH PURITY

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It is known that the deformation of metals and alloys under pressure is accompanied by the significant increase in their plastic properties. Apparently, such changes in plasticity must be reflected in the character of fracture of brittle materials under pressure, e.g., BCC metals. However, this question is practically not studied. Therefore, in this work we investigated the crystallography of fracture of molybdenum single crystals deformed at different temperatures and pressures.

The molybdenum single crystals of high purity ($R_{300} K/R_{4.2} K$ 2000) were used. The specimens were measuring $2.0 \times 0.2 \times 16$ mm. Fig. 1 shows the orientations of the longitudinal axes of the single crystals under investigation in the basic stereographic triangle. The deformation was carried out at pressure 0.1 and 800 MPa with velocity $2 \cdot 10^{-6}$ mm/s.

The features of fracture at 77 K. The fracture of molybdenum single crystals at this temperature occurs by cleavage and is of crystallographic character. The cleavage planes represent different crystallographic planes with small Miller indices belonging to the zone axis $\langle 110 \rangle$, depending on their orientation. The dependence of the active cleavage plane on the orientation of the single crystals is described in terms of the angles ζ and φ (ζ is the angle between the plane with maximum normal stress and plane $(00\bar{1})$; φ is the angle between the plane $(00\bar{1})$ and the active cleavage plane; the geometric definition of these angles is shown in Fig. 1). The cleavage planes were identified by means of applied crystallography. The angles ζ and φ were defined for each single crystal, and the orientational dependence of the active cleavage plane $\varphi = \varphi(\zeta)$ was plotted (Fig. 2). The analysis of the obtained curve reveals, that the choice of the active cleavage planes depends on two factors - the orientation of the single crystals and the value of the fracture stress for the corresponding plane.

The features of fracture at the room temperature. The fracture of molybdenum single crystals at room temperature shows

strong orientational dependence and may be ductile or brittle, depending on orientation. The fracture of the single crystals with $\zeta \leq 18^\circ$ occurs by cleavage along the plane (001). At $\zeta \geq 40^\circ$ the fracture occurs by the plastic break and is accompanied by the formation of the blade-like neck in the plane (110). The deformation of the single crystals in the interval $\zeta = 18 \pm 40^\circ$ also leads to the formation of a neck; however the final break of the specimens occurs by cleavage.

The anisotropy of the fracture features for the single crystals with BCC structure is conditioned by the change of the relation between the resolved normal stress in the active cleavage plane and the resolved shear stress in the active slip plane, when the angle φ changes. As a result, the accommodation of stress during the deformation of the single crystals with large angles ζ occurs by the plastic flow, and not by the spreading of cracks.

The plastic deformation of the BCC metals is notable for the strong temperature dependence of the critical shear stress. Therefore, when the temperature is lowered, the temperature T_{bp} of the brittle - ductile transition for the molybdenum single crystals of different orientations moves towards the greater angles ζ . This feature is common for all BCC metals. Fig.3 shows the orientational dependence of T_{bp} for BCC metals. Its analysis reveals, that at normal pressure the boundary of the change of fracture mechanism from brittle cleavage to plastic break moves towards greater angles ζ .

The features of fracture under pressure. The ductility of single crystals under pressure increases significantly, and the boundary of the change of fracture mechanism from brittle to plastic one moves continually towards smaller angles ζ . It means, that pressure smoothly displaces the curve T_{bp} (Fig.3) towards low temperatures. The formation of a neck during plastic deformation at 800 MPa is observed even for the single crystals with orientations close to $\zeta = 0^\circ$. Simultaneously with the increase of plasticity, the character of fracture changes. At Fig.4* the fractographs of the fracture surface for the single crystals with different values of ζ are represented. The analysis shows that the formation of the brittle fracture zone along the cross-section of the specimen occurs nonuniformly. At the same time, the brittle zone is observed near the side faces and the plastic break

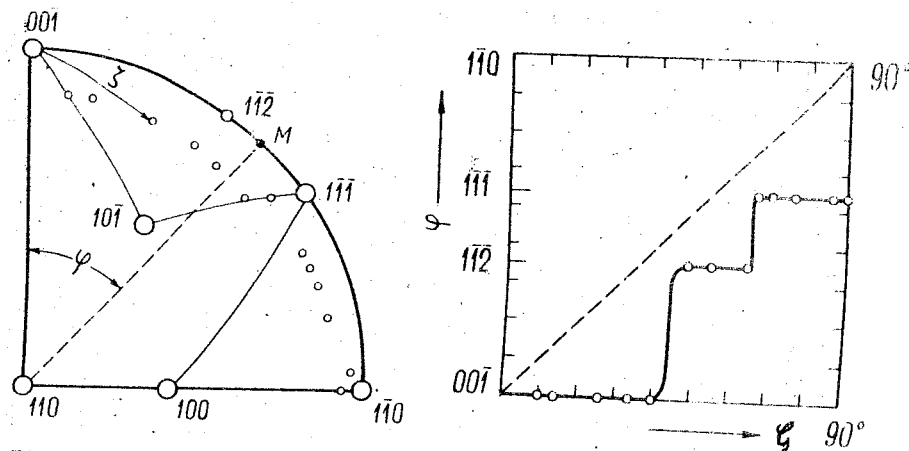


Fig.1. Orientation of the longitudinal axes of the molybdenum single crystals, M - pole of observed cleavage plane.

Fig.2. The $\varphi = \varphi(\zeta)$ curve of molybdenum single crystals deformed in tension.

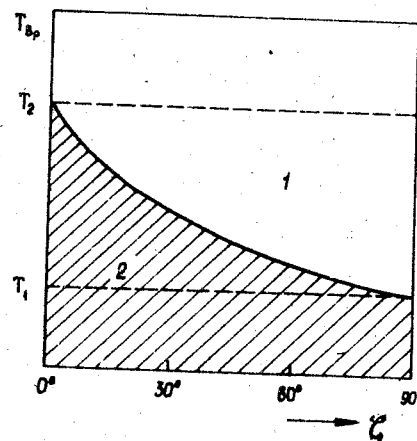


Fig.3. Dependence of T_{bp} on angle ζ : (1) - ductile fracture; (2) - brittle fracture.

*The Figure is given at the end of the book

takes place in the middle of the sample. In all cases under pressure the region of the slowing down of the crack spreading is observed. The typical look of this region is shown in Fig.5*. The formation of the region of the delayed crack spreading takes place always near the sides of the specimen. When the crack reaches the critical size, it spreads with sound velocity.

The relief of the fracture surface reflects the features of the plastic deformation proceeding.

Examination at a higher magnification shows, that the slip tracks at the upper and lower surfaces of the single crystals are continued at the fracture surface in the form of cleavage steps. It means, that the morphology of the fracture surface reflects the features of the plastic deformation proceeding. The comparable analysis of the fracture surfaces shows, that pressure essentially slows down the cross slip of screw dislocations. It follows from the fact, that steps in this case are much more straight, and the distance between the steps increases. As a whole, the morphology of the fracture surface, deformed under pressure, becomes similar to the morphology, typical for the low temperature fracture. It means, that the influence of pressure on the process of plastic deformation is physically equivalent to the lowering of temperature.

PHASE TRANSITIONS AND ELASTIC PROPERTIES OF BISMUTH UNDER PRESSURE UP TO 8.5 GPa

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Propagation velocities of longitudinal and transversal elastic waves, $V_L(P)$, $V_T(P)$, in polycrystalline bismuth were studied by means of pulse ultrasonic method at 295 K when the pressure was raised from 2.8 to 8.5 GPa in the high pressure apparatus /1/. Some peculiarities in $V_L(P)$ and $V_T(P)$ at pressures 4.2 GPa and 5.5 GPa caused by phase transitions BiIII-BiIV and BiIV-BiV were observed. These phase transitions were found for the first time by Bridgman /2/, but some authors doubted their existence. Phase transition BiV-BiVI was observed at 8.14 GPa /3/ by sharp and large decreases of transversal and longitudinal wave velocities. Velocities $V_L(P)$ and $V_T(P)$ obtained and our earlier ultrasonic piezometric data up to 3.2 GPa /4/ give the complete elastic properties variation of bismuth under pressure up to 8.5 GPa including the jumps at the five phase transitions.

The density variation $\rho(P)$ was calculated from $V_L(P)$, $V_T(P)$ and data of transition density jumps:

$$\rho(P) = \rho_0 + (1 + \Delta) \int_0^P \frac{dx}{V_L^2(x) - \frac{4}{3} V_T^2(x)} + \rho_0 \sum_i \delta_i$$

where ρ_0 - density at $P = 0$, $\Delta = \frac{9K_0^2 T}{C_P \rho_0}$ - adiabatic-isothermal correction, δ_i - relative density variation at i -th phase transition and $0 \leq \rho_i \leq \rho$. We have used the values δ_1 , δ_2 from our data /4/ and δ_3 , δ_4 and δ_5 from /2,5/. The dependence $\rho(P)$ obtained for bismuth is in excellent agreement with the values of density at pressures 2.6, 2.9, 8.8, 9.0 and 9.5 GPa measured by means of X-ray /7/ and neutron diffraction. The results of piezometric measurements /2,5,8/ disagree with X-ray and our ultrasonic data at pressures higher than 2.5 GPa. That probably may be due to wrong δ_1 , and δ_2 values obtained by /2,5,8/ (see Figure).

From $\rho(P)$, $V_L(P)$ and $V_T(P)$ all elastic properties, their pressure derivatives and Debay temperature for all six high pressure phases of bismuth were calculated. Adiabatic bulk modulus

*The Figure is given at the end of the book

$K_s(P)$ and shear modulus $G(P)$ are shown on Figure. Phase transitions BiIII-BiIV and BiIV-BiV are sluggish; they cause small increase of these moduli (1-4%). Pressure derivatives $\partial K_s/\partial p$ and $\partial G/\partial p$ for BiIII, BiIV and BiV are different. These polymorphic transitions should be considered as first-order phase transitions connected with a small distortions of bismuth crystalline lattices with different structures but close in volume.

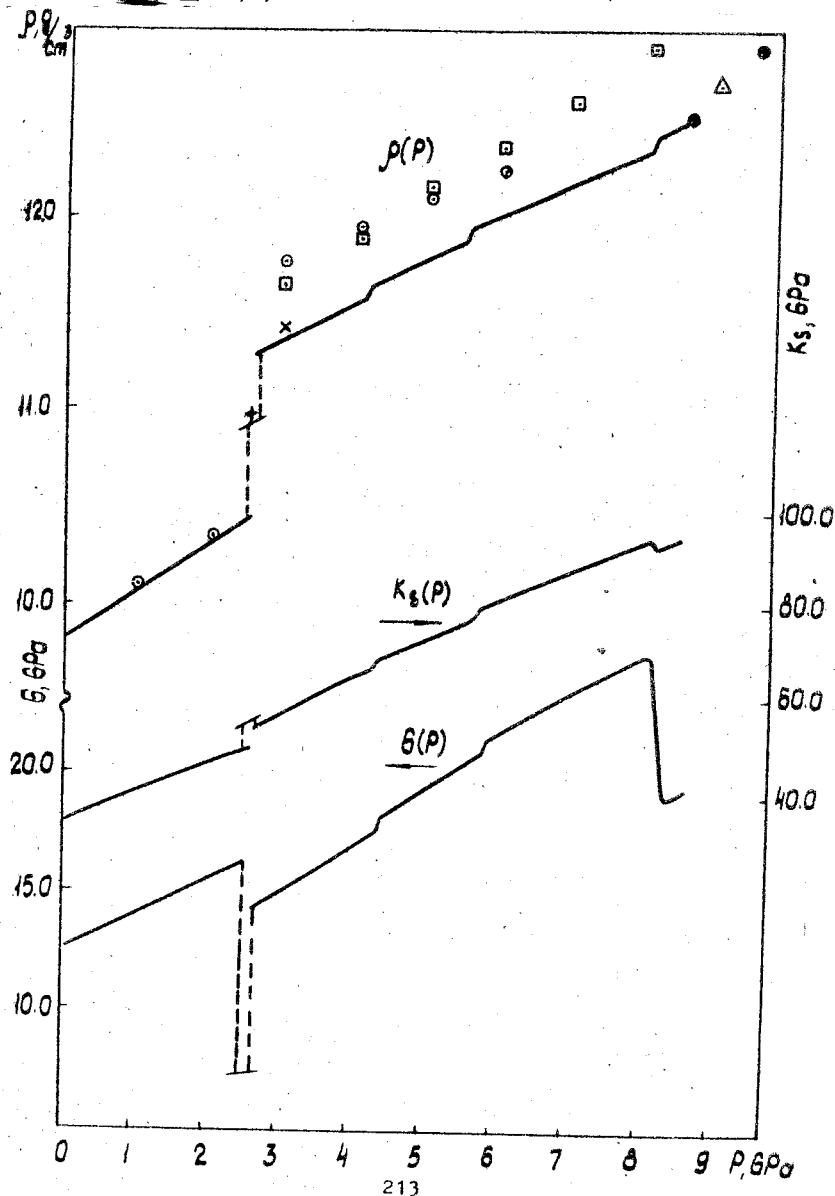
From our values $K_s(P)$ and $(\partial T/\partial p)_s$ measured by Ramakrishnan Hardy and Kennedy [9] the Grüneisen parameters γ for BiI, BiII and BiIII were calculated.

At phase transitions BiI-BiII, semimetal-metal, and BiV-BiVI when bcc metal phase BiVI arises the essential decreases of shear properties $U_t(P)$ and $G(P)$ were obtained. These phenomena correlates with increases of electroconductivity at the transitions and are connected with the growth of electron concentration leading to larger screening of nonpair ion-ion interaction, responsible for shear stability of the lattice.

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Density $\rho(P)$, bulk, $K_s(P)$, and shear, $G(P)$, moduli of bismuth at the high pressures:
our data, $\square$ - /2/, x - /5/, $\odot$ - /8/,
 $\oplus$, $\triangle$ - /7/



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The mechanical properties and peculiarities of plastic deformation of alkali halides having NaCl-type lattice are quite well studied as a function of the temperature, deformation rate and content as well as state of impurities /1/. Crystals of CsCl type are studied in this respect much less. The number of the works on high pressure effects in mechanical properties of alkali halides is quite enough, but the results are sometimes contradictory /2-4/ and the interpretation of the results is usually poorly argued /4/.

In the present article the qualitative and quantitative data on plastic deformation of CsI and LiF single crystals by uniaxial deformation as a function of hydrostatic pressure up to 1 and 1.4 GPa respectively are described. CsI crystals were compressed along $\langle 110 \rangle$ direction, the total number of the impurities ~ 100 ppm, specimens with dimensions $5 \times 5 \times 15$ mm were prepared according to /5/. The LiF specimens with the same dimensions were cleaved from one crystal with impurity content ~ 554 ppm and subsequently annealed at 450°C during 2 h. /3/. The mechanical testing was done on apparatus combined with Instron testing machine /6/. Slip bands were studied by optical and X-ray methods.

In Fig.1 a typical form of stress-strain curves of CsI crystals for different hydrostatic pressures is shown. The increase in pressure up to 1 GPa causes the following effects:

1) The pressure dependence of flow stress at $\varepsilon = 0.2\%$ can be presented as

$$\tau_{0.2}^{(p)} = \tau_{0.2}^{(0)} (1 + \alpha P) \quad (1)$$

where $\alpha = 3.5 \pm 0.1 \text{ GPa}^{-1}$, i.e. at 1 GPa the increase in $\tau_{0.2}$ is 350% (Fig.2, curve 1);

2) Work-hardening coefficients $\theta = \frac{1}{G(P)} (d\tau/d\varepsilon)$ on II

Because of nondistinct yield point for CsI the flow stress at $\varepsilon = 0.2\%$ was studied

and III stages increases with pressure in a following manner

$$\theta(P) = \theta^{(0)} (1 + \beta_1 P) \quad (2)$$

where $\beta_{II} = 1.09 \pm 0.05 \text{ GPa}^{-1}$, $\beta_{III} = 0.92 \pm 0.05 \text{ GPa}^{-1}$, original values $\theta_{II}^{(0)} = 1.3 \cdot 10^{-3}$ and $\theta_{III}^{(0)} = 0.7 \cdot 10^{-3}$;

3) Together with primary slip system $\langle 100 \rangle \{110\}$ and system $\langle 112 \rangle \{110\}$ an additional system $\langle 110 \rangle \{110\}$ is acting at high pressure;

4) By transition to III stage the "avalanch slip bands" appear producing on side faces of the specimen the slip steps of $50-300 \mu\text{m}$ in height.

It should be noted, that near these "avalanch slip bands" there is no accommodation bands and that these bands are distinct of Chernov-Lüders bands, twins and kink-bands. These bands do not cause the asterism on Laue diagrams similar to slip by the formation of punch patterns and indentation figures /7/.

In Fig.2 (curve 2) the pressure dependence of yield point for LiF crystals is presented. In the pressure interval under investigation there is no pressure dependence in $\tau = 4.55 \text{ MPa}$. The work-hardening coefficient was also independent on pressure, being $\theta^{(0)} = 1.3 \cdot 10^{-3}$.

Let us discuss the cause of the effects observed in our experiments. It is known from a literature, that

$$\tau(P) = \tau^{(0)} (1 + \frac{P}{G} \frac{dG}{dP}),$$

$$\tau(P) = \tau^{(0)} (1 + \frac{2P}{G} \frac{dG}{dP}) (1 - \frac{P}{K}),$$

where G -shear modulus, K -volume compression modulus. According to these formula at $P=1 \text{ GPa}$ a yield point should not be increased more than on 10-15% for both CsI and LiF crystals in contradiction with experimental data. Let us now take into account the known relations

$$\tau_{II} = \alpha G b \sqrt{\rho},$$

where $\alpha \approx 0.5$, b - Burgers vector value, ρ -dislocation density, and

$$\theta_{II} = \frac{1}{G} \frac{d\tau}{d\varepsilon} \text{ or } \theta_{II} = \alpha b \frac{d\rho^{1/2}}{d\varepsilon}$$

As $d\theta_{II}/dP = \alpha b d/dP (d\rho^{1/2}/d\varepsilon)$, then according to (2) one

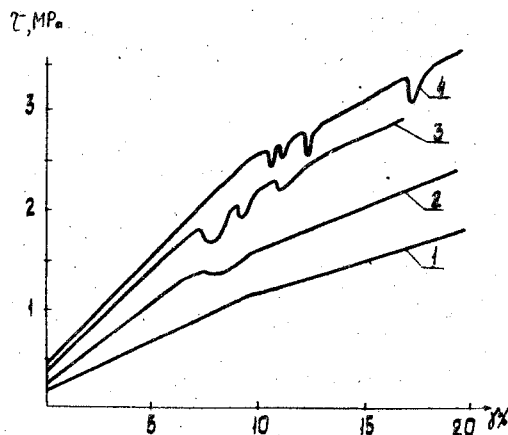


Fig. 1. Stress-strain curves of CsI crystals (in coordinates shear stress-shear strain) at different hydrostatic pressures: 1 - 0.1, 2 - 150, 3 - 450, 4 - 730 MPa.

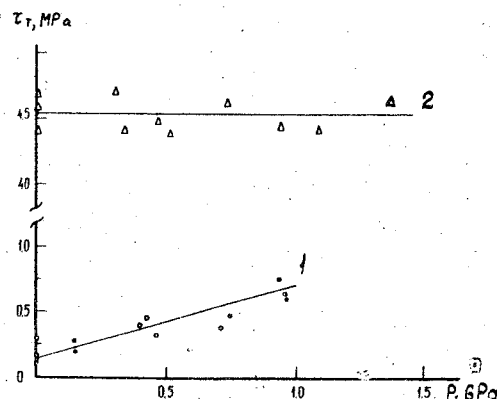


Fig. 2. Baric dependence of yield stress for CsI - 0 (1) and LiF - Δ (2) single crystals.

can write

$$\rho_{\gamma}^{(P)} = \rho_{\gamma}^{(0)} (1 + \beta P)^2 \quad (3)$$

By means of (3) it is possible to find an energy of a crystal, having at the pressure P the dislocation density $\rho_{\gamma}^{(P)}$. In accordance with nonlinear elastic theory [8] the dislocation generation causes the increase in crystal volume on a value $dV = U/G$, where $U = 1/2 (Gb^2L)$, L - dislocation segment length. The total energy at the pressure P is equal to

$$W^{(P)} = (U^{(P)} + P dV) \rho_{\gamma}^{(P)} = \frac{b^2 L}{2} (G + P) \rho_{\gamma}^{(P)},$$

and taking into account the pressure dependence of G one will get

$$W^{(P)} = W^{(0)} \left[1 + \frac{P}{G} \left(1 + \frac{dG}{dP} \right) \right] (1 + \beta P)^2,$$

where $W^{(0)} = 1/2 (Gb^2L) \rho_{\gamma}^{(0)}$. As the increase in yield point with pressure is proportional to that in $W^{(P)}$, it follows, that

$$\tau^{(P)} = \tau^{(0)} \left[1 + \frac{P}{G} \left(1 + \frac{dG}{dP} \right) \right] (1 + \beta P)^2$$

Putting in this formulae the experimental data, one will find that for CsI the yield stress should be raised by 34%, and that for LiF - by 10% in accordance with experimental data.

Thus by the description of the behaviour of alkali halides by uniaxial deformation under hydrostatic pressure one should take into account the change with pressure not only of the shear modulus, but of dislocation density too.

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PHYSICOMECHANICAL PROPERTIES AND GEOMETRICAL CHARACTERISTICS OF HIGH-STRENGTH SYNTHETIC DIAMOND GRINDING POWDERS OF NEW GRADES

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The industrial technology for the production of high-strength monocrystalline diamond grinding powders synthesized in the Ni-Mn-C growth system has been developed at the Institute for Superhard Materials of the Ukrainian Academy of Sciences. The high pressure apparatuses used for the diamond synthesis permitted to keep pressure and temperature in narrow limits during the entire synthesis cycle enabling to produce regular well-shaped single crystals.

To withdraw highly strong grains from single diamond crystals obtained under new synthesis conditions and produce grinding powder, a complex work aimed at the development of the improved process and equipment of the selective mechanical and ultrasonic grinding, classification and sorting of powders was carried out. The technology involves the employment of the powder separation by vibration tables, air separators /I/ and other special sorting methods that provide an efficient withdrawal of strongest grains and a higher uniformity of end products. As a result grinding powders of AC50, AC65, AC80, AC100, AC125 and AC160 grades are produced from synthesis products. The data of the static compression and impact load strengths for high-strength grinding powders of various grit sizes are given in Figs.1 and 2. The study on the thermal stability of grinding powders heat-treated at 1100 °C for 20 min in hydrogen was also performed. The index defined for AC50, AC65, AC80 grades 3I5/250 and 250/200 grinding powders is in the range of 2 to 2.5.

The high-strength grinding powders of new grades manifest a higher grain isometry (Table). The form factor of grains that is the ratio between the maximal grain projection length and its width does not surpass 1.18 for AC50 and AC65 grades, 1.15 for AC80, 1.12 for AC100 and AC125 and 1.10 for AC160. To provide a more complete description of grains shape the coefficient of surface development $\phi = \frac{L^2}{4\pi S}$ was used where L is the length of the

The basic geometrical characteristics of the monocrystalline grinding powders of AC50, AC65 and AC80 grades

Grade of grinding powder	Grit size, μm	Length of projection, μm	Width of projection, μm	Average grain size, μm	Form factor	Length of the projection contour, μm	Area of projection, μm^2	Coefficient of surface development
AC50	315/250	368	320	344	1.15	1114	90576	1.10
	250/200	316	267	291	1.18	919	59452	1.10
	200/160	255	215	235	1.18	743	53552	1.11
	160/125	214	180	197	1.18	610	26484	1.11
	125/100	158	134	146	1.18	461	14996	1.12
	100/80	132	114	123	1.16	381	10464	1.11
AC65	400/315	475	417	446	1.14	1394	143968	1.07
	315/250	381	333	357	1.14	1093	68924	1.07
	250/200	297	260	279	1.14	854	55292	1.10
	200/160	247	216	232	1.14	735	38928	1.10
AC80	500/400	554	501	528	1.10	1622	195920	1.07
	400/315	467	418	442	1.11	1365	137744	1.08
	315/250	359	321	340	1.12	1027	79900	1.05
	250/200	308	265	287	1.15	872	56304	1.07

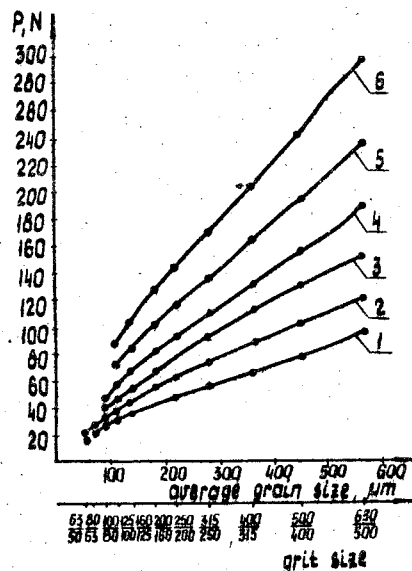


Fig. 1. Uniaxial static compression strength of grinding powders of AC50 (1), AC65 (2), AC80 (3), AC100 (4), AC125 (5) and AC160 (6) grades.

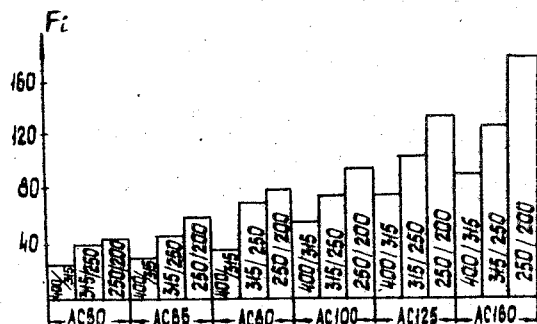


Fig. 2. Impact load (F_i) strength of grinding powders of AC50 to AC160 grades in 400/315, 315/250, 250/200 grit sizes.

projection contour, S is the area of the grain projection /2/. This coefficient amounts to 1.12 to 2.10 for AC50 grade and 1.05 to 1.06 for the AC160 grade. For the comparative assessment of the grains surface roughness a criterion of surface roughness: $K_r = \frac{\psi_1 - \psi_2}{\psi}$ is proposed, where ψ_1 and ψ_2 are the coefficients of grains sphericity defined by various methods, ψ_1 being defined by the resistance of a powder layer to the gas flow and ψ_2 by the specific area of the powder. For example, K_r of 250/200 grains varies from 1.4 (AC50 grade) to 1.15 (AC160 grade).

The high-strength grinding powders of new grades showed high performance ability. In the drilling downholes in rocks of IX drillability category with drill bits developed by the Institute the footage drilled per one bit increased by 1.5 to 2.0 times when fitted with diamonds of AC50 to AC80 grades as compared to those fitted with natural ones.

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PRESSURE DEPENDENCE PECULIARITIES OF SINGLE CRYSTAL ELASTIC CONSTANTS FOR $A^{III}B^V$ AND GROUP IV SEMICONDUCTORS

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Numerous experiments showed that tetrahedral semiconductors with diamond (Si, Ge) and zinc-blende ($A^{III}B^{V-N}$) structure transform to metallic state at first order phase transition with a structure change. As calculation demonstrated [1] the structure of high-pressure phase depends to a large extent on material ionicity: more covalent semiconductors ($f_1 < 0.3$) prefer to crystallize in the β -Sn type of structure, whereas more ionic ones ($0.3 < f_1 < 0.6$) transform to rocksalt structure.

Our goal is to investigate pressure dependence peculiarities of sound propagation velocities and effective second order elastic constants for low pressure form of some semiconducting materials with different ionicity f_1 . As it is known sound velocities determine the slope of dispersion curves at the center of Brillouin zone (BZ). Subjects of inquiry are silicon, germanium, gallium antimonide, indium arsenide with f_1 equal 0.0, 0.0, 0.261, 0.357 correspondingly [2].

Pulse-phase ultrasonic method has been used to determine pressure dependences of transit times $t_1(p)$ for five independent longitudinal and transverse waves at the carrier frequency of 7.5-10 MHz. The experimental procedure was described in [3,4]. Experiments have been carried out at hydrostatic compression of samples in the piston-cylinder device (0-25 kbar) and in the apparatus of the "toroid"-type (25-82 kbar). Transmitting liquid was benzine. [110], [100], [111] oriented samples were shaped as (16x16) mm² plates with (10-30) mm thickness and as turnicatted cone with 9 mm average diameter and (3-4) mm length.

To rule out possibility of sample failure due to known for GaSb and InAs first order phase transition with a great volume discontinuity the measurements were carried out in the region of semiconducting phase stability. Readings obtained at running up and down were practically in agreement. The sample after loading kept their dimensions and single crystal quality as Laue patterns showed.

Optimized by means of Lagrange multipliers method baric de-

pendences of transit times $t_1(p)$ were used as initial data for calculation of baric functions for density $\rho(p)$, normalized volume $V/V_0(p)$, sound velocities $v_1/v_{1,0}$, effective second order elastic constants $C_{ij}(p)$, Debye temperature $\theta(p)$, microscopic Grüneisen parameters $\gamma_1(p)$ and parameters of Murnaghan equation of state.

There are normalized sound velocities $v_1/v_{1,0}$ as a function of reduced pressure $p/K_{T,0}$ on the Fig.1 and 2. Here $K_{T,0}$ is an isothermal bulk modulus of material at ambient conditions.

The transition pressures to metallic state for GaSb and InAs were determined as sharp deviations from monotonic behavior of measured dependences $t_1(p)$ and were equal to 64 ± 4 kbar and 72 ± 4 kbar correspondingly.

$V/V_0(p/K_{T,0})$ dependences for Si, Ge, GaSb, InAs coincide what is natural because the values of isothermal bulk modulus pressure derivatives $K'_{T,0}$ for these materials are closely.

The longitudinal sound velocity v_1 in the direction [110] increases under pressure with small deviation from linearity for the all investigated materials (Fig.1). This is in agreement with the known for silicon and germanium increasing of longitudinal acoustic (LA) phonon frequencies away from the BZ center under pressure.

Analysis of pressure dependences of transverse sound velocity v_2 [110] [001] and v_3 [110] [110] (the first Muller index shows the direction of particle displacement) reveals the next singularities.

Decreasing of transverse sound velocity v_3 under compression of above mentioned materials was found to precede the transition to denser phases (β -Sn-type or NaCl-type for InAs)(Fig.2). As a result the second order elastic constant $(C_{11}-C_{12})/2$ for InAs decreases considerably in the whole interval of semiconducting phase stability, but not only in direct vicinity to phase transition as for GaSb. Diminution of this elastic constant means an increasing of the compliance of lattice to shear deformation that tries to break down the bonds of tetrahedra, i.e. covalency.

Considerable softening of another branch of transverse acoustic phonons defined by propagation velocity v_2 and elastic constant C_{44} takes place for low pressure phase of InAs. In our opinion this peculiarity is due to the fact that only InAs high pressure phase has NaCl-type structure. For silicon, germanium and gallium antimonide inequality $2C_{44}/(C_{11}-C_{12}) > 1$ remains va-

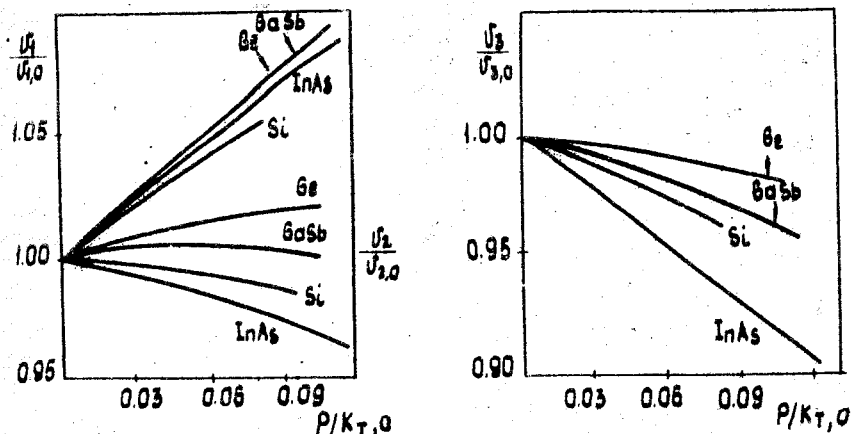


Fig.1. Reduced pressure $p/K_{T,0}$ dependences of normalized velocities of longitudinal v_1 $[110]$ and transverse v_2 $[110]$ $[001]$ waves for silicon, germanium, gallium antimonide, indium arsenide.

Fig.2. Reduced pressure $p/K_{T,0}$ dependences of normalized velocity of transverse wave v_3 $[110]$ $[110]$ for silicon, germanium, gallium antimonide, indium arsenide.

lid at transition to denser β -Sn-type phase but for indium arsenide it is to reverse the sign.

We are very much obliged to Luikh V.K. for help in the experiments.

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EFFECT OF HIGH PRESSURE ON STRUCTURE AND HIGH-TEMPERATURE OXIDATION RESISTANCE OF ALUMINUM NITRIDE CERAMICS

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Dense aluminum nitride polycrystals with up to 2% porosity barothermally sintered in high pressure apparatus at 1; 3; 4 and 5 GPa were studied. Ultradispersed AlN powder was used as the starting material.

Through X-ray diffraction analysis it has been found that barothermally sintering does not stabilize the initial wurtzite-like modification AlN_{2H} . The sintering of AlN grains is accompanied by their plastic deformation which causes large quantities of strain stacking faults and intensive formation of polytypes. The latter is attributed to the genesis of new crystalline modifications of AlN, among which the lower polytypes AlN_{3H} , AlN_{6H} and AlN_{9H} prevail. The group of the polytypes mentioned characterizes the syntaxis phenomenon /1/ in AlN which occurs on the background of the diffused reactive phase transitions $2H \rightarrow NH$. Multilayer nature of the identified polytypes of sphalerite-like structure ($3H$) is due to the formation of strain polytypes by a shear mechanism.

The studied barothermochemical mechanism of the formation of the polytypes in AlN is characterized by a high intercoherency of AlN_{NH} lattices due to the cross-linking of three-dimensional covalent networks of AlN_{NH} along $\{00L\}$ basal planes /2/.

X-ray diffraction analysis was used to analyze polytypes formed in macrovolumes of AlN (Table I). The increase in sintering pressure is found to decrease continuously the concentration of the wurtzite-like modification AlN_{2H} up to 75-80 mass % at the highest sintering pressure.

Together with the ordered distribution of stacking faults which is characteristic for strain polytypes, disordered ultradispersed stacking faults are observed in AlN as well. The concentration α of the disordered strain stacking faults in AlN_{2H} was measured using the method described in /3/.

The increase in sintering pressure was found to enhance the concentration of disordered ultradispersed stacking faults, the highest percentage of which at 5 GPa being $\alpha \geq 50\%$. The latter is

due to the relatively low energy of stacking faults in AlN as compared with the other types of plastic deformation.

Table 1. Parameters of AlN polytypes observed in products of barothermaling sintering determined by X-ray analysis

Interplanar spacings, nm	Diffraction indexes of reflections and crystallographic systems				
	(hkl) _{2H}	(hkl) _{3H} *	(hkl) _{3C} *	(hkl) _{6H}	(hkl) _{9H}
0.268	(100)			(100)	(100)
0.267					(101)
0.265				(101)	
0.262					(102)
0.254				(102)	(103)
0.248	(002)	(003)	(III)	(006)	(009)
0.243					(104)
0.236	(101)			(103)	
0.230					(105)
0.218		(102)	(200)	(104)	
0.196				(105)	
0.193					(108)
0.183	(102)			(106)	(109)
0.168				(107)	
0.160					(10,11)
0.156	(110)	(104)	(220)	(110); (108)	(110); (10,12)
0.141	(103)			(109)	
0.137					(10,14)
0.135	(200)			(200)	(200)
0.132	(112)			(116)	(119)
0.130	(201)	(105)	(311)	(203)	
0.124	(004)	(006)	(222)	(00,12)	(00,18)
0.118	(202)			(206)	(209)
0.105	(203)			(209)	
0.102	(210)			(210)	(210)

*3H and 3C symbols refer to hexagonal and cubic systems of sphalerite-like modification, respectively.

For the first time the thermal stability of the above mentioned polycrystalline AlN was studied under the conditions of isothermal heating. Figure shows the oxidation isotherms for the AlN specimens sintered at pressures of 3, 4 and 5 GPa. It is seen from comparison of scale-resistance data for these specimens and those for hot-pressed AlN specimens /4/ that the former are very stable under heating in air.

Results of kinetic studies allowed to establish laws for oxidation rate and to calculate the oxidation rate constants for AlN specimens (Table 2) and the activation energy E for oxidation of AlN sintered at 4 GPa which amounts 465 kJ/mol.

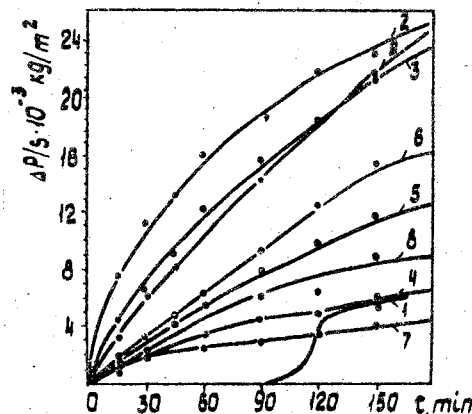
Table 2. Oxidation rate for AlN specimens sintered at 3.0, 4.0 and 5.0 GPa

Pressure, GPa	Oxidation temperature, K	Rule of oxidation	Oxidation time, min	Rate constants	
				$K_A, \text{kg/m}^2 \text{sec}$	$K_P, \text{kg}^2/\text{m}^4 \text{sec}$
3.0	1473	$(\Delta P/s)^2 = K_P \tau$	0-180	-	$3.94 \cdot 10^{-9}$
			0-60	$3.85 \cdot 10^{-6}$	$1.09 \cdot 10^{-8}$
	1573	$1/K_P (\Delta P/s)^2 + 1/K_A \Delta P/s = \tau$	60-180	$1.56 \cdot 10^{-6}$	$2.15 \cdot 10^{-7}$
			1673	$\Delta P/s = K_A \tau$	-
4.0	1473	$(\Delta P/s)^2 = K_P \tau$	0-180	-	$1.85 \cdot 10^{-9}$
			1573	$(\Delta P/s)^2 = K_P \tau$	-
	1673	$1/K_P (\Delta P/s)^2 + 1/K_A \Delta P/s = \tau$	0-180	$3.80 \cdot 10^{-6}$	$3.00 \cdot 10^{-7}$
			1573	$1/K_P (\Delta P/s)^2 + 1/K_A \Delta P/s = \tau$	-
5.0	1573	$1/K_P (\Delta P/s)^2 + 1/K_A \Delta P/s = \tau$	0-180	$5.00 \cdot 10^{-5}$	$1.12 \cdot 10^{-7}$
	1673	$1/K_P (\Delta P/s)^2 + 1/K_A \Delta P/s = \tau$	0-180	$5.00 \cdot 10^{-6}$	$1.96 \cdot 10^{-7}$

It is seen from Table 2 that AlN specimens exhibit a high oxidation resistance and that the oxidation mechanism is complicated, this is undoubtedly bound up with special features of AlN structure formation in barothermaling sintering and with intensive formation of polytypes in particular.

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Oxidation isotherms for AlN specimens sintered at 3, 4 and 5 GPa:

1 - 1473 K, 5 GPa; 2 - 1573 K, 5 GPa; 3 - 1673 K, 5 GPa;
4 - 1473 K, 3 GPa; 5 - 1573 K, 3 GPa; 6 - 1673 K, 3 GPa;
7 - 1473 K, 4 GPa; 8 - 1573 K, 4 GPa; 9 - 1673 K, 4 GPa.

THE MÖSSBAUER PARAMETERS OF (EuTb)O₃ AND (EuTm)O₃ SYNTHESIZED BY HIGH TEMPERATURE AND PRESSURE

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The rare-earth oxide solid solutions (EuTb)O₃ and (EuTm)O₃ were synthesized by using the method of high pressure and high temperature in the present paper. They were investigated by using the Mössbauer effect of ¹⁵¹Eu. It is shown that the relationship of isomer shift to atomic number of the second rare-earth element and unit-cell volume $V^{1/3}$ is still in the linear range of reference /1/. This agrees with the result that we expected.

I. Introduction

The several double rare-earth oxide solid solutions were synthesized by the authors in recent years /1-4/. In order to determine their physical properties, we have studied their structures, valence states of rare-earth ions, coordinations and hyperfine interactions. These studies are important for developing rare-earth solid state physics science.

The change in localized region of 4f valence electrons in rare-earth solid solution is very large, thus solid solution has some special physical properties. But the change caused by the interaction between two kinds of rare-earth ions in localized well double rare-earth oxide solid solution is little, so it is difficult to detect the change mentioned above. If Mössbauer method with high energy sensitivity is used, it is possible to obtain some information about hyperfine interaction. We have investigated double rare-earth oxide solid solutions (EuRE)O₃ (RE=Gd, Dy, Ho, Er, Yb, Lu) by using Mössbauer effect /1/. It is shown that isomer shift depends on unit-cell volume $V^{1/3}$ in a linear fashion. Because elements Tb and Tm obey the lanthanide contraction law, (EuTb)O₃ and (EuTm)O₃ synthesized using the same method should show this linear fashion. In order to verify our conjecture, we investigated the double rare-earth solid solutions (EuTb)O₃ and (EuTm)O₃ using X-ray diffraction and Mössbauer effect.

2. Experiment

The starting materials used were rare-earth oxides. Their purities were 99.95% for Eu_2O_3 , 99.99% for Tb_4O_7 , 99.9% for Tm_2O_3 . They were of bcc structure at room temperature. Eu_2O_3 and Tm_2O_3 were weighed and mixed according to 1:1, Eu_2O_3 and Tb_4O_7 according to 2:1 mol. Then the specimens were put into sample rooms and synthesized by using high pressure method after they were heated at 950 °C for 30 minutes. During the synthesis, at first the pressure was applied to 3.0 GPa, afterwards the temperatures were increased to 1190 °C for $(\text{EuTb})\text{O}_3$, 1205 °C for $(\text{EuTm})\text{O}_3$ and kept for 30 minutes, then samples were quenched under maintaining pressure, and finally the pressure was released when the samples were cooled to room temperature. After stripped impurity, samples were grinded to grains. The lattice parameters of the samples were determined by using X-ray diffraction. The Mössbauer spectra were recorded with OXFORD MS-500 spectrometer. The velocity for the Mössbauer spectrometer was calibrated with He/Ne laser interferometer. The Mössbauer spectra were fitted using leastsquare method.

3. Results and discussions

The solid solutions $(\text{EuTb})\text{O}_3$ and $(\text{EuTm})\text{O}_3$ synthesized using the method mentioned above were investigated by X-ray diffraction.

It is shown that solid solutions are all single phase with B-type structure. The lattice parameters were listed in Table I.

Table I. The lattice parameters of solid solutions (± 0.004 Å)

Samples	a(Å)	b(Å)	c(Å)	v(Å ³)	β (°)
$(\text{EuTb})\text{O}_3$	6.836	3.578	5.959	145.434	93.67
$(\text{EuTm})\text{O}_3$	6.742	3.522	5.922	140.518	93.10

Since the solid solutions were of B-type structure, the asymmetric factor for quadrupole splitting was not equal to zero, this made Hamiltonian describing hyperfine interaction not have the solution with general form. The approximate solution can be obtained only through numerical calculation. In addition, $\eta \neq 0$ causes the change from eight to twelve transition lines between ground state and excited state. The resonance line positions can be determined through solving Hamiltonians eigenequations, and the

intensities of resonance lines are obtained through eigenvectors of the two Hamiltonians and the multipolarity of the γ -ray connecting the two states /5/. According to the expression for the resonance energies and intensities of transition lines, Mössbauer spectra can be fitted with least square method. ^{151}Eu Mössbauer parameters derived from fitting the spectra are listed in Table 2. In order to compare it with other $(\text{EuRE})\text{O}_3$ solid solutions, we also wrote out parameters of reference /1/ in Table 2. The Mössbauer spectrum of $(\text{EuTb})\text{O}_3$ at room temperature was shown in Fig.1.

Table 2. Mössbauer parameters of solid solution at room temperature

Samples	δ (mm/s)	$eV_{zz}Qq$ (mm/s)	η
$(\text{EuGd})\text{O}_3$	0.46(0.01)	-6.34(0.23)	0.76(0.05)
$(\text{EuTb})\text{O}_3$	0.47(0.01)	-9.63(0.31)	0.32(0.07)
$(\text{EuDy})\text{O}_3$	0.48(0.01)	-6.41(0.14)	0.82(0.03)
$(\text{EuHo})\text{O}_3$	0.49(0.01)	-7.49(0.26)	0.88(0.04)
$(\text{EuEr})\text{O}_3$	0.50(0.01)	-6.23(0.28)	0.83(0.04)
$(\text{EuTm})\text{O}_3$	0.51(0.01)	-8.95(0.37)	0.18(0.16)
$(\text{EuYb})\text{O}_3$	0.52(0.01)	-4.98(0.25)	0.59(0.08)
$(\text{EuLu})\text{O}_3$	0.53(0.01)	-6.94(0.22)	0.81(0.03)

It was seen from Table 2 that there was a definite relation between the atomic number of the second rare-earth element and isomer shift. The relation between isomer shift and unit-cell volume $V^{1/3}$ was shown in Fig.2.

The following discussions can be made on the experimental data:

(1) $(\text{EuTm})\text{O}_3$ is a new phase material. Schneider et al /6/ have ever synthesized $(\text{EuTm})\text{O}_3$ solid solution with C-type structure. However, it was shown from X-ray diffraction that the solid solution $(\text{EuTm})\text{O}_3$ synthesized using high pressure method was of B-type structure, so $(\text{EuTm})\text{O}_3$ obtained in the present work was of new phase.

(2) In the solid solutions, Eu atoms are in one of the crystallographically equivalent positions. This could be seen from the fitting of the spectra.

(3) Eu ions in solid solutions investigated in this work are in trivalent oxidation states. Using source EuF_3 , the isomer shift for Eu^{2+} -containing compounds are in the range of -11.2 - -13.9 mm/s, the corresponding parameters for Eu^{3+} -containing compounds

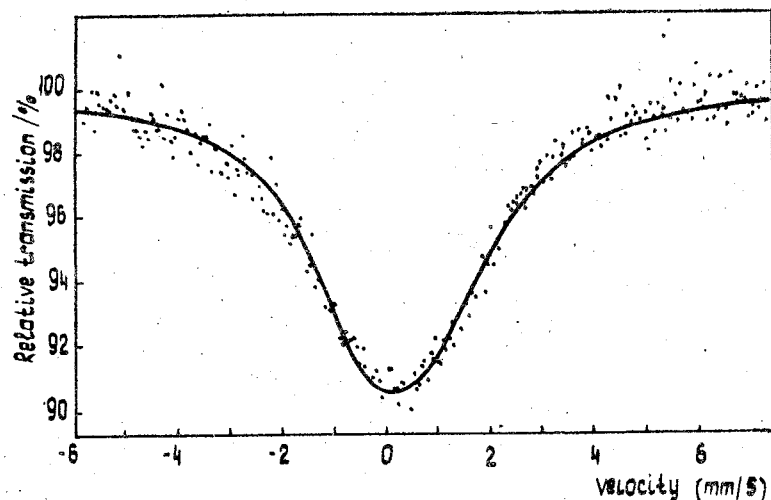


Fig. 1. Mössbauer spectrum of $(\text{EuTb})\text{O}_3$ at room temperature.

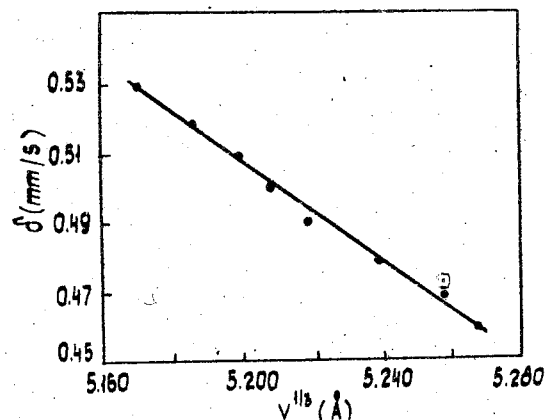


Fig. 2. The relation between isomer shift and unit-cell volume $V^{1/3}$.

are in the range of -0.13 – 1.5 mm/s [7]. Hence the valence state for Eu ion can be obtained.

(4) In reference [1], the equation obtained by fitting points in Fig. 2 with least-square method was:

$$\delta \text{ (mm/s)} = 4.383 - 0.745 V^{1/3} (\text{\AA})$$

$(\text{EuTb})\text{O}_3$ and $(\text{EuTm})\text{O}_3$ isomer shifts which were obtained by taking their unit-cell volumes in the above equation were 0.465 mm/s and 0.510 mm/s respectively, while the isomer shifts obtained from the experiment were 0.47 mm/s and 0.51 mm/s respectively. Thus $(\text{EuTb})\text{O}_3$ and $(\text{EuTm})\text{O}_3$ were still in the linear range which we had determined in the $(\text{EuRE})\text{O}_3$ solid solutions. So isomer shifts depended on unit-cell volumes $V^{1/3}$ in a linear fashion for ABO_3 -type double rare-earth solid solutions ($A=\text{Eu}$, $B=\text{heavy rare-earth elements}$).

(5) The quadrupole splitting constants obtained in this work are negative, which indicates that the electric field gradients were also negative, and they had the same sign as that of lattice contributions. This also shows that the contribution of change from second-order $4f$ electrons to EFG are smaller than that of lattice contributions.

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THE EFFECT OF HIGH PRESSURE ON GRAIN BOUNDARY MIGRATION RATE

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Introduction

The migration of grain boundaries plays a major role in many significant technological processes. However, its mechanism has not been explained fully yet. If, while examining the grain boundary migration, an additional thermodynamic variable i.e. pressure is applied, it may give ground to extending the physical basis for conclusions concerning the structure of grain boundaries and their migration mechanisms. This work aims at examining the influence of pressure on the grain boundary migration process and at determining the activation volume for the process.

In accordance with the absolute reaction rate theory [1] if the boundary migration process consists in creating activated atoms complexes resulting in the shift of atoms from one grain to another, the kinetics of such a process can be presented in this equation:

$$v_m = A \exp (-G/RT) \quad (1)$$

where: v_m - grain boundary migration rate, A - constant,
 T - temperature, R - gas constant, $G = U - TS + pV_{act}$ -
Gibb's free energy of the "activated complex"
 U , S - internal energy and entropy of complex
 p - external pressure, V_{act} - activation volume.

The quantity V_{act} may be experimentally determined:

$$(p_1 - p_2)V_{act} = RT \ln(v_{m1}/v_{m2}) \quad (2)$$

in which p_1 and p_2 , v_{m1} and v_{m2} are two different pressure and corresponding boundary migration rates.

While introducing the above dependencies it was taken into account that both entropy and internal energy are slow-variable functions of pressure [2]. Value analysis of activation volumes

acquired during the research of grain boundary migration in hydrostatic high pressure conditions makes it possible to measure the local expansion of lattice during atoms shift in connection with grain boundary migration. Experimental measurement of activation volume may lead to concluding as to mechanisms of grain boundary migration. The idea behind it is a comparison of experimentally achieved activation volume with a known volume of crystal defects which may create an "activated complex" on a grain boundary that is a condition for the process to take place.

Experimental

A high pressure equipment produced by High Pressure Research Center Polish Academy of Sciences was used during the research. Experiments were divided into three groups to be able to determine the influence of grain boundary structures and the driving force of migration process on migration mechanism.

1. Examination of the grain growth in copper MIE after the critical strain.

Rolled copper after being recrystallized at temperature of 1173 K and deformed to critical strain 4% had an average grain size $73 \pm 3 \mu m$. The samples were annealed at temperatures and pressures listed in table for 60 minutes. The table also shows the results of average grain size measurement.

2. Examination of the recrystallization and recovery of aluminium of 4N purity.

Cylinders 30 mm in diameter were reduced by hydrostatic extrusion to 3 mm in diameter. Strength samples were taken from the bars obtained by such means. The samples were annealed at temperatures and pressures listed in table. Next, mechanical properties were investigated with a help of INSTRON strength machine with a 10 mm based extensometer. Moreover, grain sizes were measured by the use of an electron transmission microscope and an optical microscope. The results are shown in table and diagram.

3. Examination of grain growth in 4N purity aluminium.

The mode of samples preparation and the method of results evaluation was identical with the one presented above except for initial recrystallisation annealing which was done at the temperature 553 K at low pressure. $3.1 \mu m$ size grains were obtained as a result. Results of grain size measurements are shown in ta-

ble. Mechanical properties of examined samples did not differ among themselves in a statistically significant manner.

Correlation between grain size and temperature, pressure and time annealing

Sample symbol	Temperature (K)	Pressure (GPa)	Time (min)	Grain size (μm)
A11	553	0.05	60	3.1 ± 0.5
A12	553	1.0	60	3.1 ± 0.6 *
A13	553	0.05	25	3.1 ± 0.4
A14	553	1.0	480	4.2 ± 1.0
A21	623	0.05	60	32.0
A22	623	1.0	60	21.9
A23	623	0.05	300	52.2 ~~xxx~~
A24	623	0.5	300	54.1 ~~xxx~~
A25	623	1.0	300	35.7 ~~xxx~~
M1	837	0.05	60	69.2
M2	837	0.5	60	90.1
M3	837	1.0	60	69.7
M4	1083	0.05	60	202.7
M5	1083	0.5	60	224.6
M6	1083	1.0	60	200.1

Remarks: letter A designates aluminium samples, letter M - copper samples, * - material after annealing contained non-recrystallized areas; grain size were measured in recrystallized areas only, xx - before annealing in high pressure samples were annealed at temperature 553 K for 60 min.

Discussion

The analysis of the above presented results points to the fact that kinetics of grain boundary migration depends on pressure to a much smaller degree than the kinetics of recrystallization and recovery. For example, yield stress for a sample annealed at the pressure of 1 GPa is about 30% higher than a sample annealed at low pressure.

On the basis of data presented in table the activation volume for recrystallization process may be calculated. It is assumed that the structure of sample A14 (see table) after annealing at the pressure of 1 GPa is identical with the structure of sample A11 annealed at low pressure for one hour. An assumption like this one is justified since both the grain size and mechanical properties (diagram) of both samples are identical within error limit.

On the basis of equation (2), it may be calculated that such relation of the migration process rate correlates with $1.5 \times 10^{-29} \text{ m}^3$ per atom of activation volume i.e. approximately 0.8 atomic volume. It is close to activation volume for selfdiffusion and indicates that the kinetics of formation of recrystallization nuclei and migration of subboundaries is controlled by the kinetics of vacancies migrations /3/. Differences in size in samples A21 and A22 can be explained in a similar manner.

In case of migration of the already existing boundaries, the activation volume for grain boundary migration process is much smaller than the vacancy volume: $V_{\text{act}} < 0.1$ atomic volume. This result contradicts the theories of grain boundary migration that attach a significant role to vacancies as, for example, it was analyzed in papers /4/ and /5/. It supports, however, that the process of atomic shift takes advantage of the already existing structural porosity within the grain boundary /6/. As far as the observed phenomena are concerned, the relations between grain boundary migration rate and the pressure at which the samples were annealed (table) will be the subject of further research.

Conclusions

Activation volume for the formation of recrystallization nuclei and recovery is approximately 0.8 atomic volume. On the other hand, activation volume for grain boundary migration (grain growth) in copper and aluminium at different purities and different driving forces is less than 0.1 atomic volume. Thus, it may be concluded, that the kinetics of recovery and formation of recrystallization depends on migration rate of lattice gaps, while vacancies do not play a significant role in the case of grain boundary migration.

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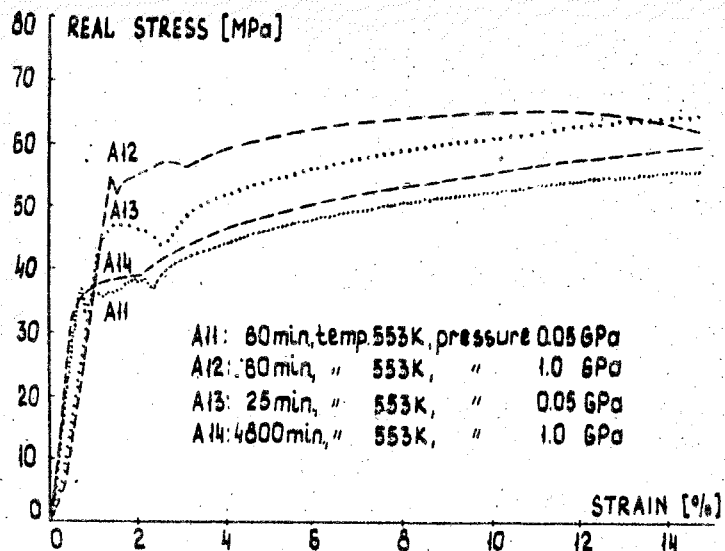


Diagram 1: The relation between real stress and strain for aluminium samples annealed at high pressure

The relation between real stress and strain for aluminium samples annealed at high pressure.

ENHANCED GROWTH OF COPPER GRAINS ANNEALED AT HIGH PRESSURE

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Introduction

Grain boundary migration goes with most thermally activated processes of polycrystal microstructure transformations. Publications on the influence of hydrostatic pressure on grain boundary migration are not numerous (about 10-15). The first published results of growth and secondary recrystallization research are contradictory pointing to both positive and negative effect of hydrostatic pressure on the grain boundary mobility [1,2,3]. The effect of hydrostatic pressure on microstructure transformations and grain boundary properties has been discovered lately [4]. New kind of experiments have been carried out under pressure to analyze grain boundary migration rate [5,6].

It is the objective of this work to explore the effect of pressure on high-angle grain boundary migration in copper which have been deformed to critical strain. Presence of large gradients of stored strain energy indicates that in this particular case grain growth results from grain boundary migration under high driving forces.

In a recently published work [6] by the authors, the research was focused on the low-angle grain boundaries migration in recovery and recrystallization processes under small driving forces.

Experimental

The material used was technically pure copper containing oxides precipitations. Strength samples were cut from copper MIE rolled and recrystallized at temperature 1173 K for 60 minutes. The samples were deformed to critical strain $\epsilon = 4\%$ by means of uniaxial tension at the initial strain rate $\dot{\epsilon}_i = 2.1 \times 10^{-4} \text{ s}^{-1}$ in INSTRON strength testing machine. Average grain size in the initial stage was $73 \pm 3 \mu\text{m}$. Next, strength samples were cut into 5 mm in diameter and 10 mm length cylindrical samples with an electro-spark saw.

The samples were annealed under high pressure in apparatus

produced by High Pressure Research Center. Prior to high pressure annealing, the chamber was vacuum pumped to 1.3 Pa (10^{-2} Tr) and system was degassed at 423 K for 15 min . The grain boundary migration studies were performed in two temperatures 1083 K and 873 K under pressures up to 1.5 GPa both in recrystallized material and in the one that after recrystallization was critically strained. Argon was high pressure medium. The pressure was measured by manganin coil with accuracy app. 10 MPa . Temperature was stabilized with accuracy $\pm 5 \text{ K}$ (PtRh6-PtRh30 thermocouple). From pressure annealed samples metallographic cross-section were prepared by mechanical polishing, chemical removing (reagent - $30 \text{ cm}^3 \text{ HNO}_3$, 10 g FeCl_2 , ethyl alcohol) and chemical etching (reagent - 20 g chromic acid anhydride, $5 \text{ cm}^3 \text{ HNO}_3$, $75 \text{ cm}^3 \text{ H}_2\text{O}$). The average grain sizes were determined by the method of random secants on the metallographic microscope NEOPHOT (app. 180 grains were measured on each cross section).

Results

Diagram shows measurements results of grain size as a function of annealing pressure and temperature. Annealing time was constant i.e. 60 minutes . Grain size at the initial stage (i.e. after initial annealing at 1173 K for 60 min) was $73 \pm 3 \text{ }\mu\text{m}$. Estimated on the basis of the diagram percentage of increase of migration rate per 0.1 GPa is:

- for recrystallized material - app. 1.5% at temp. 873 K , app. 11% at temp. 1083 K ,
- for recrystallized and deformed to critical strain - app. 3% at temp. 873 K , app. 4% at temp. 1083 K .

Discussion

Grain boundary mobility in recrystallized material depends on the grain boundary atomic structure. Under high pressure conditions, the distances between atoms in crystallographic lattice become shorter and by the same way free boundary volume gets smaller. Shifts of atoms through the boundary with a reduced "porosity" are hindered. Therefore, grain boundary migration rate during grain growth should also become smaller. This argument is confirmed by the research of secondary recrystallization process in high purity polycrystal /5/.

Research of technical purity polycrystal (MIE copper for discussed experiment) annealed under high pressure point to an oppo-

site phenomenon i.e. growth of average grain size. This phenomenon can be interpreted as a pressure induced increase of driving force of grain boundary movement. Hence, the well known kinetics equation of grain boundary migration /7/ may be modified for high pressure condition as:

$$v(p) = M(p) \times F(p)$$

$$v(p) = [M_0 \exp(-G/RT)] \times [F_0 (1 + \alpha p)] \quad (I)$$

where $v(p)$ - grain boundary migration rate under pressure; $M_0, M(p)$ - grain boundary mobility in pressureless and pressure conditions; $F_0, F(p)$ - driving force in pressureless and pressure conditions; p - external pressure, α - factor of proportionality; $G = U - TS + pV_{\text{act}}$ - Gibbs's free energy /6/; R - gas constant, T - temperature.

It can be assumed that the growth of grain boundary migration rate of high-angle grain boundaries is controlled under pressure mainly by the increase of driving force. Grain boundary mobility with a considerable amount of precipitation in its microstructure is usually radically reduced, for pressure as well. Hence, $M(p)$ in equation (I) is for a tested material negligibly small.

Pressure induced increase of energy gradient between boundary and inside of a grain is responsible for the driving force increase in the migration process. This results from two reasons: 1. Attractive force between grain boundary and lattice dislocations increase under pressure. This is a result of growth of elasticity constants /8/ and the fact that boundaries are the places for stress relaxation and dislocation spreading /9/. 2. Dislocations generated on precipitations under pressure in MIE material are more numerous than in pressureless conditions (higher lattice stress) /10,11/. Moreover, pressure causes growth of stresses stored inside a grain derived from dislocations (lattice dislocation energy growth) /3/.

A hypothesis can be put forward that factor 2 is responsible for the growth of energy stored inside a grain in recrystallized material. Factor 1 and 2 are responsible for phenomena which occur while the recrystallized material is annealed under pressure and is additionally deformed to critical strain.

Factor 2 makes that material act as if the real strain was larger then it results from applied strain (specially when the material with high density of dislocation is considered - material deformed to critical strain) /12/. This discrepancy increase with the pressure increase. It is reflected in the shift of a slo-

AVERAGE GRAIN SIZE
D [μm]

Material - MIE technical purity
1, 2 - recrystallized
3, 4 - recrystallized and deformed
to crystal strain

4, T = 1083 K
2, T = 1083 K
3, T = 873 K

1, T = 873 K

PRESSURE [GPa]

Average grain size as a function of the pressure under which the annealing treatment was carried out

ped segment the curve 4 in relation with 2 (see diagram). It can be observed, however, that the "saturation phenomenon" excludes the final grain size to be larger than app. 240 μm . There might exist a maximum strain of material at which, instead of grain growth i.e. a contribution of the migration of already existing grain boundaries, a generation of new grains begins. This supposition needs to be researched much precisely. Except for the two phenomena discussed above, temperature factor should be considered since it causes a higher grain boundary mobility at temperature 1083 K than at 873 K (curve 1 and 2, 3 and 4).

Conclusions

The research of grain growth in MIE copper of technical purity was carried out under pressure up to 1.5 GPa and temp. 1083 K and 873 K. It was found out that in material of high density of dislocations an increase of high-angle grain boundaries migration rate occurs. Such a phenomenon is interpreted as an increase of the driving force of the migration process.

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The physical processes occurring at the shock wave front depend on the strength properties of metals and are largely determined by the presence and behaviour of polymorphous phase transformations under shock wave loading with pressures up to 30-40 GPa. The material undergoing a phase transformation under shock wave loading can turn out to be in a different structural state from that in which it is a phase transformation induced by static pressure or heating [1]. This change of state results from extreme conditions due to short pressure pulse duration (less than 10^{-8} sec), high strain rate at the shock wave front, nonuniform high temperatures in the specimen, and high cooling rate after adiabatic heating. The investigation of microstructures subjected to dynamic loading is one of the most promising directions in the study of the physical processes that occur in materials at shock waves propagate, such research is more convenient to carry out with alloys exhibiting residual phase transformation [2].

The influence of static (up to 20 GPa) and dynamic pressure at a bcc-fcc (α - γ) phase transformation in Fe-31.8 wt.% Ni-0.001 wt.% C alloy was investigated. After forging, billets designed for making specimens were heated to 1373 K and quenched in water. The martensite was obtained by cooling to the martensite transformation point M_s , at 218-214 K, or to the liquid nitrogen temperature.

Dynamic impact compression at a pressure of 13 GPa was affected on a 40 mm dia and 20 mm thick specimen press-fitted in a low-carbon steel preservation ring. Experiments at a quasihydrostatic pressure up to 8 GPa were conducted on cylindrical specimens 4 mm high and 5.5 mm in diameter compressed in a toroidal container which was placed between anvils with the corresponding profile. Pressures of up to 20 GPa were obtained on a hydraulic press Bridgman anvils. After pressure treatment, the specimens were studied with X-ray, metallographic and electron microscopy methods. The microhardness was determined with a PMT-3 meter by indenting a diamond pyramid under a 50 g load.

As the Fe-31.8 wt.% Ni alloy is cooled to M_s temperature large lenticular martensite crystals (α -phase) form which have a midrib in the centre in the austenite matrix (γ -phase). Quasihydrostatic pressure causes a reverse α - γ martensite transformation in such crystals of Fe-31.8 wt.% Ni alloy. The degree of transformation depends on the magnitude of pressure (Fig.1). First regions of the austenite that forms as a result of the α - γ transformation are observed after applying a pressure of 2-3 GPa. A pressure of 8 GPa reduces the amount of martensite by nearly a factor of two. Total completion of the bcc-fcc transformation in the Fe-Ni alloy investigated was attained on increasing the pressure up to 20 GPa.

The austenite arising in martensite crystals on exposure to pressure has the form of long narrow strips (Fig.2) which have the same etching capacity as the retained austenite. The strips of the new austenite start at the boundaries of the martensite and retained austenite or at the boundaries of contiguous martensite crystals of different orientations and at the boundaries of the austenite strips that appeared earlier. The strips either pass through the entire martensite crystal or end at the midrib. Strips of different width have different directions divide the martensite crystals into small fragments.

On exposing a Fe-31.8 wt.% Ni alloy specimen as a cube to a quasihydrostatic pressure of 8 GPa, scanning electron microscopy revealed, within large lenticular martensite crystals, narrow strips of the new austenite that were present on two surfaces of the specimen.

The rise in microhardness to 1.65 GPa in the retained austenite after applying a pressure of 8 GPa is associated partly with stress accommodation during the bcc-fcc transition and partly with the deformation resulting from the anisotropy of compression of the martensite and austenite. Strengthening of the austenite which forms as a result of the reverse transformation is roughly the same, whether the bcc-fcc transition takes place under pressure or during heating.

An electron microscopy investigation of Fe-31.8 wt.% Ni alloy showed that the crystallographic orientations of the martensite and the pressure-induced austenite obey martensitite orientation relations. The most frequent case is one where the retained austenite seems to "grow through" the martensite crystal as narrow

*The Figure is given at the end of the book

strips. The plates of the new austenite can be oriented as the retained austenite, but in some cases they can have a different orientation, including a nontwinning relative to the retained austenite. The dislocation density in the austenitic regions that have suffered a bcc-fcc phase transformation is appreciably higher than that in the retained austenite.

A bcc-fcc phase transformation in Fe-31.8 wt.% Ni alloy is induced by dynamic loading up to a pressure of 13 GPa. Metallographic investigations show that the bcc-fcc phase transformation in this case displays features peculiar to both the bcc-fcc transformation induced by quasihydrostatic pressure and the phase transformation induced by heating [2]. However, this transformation exhibits also peculiarities that are typical only for dynamic loading.

A bcc-fcc transformation under dynamic loading, just as a transformation under quasihydrostatic pressure, is initiated by the formation narrow austenite plates that spring up at the boundaries of martensite crystals (Fig.3). However, in comparison with a bcc-fcc transformation induced by quasihydrostatic pressure (Fig.2), these plates are narrower and their boundaries are frequently bent. The change in morphology may be accounted for the increase in temperature due to adiabatic heating on the shock wave front, by an increase in the number of nuclei, and the small interval of time for their propagation.

On complete bcc-fcc transformation gives rise to an ultradisperse microstructure that succeeds the martensite crystals in the specimen subjected to dynamic loading and consists of γ -phase crystals of different orientations.

Conclusions

1. In an iron-nickel alloy containing lenticular martensite quasihydrostatic pressure causes at room temperature a bcc-fcc martensite transformation. The transformation proceeds by the nucleation and growth of austenite plates that dissect martensite crystals into individual fragments. The degree of transformation depends on the magnitude of pressure.
2. The bcc-fcc phase transformation induced in Fe-31.8 wt.% Ni alloy by dynamic pressure has features of a transformation induced by both quasihydrostatic pressure and heating and can oc-

*The Figures are given at the end of the book

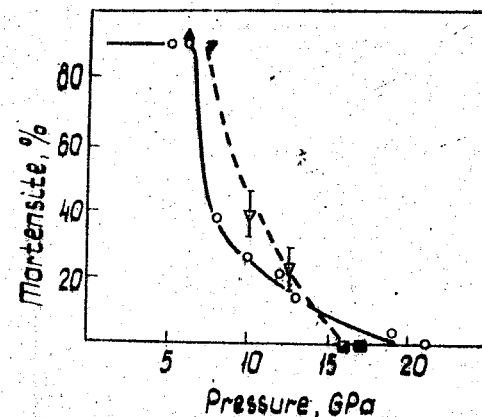


Fig. 1. Bcc-fcc phase transformation induced by quasihydrostatic pressure (solid line) and shock pressure (dotted line) in Fe - 32 wt.% Ni alloy. Empty symbols denote our experimental results. Black symbols stand for results reported in the literature.

cur by the formation of narrow strips of new austenite at boundaries of bcc crystals.

3. With the Fe-31.8 wt.% Ni alloy subjected to dynamic loading, bcc-fcc transformation gives rise to a disperse structure that succeeds the martensite crystals and consists of either a mixture of the bcc and fcc phases or disperse fcc-phase crystals.

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PHASE TRANSFORMATIONS IN FINELY DISPERSED STRUCTURES OF Fe ALLOYS DURING DEFORMATIONS UNDER PRESSURE

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By appreciably increasing the defect density, severe plastic deformation under high pressure changes the structural and phase states of the material and its physical and mechanical properties. These changes are characteristic of heavy-duty processes such as hydroextrusion, processing by burst, friction of two surfaces, etc. Therefore it is of practical interest to investigate phase and structural transformation induced in metals and alloys by plastic deformation and high pressure.

The effect of plastic deformation (by shear under pressure in Bridgman anvils) on structural and phase transformations in Fe-32% wt.Ni, Fe-29% wt.Cr-8% wt.Ni and Fe-40% wt.Mn alloys was investigated. After quenching, Fe-Cr-Ni and Fe-Mn alloys in the initial state contained 100 % bcc and 100 % fcc phases, respectively. After quenching, the Fe-Ni alloy was cooled to 77 K to obtain about 90 % martensitic bcc phase.

The pressure was generated with VK-6 alloy Bridgman anvils with the diameter of the support surfaces equal to 3-5 mm. Plastic deformation was accomplished by turning one anvil about another by an angle φ at room temperature and under a pressure of up to 16 GPa. In all cases, an axial pressure was first generated on the sample and then a given degree of deformation was reached by maintaining the axial pressure constant. The deformation was assessed by the formula [1]:

$$\varepsilon = \ln \frac{\varphi r}{d},$$

where d is the thickness of the sample, and r its radius. For 5 mm dia anvils the deformation was assessed at $r=2$ mm.

At degrees of deformation $\varepsilon \leq 2$ (less than a full revolution of the anvils) a finely dispersed structure with crystals sized 0.1 to 0.2 μm forms in the bulk of the specimen, irrespective of the phase composition (of the alloys investigated). In that state the microhardness increased to 5-6 GPa in comparison with 1-2 GPa in the as-quenched state. Further deformation ($\varepsilon > 2$) up to 35 full revolution of the anvils, did not change the structural

state and the microhardness was constant. Plastic deformation and damping of mechanical energy in to sample after the formation of a finely dispersed structure occur by grain-boundary slip [2].

Electron diffraction patterns of that structure have continuous Debye rings. That structural state is an illustration for the dissipative thermodynamic system realized during shear under pressure.

Changes in the phase composition of the samples during deformation under pressure occur both during the formation of a dissipative finely dispersed structure (for $\varepsilon \leq 2$) and during further deformation until an equilibrium under these conditions phase composition is attained. The results depicted three phase diagrams in pressure-true deformation coordinates confirm (Figs. 1 to 3) that the processing used in our investigations alters the phase state of the alloys dramatically.

Shear deformation under pressure reduces substantially (by 5 GPa) the interval of pressures of the bcc-fcc phase transformation in Fe-32% Ni alloy (Fig.1) and due to the production of a finely dispersed structure in the alloy, make the alloy stable with respect to the fcc-bcc transformation when subsequently cooled down to 4 K [3].

The processing employed by us allowed us for the first time to transform a stable fcc Fe-40% Mn alloy to an hcp state (Fig.2), in which the alloy persists when subsequently heated up to 600 K (Fig.3). Over the temperature range 600-750 K a reverse phase transformation occurs. After heating to 800 K and higher, only the fcc phase is observed in the sample (Fig.4).

In the Fe-29% Cr-8% Ni alloy that after quenching contained 100 % of the bcc phase, bcc-fcc and bcc-fcc-hcp phase transformations were observed (Fig.3). The crystal lattice parameter of the fcc* phase that appears in the alloy subsequent to deformation under pressure is 1.5% larger than that of the fcc phase of this alloy and is equal to 0.3651 ± 0.0015 nm [4].

Subsequent heating of Fe-Cr-Ni samples containing bcc, hcp and fcc* phases (Fig.3) to 600-700 K lowers the diffuseness of the X-ray without changing the peak height. The hcp-fcc phase transformation begins in the at 700-750 K temperature range and terminates at 900 K. In samples containing an fcc* phase the X-ray lines of the fcc* phase decrease in intensity and lines of the fcc phase appear at temperatures above 800-850 K (Fig.5).

Thus during shear under pressure (at deformation $\varepsilon \leq 2$) a finely dispersed dissipative structure forms in the alloys investigated.

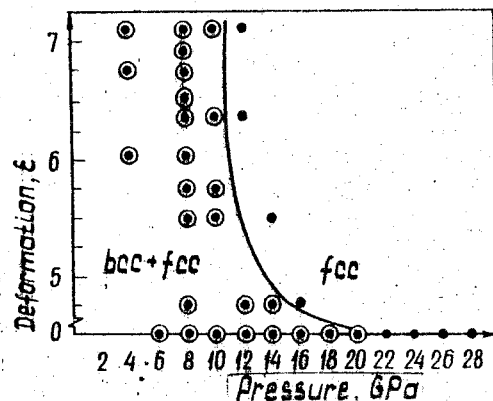


Fig.1. Phase diagram for Fe-32 wt.% Ni alloy: o - bcc phase; ● - fcc phase.

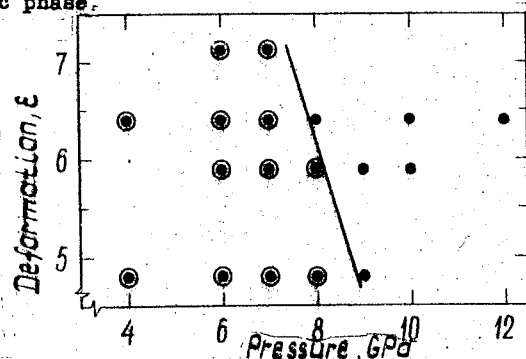


Fig.2. Phase diagram for Fe-40 wt.% Mn alloy: o - fcc phase; ● - hcp phase.

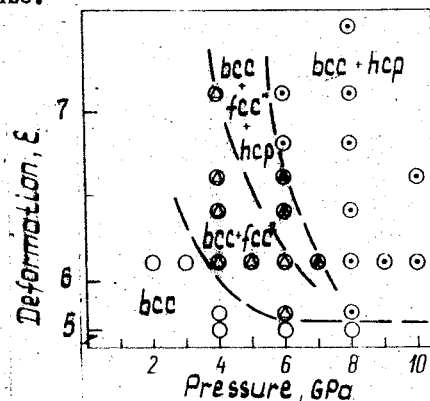


Fig.3. Phase diagram for Fe-29 wt.% Cr-8 wt.% Ni alloy: o - bcc phase; Δ - fcc* phase; ● - hcp phase.

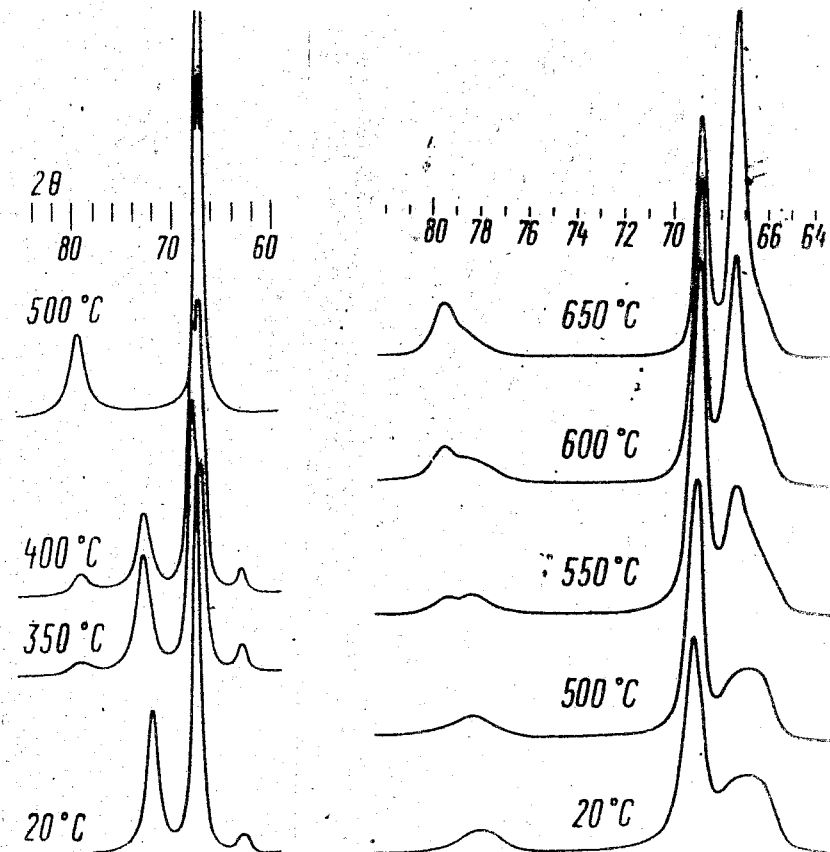


Fig.4. X-ray diffraction patterns for samples of Fe-40 wt.% Mn alloy after heating to: 620, 670, 800 K in the hcp state (P=10 GPa, $\epsilon=6.4$).

Fig.5. X-ray diffraction patterns for samples of Fe-29 wt.% Cr-8 wt.% Ni alloy in the bcc + fcc* state after heating to different temperatures.

tigated which consists of 0.1-0.2 μm crystallites. In the process of deformation of this structure the noncompensated rotation of neighbouring crystallites gives rise to internal stresses which, along with pressure, determine the phase state of the alloy. This results in phase transformations and in the establishment of an phase constitution of the alloy equilibrium for deformation under pressure.

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PRESSURE SYNTHESIS OF SUPERCONDUCTORS

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The investigation of the formation laws of various class of superconducting compounds are being carried out at the Institute for High Pressure Physics of the USSR Academy of Sciences for many years. By high pressure-high temperature treating it is possible to create new superconductors and enhance the critical parameters of superconducting state. The properties of metastable under room conditions carbides, ternary molybdenum sulfides and compounds with A-15 structure were studied.

For the synthesis of high pressure phases and high pressure treatment there was employed apparatus of the "thoroid"-type with a graphite heater and boron nitride or refractory metals ampule inside it, standard method for the temperature and pressure measurements was used.

The pressure annealing of the arc melted alloys under conditions ($3-7 \cdot 10^9$ Pa, 1600-1700 K, 5 min) offers to obtain the continuous series of monophasic solid solutions $(\text{Lu}, \text{Th})_2\text{C}_3$ with a Pu_2C_3 - type structure on the base of superconducting high pressure phase of Lu_2C_3 with a cubic structure of Pu_2C_3 . The composition dependence of T_c for this series may be presented as a curve with a maximum, fig.1, the lattice parameter obeys to Vegard's rule. In this case the critical temperatures of the binary compounds were 13.9 K and 4.0 K respectively and maximum T_c for the $(\text{Lu}_{0.8}\text{Th}_{0.2})_2\text{C}_3$ is 16 K. This maximum may be enhanced by increasing T_c of binary compounds, the best samples of Lu_2C_3 compound have $T_c = 15$ K [1].

The superconducting high pressure phases of Chevrel compound SnMo_6S_8 and PbMo_6S_8 which are known as having the highest critical magnetic fields were obtained under conditions ($3-7 \cdot 10^9$ Pa, 1500-1900 K, 5 min). The crystal structure of these metastable compounds (it is monoclinic, space group $\text{P2}_1/\text{m}$, $Z=2$) was determined on the base of refined structure of Mo_2S_3 -monocrystal produced under high pressure-high temperature conditions and analysed by automatic x-ray Syntex-P2 diffractometer [2]. The lattice a and c parameters of the compounds are similar to ones of the Mo_2S_3 but parameters b are twice. The structure is formed by

sulfur octahedra layers which are parallel to the "b" direction of the lattice. The chains of the molybdenum atoms surrounded by the sulfur atoms bind the layers. In each cell there are sulfur octahedra filled by molybdenum atoms and two empty ones which form open channels in the [010] direction of the lattice are pointing at the fig.2. The ordered penetration of the third component to take place into these channels. The high pressure phases with stannum and plumbum have higher T_c than initial Chevrel compounds 14.7 K and 15.7 K, respectively, but they have common critical fields. The high pressure phase HgMo_6S_8 is superconducting with $T_c=7.1$ K but Chevrel ones are not superconducting up to 7 K.

After treatment under $(3-6 \cdot 10^9 \text{ Pa}, 700-1000 \text{ K}, 5 \text{ min})$ and common annealings at $1100 \text{ K} \times 30 \text{ h}$ the critical current density for $1.2\text{Mo}_{6.4}\text{S}_8$ and $\text{Sn}_{1.2}\text{Mo}_{6.2}\text{S}_8$ increases by a factor of a few tens and achieved a value of $1 \cdot 10^4 \text{ A/cm}^2$ and $3 \cdot 10^4 \text{ A/cm}^2$ (4.2 K, 14 T), respectively. The changes of other parameters were not more than 10%. Dependencies for the critical current densities $J_c(B)$ for $1.2\text{Mo}_{6.2}\text{S}_8$ samples are shown in fig.3. $J_c(B)$ varies in proportion to the total amount of pinning centers in the samples and their interactions with the fluxoids. The last in turn are dependent on mechanical stresses, the crystallite and hole sizes, composition, etc., and these parameters depend on pressure and temperature [3].

The high pressure-high temperature treatment gave a great influence on berthollide A-15 niobium compounds. The 5-10 minutes annealings ordering of sublattice A and B under pressure gave a significant enhancement T_c that could be obtained by a classical many-stage annealing treatment under common conditions for a 100 h. For instance, the pressure annealing of the Nb_3Ga compound allows to obtain the increase T_c from 18 K to 20.4 K at the conditions $(10^9 \text{ Pa}, 2100 \text{ K}, 5 \text{ min})$.

The high pressure displaces the homogeneity boundaries of the Nb-Ge compound to its stoichiometric composition and the possibility of filling the sublattice B appears. The high pressure synthesis under the conditions $(7-9 \cdot 10^9 \text{ Pa}, 2100 \text{ K}, 5-10 \text{ min})$ the understoichiometric Nb-Ge alloys as a starting material with admixture of germanium gave the enhancement of bulk samples T_c up to 22.3 K at a set of a lattice parameter reduction to $a_0 = 5.135 \text{ \AA}$.

The giving instances show that the high pressure-high temperature treatment resulted in various effects, allowing to create new superconducting compounds and to improve the critical parameters.

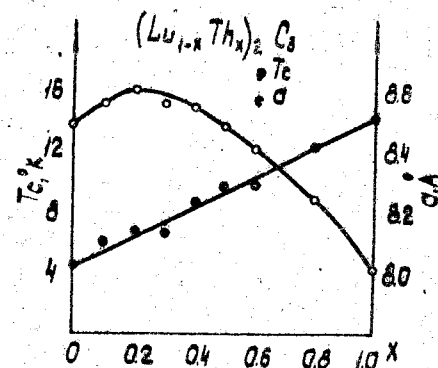


Fig.1. $T_c(x)$ and $a_0(x)$ dependences for the series of solid solutions $(\text{Lu,Th})_2\text{C}_3$.

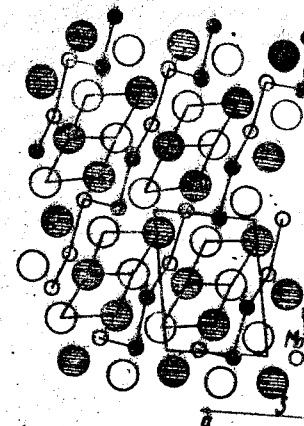


Fig.2. The projection of the Mo_2S_3 crystal structure on the (101) plane. The full atoms are lying in the layers $y=3/4$, the empty ones are lying in the layers $y=1/4$. The elementary cell is pointed out with two empty sulfur octahedra.

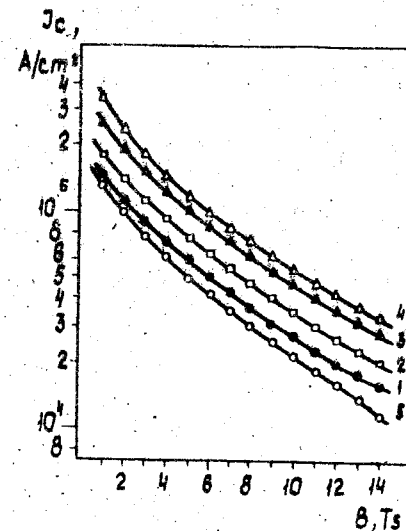


Fig.3. $J_c(B)$ -dependences for samples SnMo_6S_8 : 1-control case; 2 P-T-treatment without annealing, 3, 4, 5 P-T-treatment and annealing at 900 K, 1150 K and 1400 K for 24 h, respectively.

vers of superconductors. It can be supposed that this method will be perspective one for the investigation of a new class of high temperature metal-oxide superconductors.

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ON DIAMOND FORMATION BY CHEMICAL REACTIONS AT STATIC PRESSURE

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Looking for alternatives to the synthesis of diamond there have been many trials to obtain diamond from chemical reactions. Only by using of very high pressures and temperatures Wentorf /1/ found a successful formation of small-crystalline diamond from organic compounds in the region of 15 GPa/2000 °C.

A carbon deposition by chemical reactions has been reached at comparatively low conditions of pressure and temperature, that means it is possible to deposit the carbon in the diamond-stable region under these low conditions.

There are the following advantages for a possible diamond formation by chemical reactions:

- carbon deposition "in statu nascendi"
- diamond-stable region at conditions of moderate pressure and temperature
- in the case of silicon, germanium and hexagonal boron nitride the amorphous forms can be converted at lower phase transition pressures.

Amorphous boron nitride can be transformed into cBN above 6 GPa/800 °C /2/ and the transition into the metallic phases occur in a-Si at 10 GPa and in a-Ge at 6 GPa, whereas in the crystalline state their transition pressures are 15 and 10 GPa, respectively /3/.

Because in the most reactions described in literature in spite of carbon deposition in the diamond-stable region no diamond formation was observed, there is an evident strong cinetical prevention for the diamond formation.

An overcome of the kinetical prevention would allow conclusions on the mechanism of different diamond syntheses.

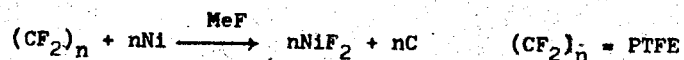
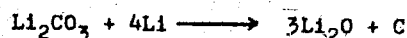
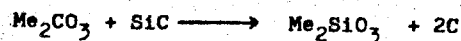
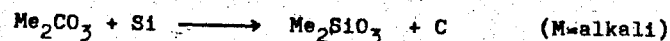
We investigated the carbon deposition from chemical reactions in a belt apparatus in the region to 4 GPa and 800 °C, be-

cause only a synthesis at moderate pressures and temperatures can be an alternative to the well-known catalytic transformation from graphite.

The reactions were selected with the aim to decrease the kinetical barrier in the following point of view:

- reactants with different hybridization of the carbon, e.g. sp^2 -, sp^3 - or mixed hybridization,
- reactions with or in presence of catalytic active elements or compounds, e.g. Fe, Ni which catalyze the graphite transformation or SiC, which acts as seed-interface by CVD-diamond deposition,
- reactants with diamond-similar structure and the possibility of a heterogeneous nucleation process, e.g. on Ni or Fe,
- compounds with positively charged carbon, because for positively charged carbon a smaller atomic volume can be expected,
- compounds with 6-C-rings, because 6-C-rings can be transformed into dense structures by martensitic transformations.

The following reactions were investigated in the field to 4 GPa/800 °C as shown in Fig. 1.



decomposition of

Hexachloro-benzene
Hexachloro-p-xylene
Ferrocene

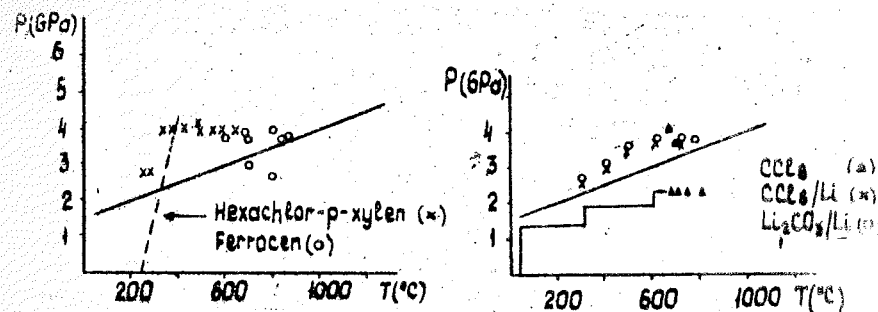


Fig. 1. Experimental conditions of different systems.

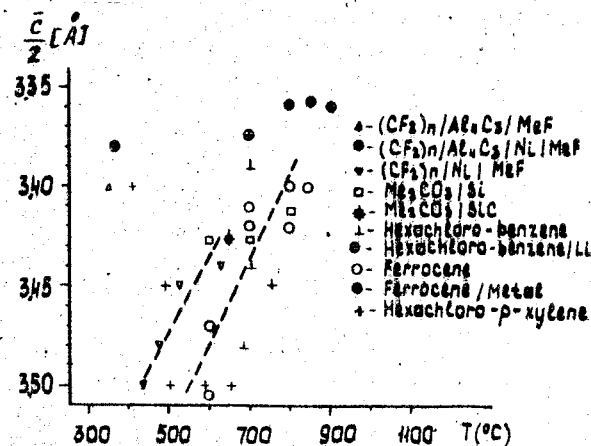


Fig. 2. Layer distance from obtained graphitic carbon of different systems and temperatures.

Results

Only graphitic carbon, predominantly low crystalline, but not diamond were found in the products of these reactions. Investigations were carried out by X-ray analysis and EDS. Fig. 2 shows the values of carbon layer distance, which were observed under different conditions and reactions. In spite of the scattering of values the stronger tendency of graphitization at upper temperatures, especially in metal-containing systems, can be clearly observed.

These results agree with about 50 such investigated reactions in literature and only at essentially higher pressure and temperature conditions a successful diamond formation is described by chemical reactions.

Conclusions

In the field to 4 GPa, 800 °C no diamond formation by chemical reactions at static pressure is observed.

The formation of diamond was obtained only by an essential increase of pressure and temperature, in the case of amorphous carbon at 15 GPa/1000-1500 °C after a partial graphitization at 15 GPa/500 °C /4/. These high conditions of transformation are comparable with those necessary for wellcrystalline graphite. This suggests a solid-solid-transformation mechanism on the martensitic way. Lower conditions for diamond formation can be expected in chemical reactions, which contain metallic components (active for catalytic graphitization) and organic compounds containing hydrogen, which are easily graphitizable.

The behaviour of a-C is not analogous to a-Si, a-Ge and a-hBN regarding phase transitions.

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INTRAMOLECULAR EXCITED-COMPLEX STATE AT HIGH PRESSURE

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Abstract

The formation of intramolecular excited-complex (IEC) state in some bichromophic compounds has been investigated at high pressures. The peak shift with pressure was determined. The formation is highly dependent on solvent viscosity due to a large amplitude twisting molecular motion. Applicability of this viscosity dependence to the hindered-rotation model based on Kramers' theory as well as the free volume limited model was discussed for the intramolecular excimer (IE) formation in 1,3-di(I-pyrenyl)propane (DPP).

I. Introduction

The intramolecular excited-complex (IEC) state in bichromophic compounds is characterized by a new red-shifted emission. Application of high pressure to these systems may offer a useful means for distinguishing their electronic states, since the energy shift with pressure may be dependent on the characteristic properties.

Furthermore, as the formation processes of some IEC states involve large amplitude intramolecular twisting motion, they are expected to be highly dependent on the frictional forces exerted by solvents. The application of high pressure achieves a large amount of continuous variation in solvent viscosity with almost constant interactions of solvent shell with the aromatic chromophores. In most studies on the influence of solvent viscosity utilizing homologous solvent series or mixed solvents to achieve the viscosity variation, there may exist a problem of specific interactions with chromophores.

The peak shift with pressure and the effect of solvent viscosity on the rate of the IEC state formation in some bichromophic compounds have been studied /1-5/. The present paper describes mainly the results of intramolecular excimer (IE) formation in 1,3-di(I-pyrenyl)propane (DPP).

2. Experimental

DPP was synthesized by using the methods as described in literature /6/, and also an authentic sample was obtained from Molecular Probes, Inc. It was confirmed that no impurity was detectable in TIC as well as in absorption and emission spectra. Solvents of spectroscopic grade were purified by the ordinary method. All solutions are dilute enough for intermolecular molecular contribution to vanish. They were degassed by repeated freeze-pump-thaw cycles just before measurements.

The high-pressure cell, emission equipment, and methods of analyzing data have been described elsewhere /1,7/. The measurements at high pressures were carried out at 303 K.

3. Results and Discussion

Peak Shifts with Pressure. Table lists the peak shifts of IEC bands with pressure for some bichromorphic compounds, which were determined from the initial slopes after fitting to polynomials. The IEC band shows a larger red-shift than the locally excited (LE) band by an order of magnitude. The LE band changes linearly, whereas the IEC band saturates with pressure. It is found that the amount of the shift for the intramolecular excimer (IE) band in DPP is comparatively smaller than the IEC bands for "TICT" compounds /8/. The amount of the shift in DPP is insensitive to solvent polarity for both IEC and LE bands. The value of $d\bar{\nu}_{\max}/dP$ for the locally excited (LE) band in DPP is $-9 \sim -16 \text{ cm}^{-1}/\text{kbar}$, which is assigned as $1_L \rightarrow 1_A$ transition. For $1_L \rightarrow 1_A$ transition it is several times larger in polar solvents /9/. By further detailed analysis of the energy shift with pressure in various IEC compounds, we will surely find it a more useful and definite measure to determine the nature of fluorescent electronic states.

The peak shift of the IEC band with pressure

	$d\bar{\nu}_{\max}/dP$ ($\text{cm}^{-1}/\text{kbar}$)
1,3-Di(I-pyrenyl)propane (DPP)	$-84 \sim -170$
9,9'-Bianthryl (BA)	-220
p-(9-Anthryl)-N,N-dimethylaniline (ADMA)	-300
p-(9-Anthrylmethyl)-N,N-dimethylaniline (AMDMA)	-300
4-(Dimethylamino)benzonitrile (DMABN)	-208

Pressure Effects on the IE Formation in DPP. When the ordinary scheme /10/ is adopted for the formation of the intramolecular excimer (IE), the standard steady-state kinetic analysis for the ratio of the quantum yields from IE state, ϕ_{IE} , and LE state, ϕ_{LE} , leads to the following expression:

$$\frac{\phi_{IE}}{\phi_{LE}} = \frac{k_5}{k_I} \cdot \frac{k_3}{k_4 + k_5 + k_6}, \quad (1)$$

where k_I and k_5 are the fluorescence decay rate constant for the LE and IE states, k_3 is the rate constant for the formation of the IE state, k_4 is the rate constant back to the LE state, and k_6 is the decay rate constant of IE state by internal conversion. When the solvent viscosity is high at high pressures and/or low temperatures, a limiting condition should be applied, i.e., $k_4 \ll k_5 + k_6$. In this case, eq.(1) reduces to

$$\frac{\phi_{IE}}{\phi_{LE}} = \frac{k_5}{k_I} \cdot \frac{k_3}{k_5 + k_6}, \quad (2)$$

Since k_5/k_I is expected to be independent of pressure just as it is independent of solvent and temperature, and in addition, since the pressure dependence of $1/(k_5+k_6) = \tau_{IE}$ can be assumed to be relatively small, the observed pressure dependence of the quantum yield ratio reflects the pressure dependence of k_3 . In another extreme where $k_4 \gg k_5+k_6$, eq.(1) reduces to $\phi_{IE}/\phi_{LE} = (k_5/k_I)(k_3/k_4)$. A transfer of kinetics between these extremes has been observed in the IEC formation of 9,9'-bianthryl (BA) and 4-(9-anthrylmethyl)-N,N-dimethylaniline (AMDMA) by application of high pressure /4/.

Fig.1 shows the effect of pressure on the ratio of the quantum yields for DPP in various solvents. The decrease with pressure indicates that the condition studied is in the viscosity-controlled extreme given by eq.(2).

Fig.2 displays the plot of the yield ratio against inverse of solvent viscosity, $1/\eta$, for three solvents, i.e., methylcyclohexane, i-butanol, and 2, 6, 10, 14-tetramethylpentadecane (TMPD). The rates of the IE formation deduced from the yield ratio are well-correlated with solvent viscosity. It is also clear that over our viscosity range the plots have a definite curvature, implying

that the simplest approach of a diffusion-controlled collision process, which is expressed to be proportional to T/η , is not applicable.

At first the result was analyzed in terms of "free volume limited model" /II/, by which the IE formation of DPP is expressed as follows;

$$\frac{\phi_{IE}}{\phi_{LE}} = C\eta^{-\alpha}, \quad (3)$$

where $C = (k_5/k_1) \{C'/(k_5+k_6)\}$, C' is a constant, and α is a parameter representing a measure of the fraction of the critical volume required for the motion in the solvent that is needed by the solute to undergo some relative motion of the two chromophore groups. The greater free volume needed to the chromophore would be expected to be reflected in a larger value for α . The dashed line in Fig.2 shows the best fit to this model with $\alpha = 0.736$.

Another approach which attempts to incorporate the intramolecular restrictions to rotation is "hindered-rotation model" based on Kramers' theory /I2/. On the basis of this model, the rate of the IE formation after a single hindered rotation over a potential barrier E_0 is presented to have the following form:

$$\frac{\phi_{IE}}{\phi_{LE}} = A \{(\eta^2 + B)^{1/2} - \eta\} \exp(-\frac{E_0}{RT}), \quad (4)$$

where $A = (k_5/k_1) \{k_3/(k_5+k_6) (r/\mu) (\omega_A/\omega_B)\}$ and $B = (\mu/2\pi r)^2 \omega_B^2$, and ω_A and ω_B are the frequencies corresponding to the initial potential well and the top of the barrier potential, respectively. In the course of the derivation of eq.(4), a hydrodynamic assumption of a slipping boundary condition: $\beta = 4\pi\eta r$ was adopted. The solid line in Fig.2 represents the best nonlinear least-squares fit of the data to this model expressed by eq.(4). The resultant parameters are $A = 0.696$ and $B = 131 \times 10^{-6} \text{ kg}^2/\text{m}^2 \text{ s}^2$. Moreover, by introducing the values of μ and r , the value of ω_B can be estimated from the obtained value of B . Assuming the effective value of r in between the long and short axes of pyrene molecule, we obtain $\omega_B = 7.6 \times 10^{13} \sim 15 \times 10^{13} \text{ s}^{-1}$.

Based on a goodness-of-fit in Fig.2, it is concluded clearly that the IE formation of DPP is better described by the hindered-rotation model.

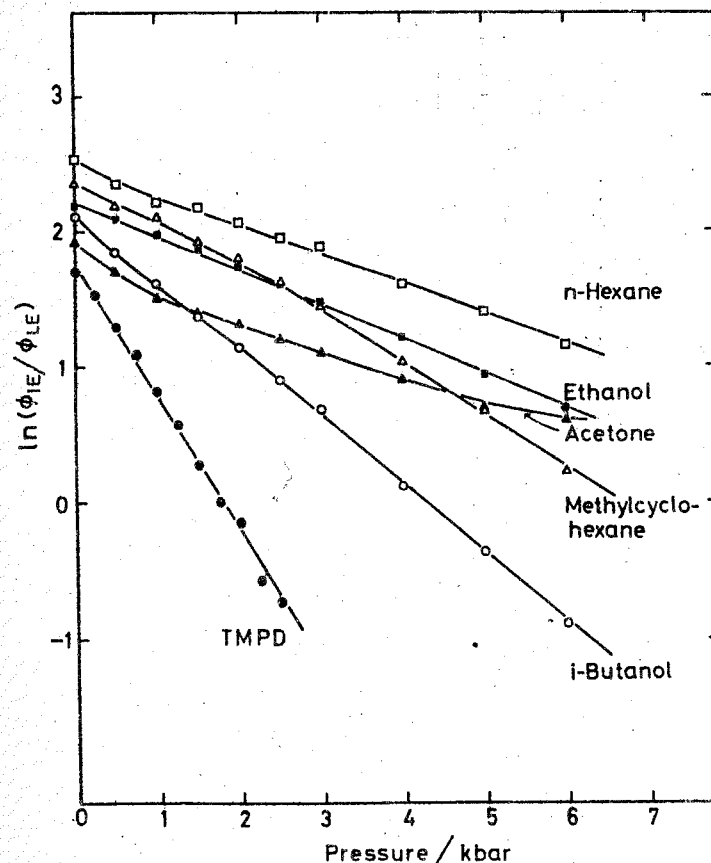


Fig.I. Pressure dependence of the quantum yield ratio in various solvents at 303 K.

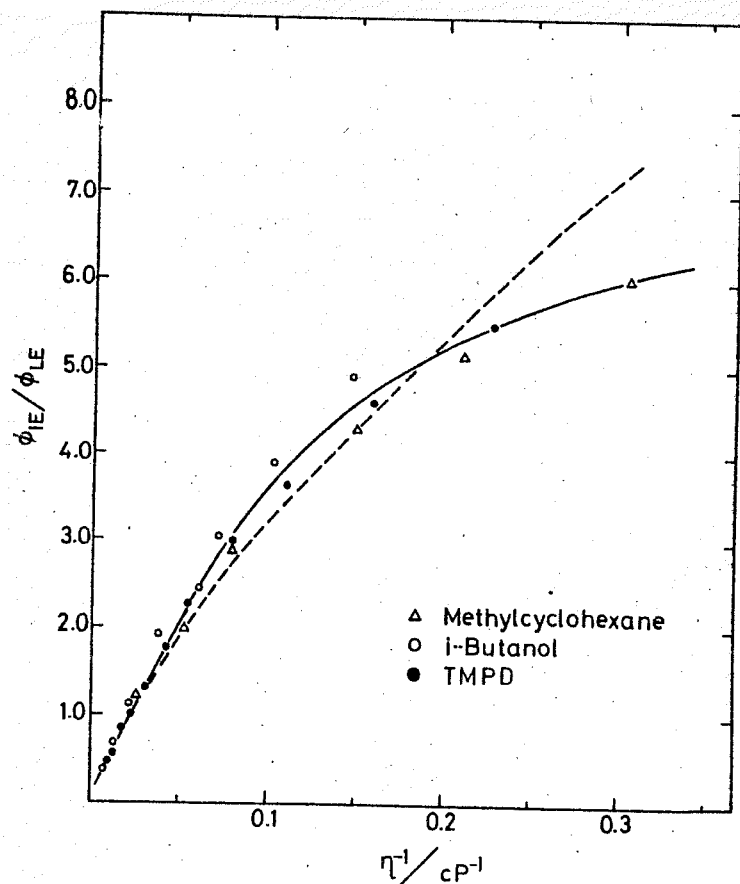


Fig.2. The plot of quantum yield ratio against $1/\eta$. The solid line represents the best fit for the "hindered-rotation model" and the dashed line represents the best fit for the "free volume limited model".

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Abstract

High pressure Raman studies were performed on isoelectronic molecular crystals CO₂ and N₂O at room temperature and low temperatures up to 20 GPa. Changes in the spectral features of external modes indicate phase transitions around 6 GPa (?) and around 11 GPa in CO₂ and around 5 GPa in N₂O. The temperature shift of the lattice modes strongly decreases under compression and is discussed with respect to anharmonic effects. The pressure tuning of the Fermi resonance is determined. In both systems Fermi resonance decreases with increasing pressure.

Introduction

In the solid state CO₂ and N₂O form molecular crystals. In these crystals the molecule retains its identity to a great extent due to the strong intramolecular forces, as compared to the weaker intermolecular forces. The study of vibrational features and their pressure dependence can yield important information on the nature and form of these forces and is also a valuable tool for determination of p-T-phase diagrams. Since CO₂ and N₂O have similar molecular properties and form an isoelectronic pair, comparative studies can reveal how subtle differences affect physical and chemical behaviour. Extensive high pressure Raman studies at room temperature were reported for CO₂ [4,5] but not for N₂O. One phase is reported for each CO₂ and N₂O at ambient pressure [1,2]. The molecules are

arranged in a fcc-lattice (4 molecules per unit cell) with the molecular axes aligned along the body diagonals. In the CO₂-crystal (space group Pa3) the centers of the centro-symmetric molecules occupy the fcc-lattice points. The N₂O-molecules are asymmetric, but since the orientation of the molecules is at random in solid N₂O, its average structure may be regarded as isomorphous with that of CO₂ [3].

Experimental

Solid CO₂ and N₂O were loaded into the pressure chamber of a diamond anvil cell and investigated by Raman spectroscopy [6].

Results

Typical Raman spectra in the lattice region of N₂O under pressure and 20 K are shown in Fig. 1. Between 5 and 10 GPa drastic changes occur. At least two new bands appear in the region of the higher energy libron while the librational modes of phase I vanish. The general features of the internal modes remain unaffected by the phase transition, however, splitting (ν_2) and slight changes in frequency and slope (ν_1, ν_3) accompany the phase transition (Fig. 2). Both components of $2\nu_2$ show a decrease in intensity under compression, which is very marked for the lower energy component.

In the lattice vibration region the Raman spectra of CO₂-I are very similar to the spectra of N₂O-I. Above ≈ 6 GPa additional lines were observed (Fig. 3), which may indicate slight distortions of the fcc-lattice (e.g. tetragonal) or of the molecular symmetry. Similar spectra were also observed in the lower pressure range (phase I) if large pressure inhomogeneities are introduced by pressure cycling at low temperatures (Fig. 4). Therefore, high pressure studies on single crystalline samples in a hydrostatic pressure transmitting medium are necessary to solve the puzzle of a possible phase IV between ≈ 6 GPa and ≈ 10 GPa in CO₂. In agreement with recent studies [5] the transition to phase III was observed in the pressure range 10-15 GPa. The Raman spectra in the lattice region of this phase (Fig. 5) look very similar to the spectra of N₂O-II. This indicates that the crystal structures of CO₂-III and N₂O-II may be identical or very similar.

A negative isobaric temperature shift is observed for the lattice modes in the lower pressure range (Fig. 6). The temperature dependence is a consequence of anharmonicity of the intermolecular potential. The T-shift is commonly divided into two contributions according to

$$\left. \frac{d\omega}{dT} \right|_P = \left. \frac{\partial \omega}{\partial T} \right|_V - \alpha_P B_T \left. \frac{d\omega}{dP} \right|_T.$$

α_P denotes the thermal expansivity and B_T the bulk modulus. The first term on the right is due to cubic and quartic anharmonicities (explicit term), and the second term describes the effect of thermal expansion (implicit or volume term). In the low pressure regime the thermal expansion is mainly responsible for the total T-shift, since the contribution of the explicit term is negligible, as can be seen from Fig. 7. With increasing pressure the total T-shift strongly reduces and is negligible around 10 GPa for CO₂. Assuming the explicit T-shift to be unaffected by compression this means a drastic reduction to ≈ 0 of the thermal expansivity α_P , because $B_T \left. \frac{d\omega}{dP} \right|_T$ does not decrease under compression. On the other hand available equation of state (EOS) data at room temperature [7] and 0K [8] indicate a smaller decrease of α_P with pressure. A rough estimate shows that the implicit contribution does not change drastically under compression. This result then suggests an increase of the explicit term under compression, as can be noticed in Fig. 7. Thermal expansion and volume shift of frequencies are closely connected with anharmonicity. Since the Grüneisen parameter γ remains constant over the considered pressure range a drastic reduction of anharmonicities, as suggested by $\alpha_P \approx 0$, may be ruled out.

The internal modes of both substances are modified by Fermi resonance (FR). The symmetric stretch ν_1 interacts with the overtone of the bending mode $2\nu_2$ via the anharmonic coupling constant k_{122} . This interaction manifests itself through a marked shift of both modes ($\nu_1 \rightarrow \nu_+$, $2\nu_2 \rightarrow \nu_-$) and through borrowing of intensity by $2\nu_2$ at the expense of ν_1 .

Knowledge of mode frequencies (ν_+ , ν_- , ν_2) and the intensity ratio $R = I(\nu_+)/I(\nu_-)$ allows the analysis of FR and its pressure tuning according to FR-theory [9,10]. The FR quantities for CO₂ and N₂O are summarized in Table. δ denotes the separation of perturbed modes $\nu_+ - \nu_-$, Δ the separation of unperturbed modes $\nu_1 - 2\nu_2$ and W the Fermi interaction parameter. At ambient pressure FR is much stronger in CO₂ than in

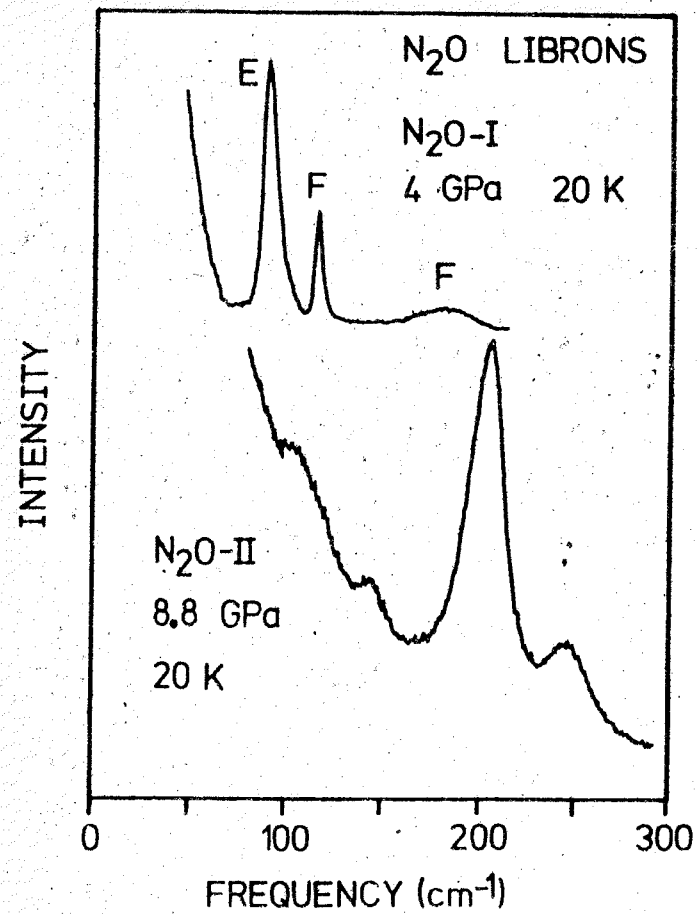


Fig. 1. Low energy Raman spectra of N₂O.

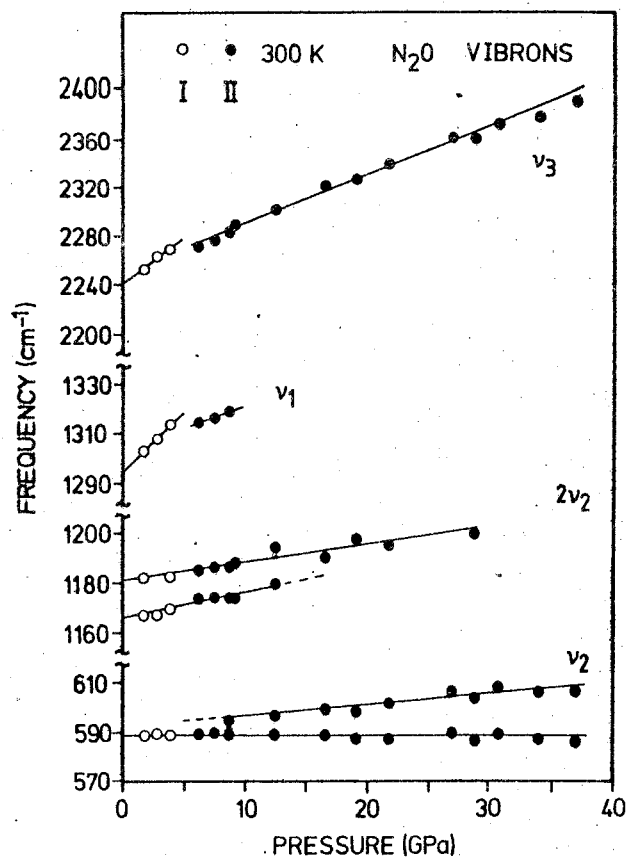


Fig. 2. Pressure shift of internal modes of N_2O .

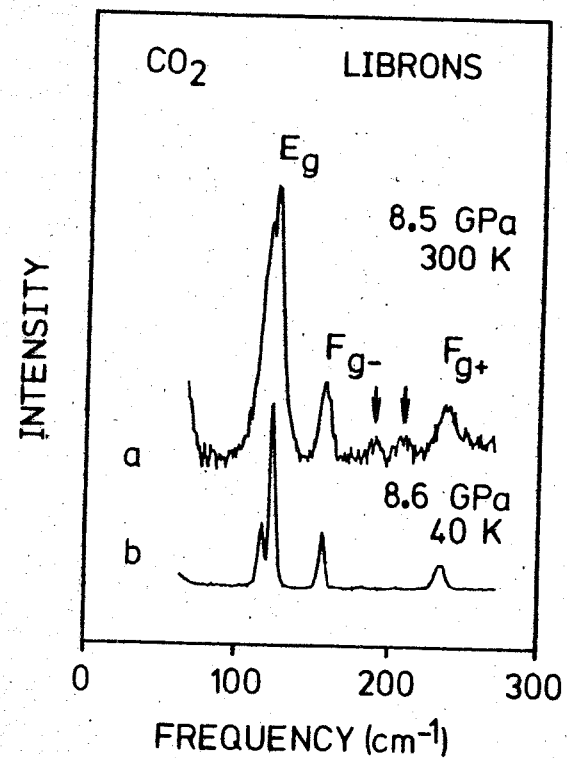


Fig. 3: Low energy Raman spectra of CO_2 :

- a) pressurized at room temperature;
- b) pressurized at room temperature and subsequently cooled down.

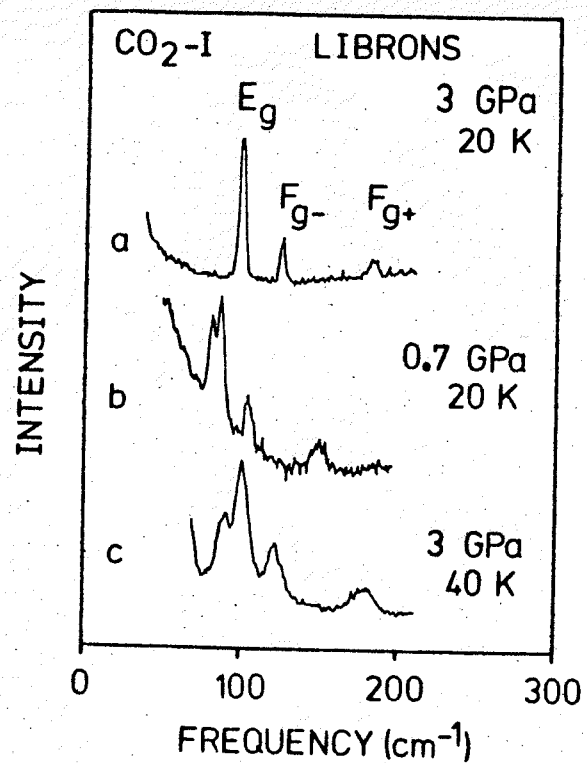


Fig. 4. Low energy Raman spectra of $\text{CO}_2\text{-I}$ at low temperature :

- a) pressurized at room temperature to 3 GPa and cooled down ;
- b) unloaded at 20 K to 0.7 GPa ;
- c) pressurized to 13 GPa, unloaded to 1 GPa and pressurized to 3 GPa at 40 K .

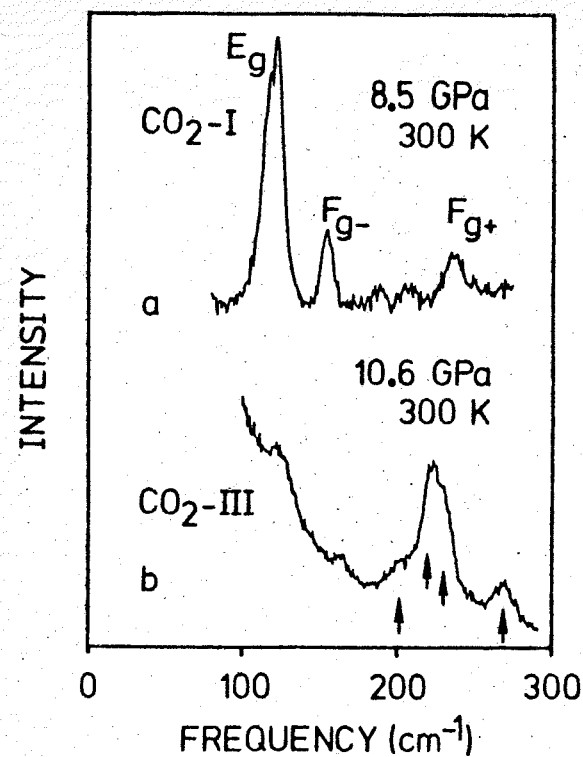


Fig. 5. Low energy Raman spectra of solid $\text{CO}_2\text{-I}$ and $\text{CO}_2\text{-III}$ at room temperature .

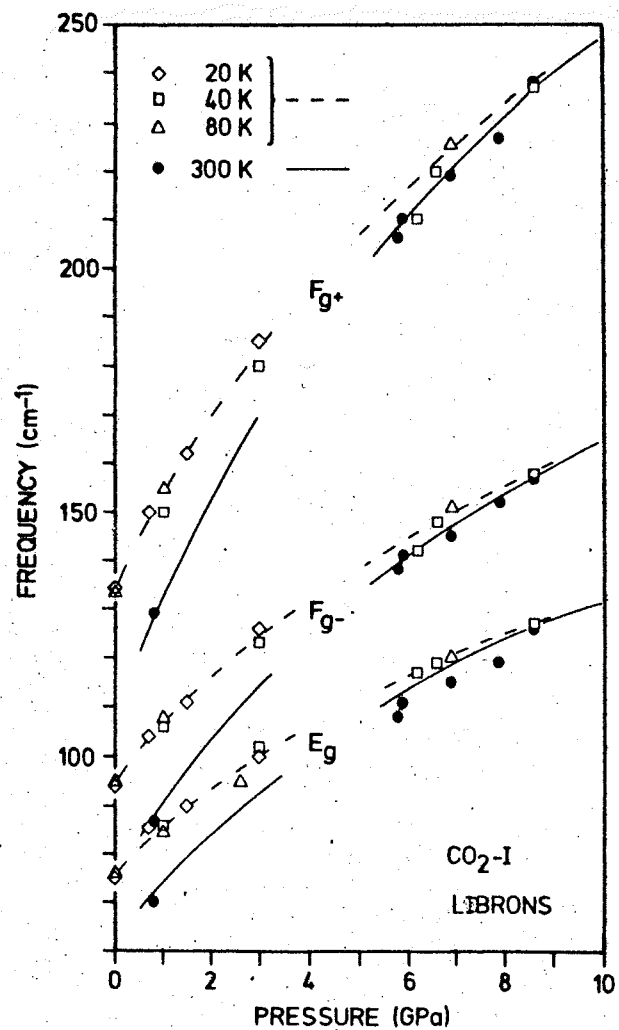


Fig. 6. Pressure shift of external modes of solid $\text{CO}_2\text{-I}$ for various temperatures.

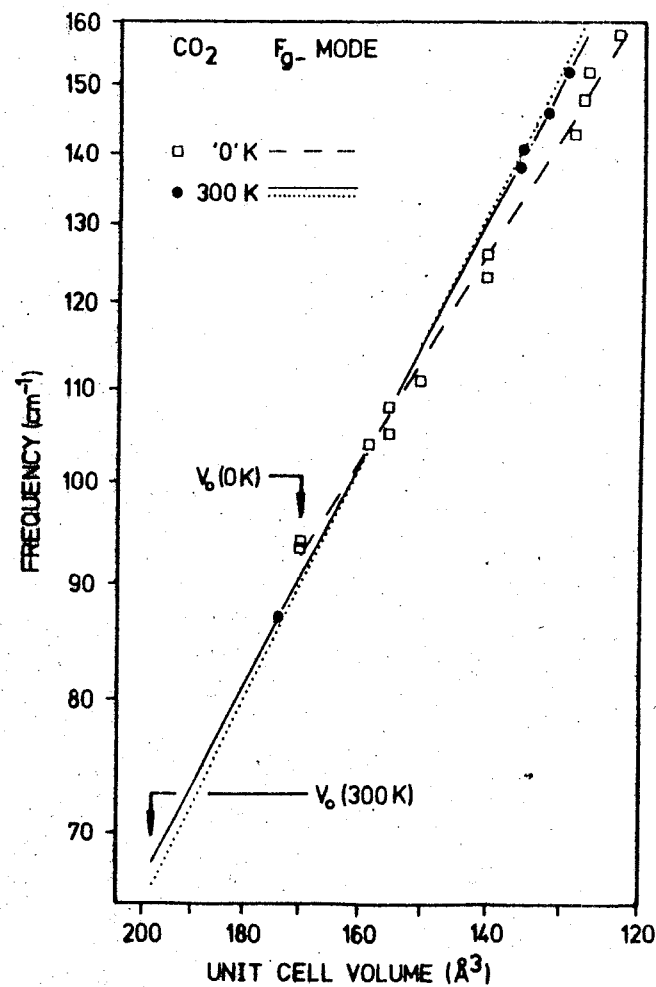


Fig. 7. Volume dependence of the librational F_{g-} mode of solid $\text{CO}_2\text{-I}$. The lines were obtained by least square fitting. Solid and dashed line, present work, dotted line, from Ref. 4.

Effect of pressure on Fermi resonance quantities of solid CO₂ and N₂O.

Substance	CO ₂		N ₂ O	
Pressure	0 GPa	5 GPa	0 GPa	5 GPa
δ (cm ⁻¹)	110	122	129	151
Δ (cm ⁻¹)	50	75	105	133
W (cm ⁻¹)	50	43	38	36
$(W/\Delta)^2$	1	0.3	0.13	0.07

N₂O, as indicated by the larger FR-strength $(W/\Delta)^2$. This difference is mainly due to smaller value of Δ for CO₂. Under pressure W decreases, more pronounced for CO₂ than for N₂O. increases under compression for both substances. The FR-strength has reduced by a factor of 2-3 at 5 GPa. The main reason is not a drastic reduction of anharmonic coupling constant k_{122} but a rather strong increase of Δ .

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OPTICAL STUDIES OF SOLID OXYGEN TO 130 GPa INDICATIONS OF A POSSIBLE METALLIC STATE AT ABOUT 130 GPa

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ABSTRACT

Studies of optical properties of solid oxygen, optical density and reflectivity, have been carried out up to 81.6 GPa and up to 130 GPa respectively in a diamond-anvil high pressure cell. Linear extrapolation of the absorption edge obtained from optical density data indicates a band gap closure at $P = 130 \pm 20$ GPa. In addition, the diamond-sample interface reflectivity at .52 eV (2.4 μm) shows a steady increase from nearly zero at 70 GPa to 35% at 130 GPa. This may indicate the onset of a metallic state at ultra high pressure.

Developments of ultra high pressure techniques using the diamond anvil cell (DAC) have made possible the investigation of insulator-to-metal transition in solids [1]. Metallization of CsI [2], BaTe [3,4], HI [5] and BaSe [6] have been recently reported. Earlier, molecular solid iodine was also metallized in the DAC [7] and was also found to be a superconductor at 45 GPa [8].

Among other possible and interesting solids that could be metallized with sufficiently high pressure, oxygen is to be considered. Extensive studies have been done on this molecular crystal in the modest pressure range ($P \leq 40$ GPa). Theoretical calculations have confirmed the low pressure and low temperature phase diagram [9]. Low pressure structural studies have been carried out by several groups and have revealed the existence of three subsequent structures at room temperature and up to 9.9 GPa [10-14]: the β -phase at 5.5 GPa (rhombohedral), the "orange"-phase or δ -phase at 9.6 GPa (orthorhombic) and the ϵ -phase at 9.9 GPa (unknown structure, maybe an orthorhombic distortion of the δ -phase [14]). Optical properties have also been largely studied up to modest pressures ($P \leq 38$ GPa). Nicol and Syassen [15] have pointed out the anisotropy of the β - and ϵ -structure by transmission spectroscopy. At the same pressure e.g. at 37 GPa (ϵ -phase) crystals grown in the DAC with their c-axis perpendicular and parallel to the diamond culet show dark and light coloration respectively. In the former case the polarization of the incident light being in perpendicular to the c-axis and inversely in the later case indicating the planar nature of the solid ϵ -phase.

This paper describes the results of optical density measurements via transmission spectroscopy up to 81.6 GPa and near-infrared reflectivity up to 130 GPa on solid oxygen. Results are interpreted in terms of the appearance of a metallic state in the 100 GPa range.

A 50 μm cylinder drilled in a T301 stainless steel gasket was used as the pressure chamber. The diamonds, 1/3 carat stones, were either flat with a 300 μm culet for transmission spectroscopy or beveled by 5 degrees with a 100 μm tip and a 300 μm culet for reflectivity spectroscopy.

Because solid oxygen becomes opaque at modest pressures ($P \geq 40$ GPa) [15], care was taken to ensure that ruby fluorescence, used for pressure estimation [1], could be recorded up to very high pressures ($P \geq 100$ GPa). In fact, pressures were measured up to 100 GPa at which loss of ruby luminescing efficiency and stress-induced diamond luminescence made impossible the line shift measurement. Instead pressure-calibrated diamond displacement, a technique known to give a fairly accurate pressure estimation [16] was used from 100 GPa to 130 GPa.

Oxygen was loaded in its liquid state. Once at room temperature, the sample was brought to its β -phase at 5.5 GPa. Samples obtained with this method proved to have their c-axis oriented perpendicularly to the diamond culet as their dark coloration showed at higher pressures [15]. Although most parts of the sample were of uniform dark coloration, regions around the ruby were lighter. We assumed that the crystal orientation was the same up to the highest pressure reached.

The sample was illuminated by the white light of a 100 W tungsten halogen lamp. Transmitted light was then collected by a sapphire microlens assembly designed to meet the requirement of the long working distance of the DAC used. Intensity of the transmitted light was then measured as a function of energy by means of different combinations of gratings and detectors to cover the 0.5 eV to 3.0 eV energy range. Near infrared and visible light signals were detected by a two-stage thermoelectrically cooled PbS detector and a Si PIN diode respectively.

Optical density as a function of photon energy was obtained by taking the logarithm of the ratio of the transmission through the same diamond with no sample present to the transmission through the sample (50 μm). Reflectivity measurements were made by techniques similar to those described by Syassen and Sonnenschein [17]. Near-infrared reflectivity as a function of photon energy was measured at the diamond-sample interface (R_d , hereafter) [17]. The sampled area was not larger than 300 μm^2 , ~ 20 μm in diameter. Small corrections were applied to the spectra to take into account the absorption of diamond at low photon energy which was directly measured.

Results of the transmission measurements up to 81.6 GPa are shown on Figure 1. The three distinct groups of curves correspond to three different combinations of gratings and detectors used to cover the visible and the near infrared spectral range i.e. from 0.5 eV to 3.0 eV. In principle, one should be able to extract the absorption edge from the data by noting the intersection of the optical density-(OD) curves with a line of constant and relatively high OD e.g. 3.0. However this method would lead to erroneous results if applied to the present data for the following reasons:

1. The baseline of an OD curve i.e the level where the OD is nearly independent of energy, increases with pressure. This is attributed to pressure-enhanced-grain-boundary scattering.
2. As pressure increases, the sharp OD rise associated with the absorption edge is less prominent due to the pressure gradient over the sample area and to inhomogeneity of the sample thickness as a result of the cupping of the diamonds.
3. At higher pressures, data points are somewhat scattered mainly due to signal weakness.

In order to pinpoint the onset of the absorption edge, wherever data made it possible, unnormalized data rather than the OD's were considered. The absorption edge has been defined to correspond to the energy at which the sample starts transmitting (arrow on the inset of Figure 2). Absorption edges are plotted as a function of pressure on Figure 2. In addition to our results, three data points, deduced by the authors from OD curves of Nicol and Syassen [15], are plotted ($\square$). They correspond to the largest OD's at 16, 22 and 37 GPa of a "dark" sample.

Although data points are somewhat scattered, a linear extrapolation based on the data points above 50 GPa indicates a null energy at about $P = 130 \pm 20$ GPa. This gives a rough estimate of the pressure at which the band gap closure should occur.

Results of R_d as a function of energy and pressure are illustrated in Figure 3. Reflectivity curves at pressures below 70 GPa are not shown because of their nearly zero levels. However, starting from 70.3 GPa, reflectivity levels increase as photon energy decreases and the slope dR_d/dE becomes larger as pressure increases. At .52 eV (2.4 μm) R_d reaches nearly 35% at the highest pressure achieved i.e. 130 GPa. In fact, from

its very low value at 70 GPa the reflectivity rises steadily to 35% up to 130 GPa. To our knowledge solid oxygen is the only material, which was once an insulator, that has shown such a high degree of reflectance in the 100 GPa pressure range. An additional feature of the R_d curves is worth noting. Between .52 eV and .75 eV, a "band" seems to become more prominent as pressure is applied. Whether this is due to an intrinsic physical property of solid oxygen or due to an experimental artifact is still unknown. Further investigations are underway to clarify this point.

Undoubtedly, solid oxygen shows the signs of an "good" near-infrared reflector in the 100 GPa pressure range. However the energy dependence of R_d cannot be compared to the Drude-type behaviour of a real metal: in that case one would expect to measure a somewhat large increase of R_d level as the energy of the reflected light approaches the plasma edge. For oxygen, although the R_d levels are high, up to 35 % at 0.52 eV and at 130 GPa, the increase of reflectivity from 1.5 eV to .52 eV is modest (see Figure 3).

Because of the short spectral range covered by the reflectivity data, a Kramers-Kronig analysis would certainly have lead to unreliable results for the index of refraction and the extinction coefficient. For that reason no attempt was made to get a Kramers-Kronig inversion. However, if oxygen were considered a semiconductor and hence described by a Lorentz model, it would be reasonable to assume that the imaginary part of the refractive index is negligible at 0.52 eV, see e.g. the case for silicon [18]. In that case, it is possible to calculate the refractive index of oxygen from the reflectivity data at the diamond-oxygen interface, i.e. from 0.35 at 130 GPa; the result is $n = 9.4$ indicating a very small band gap. However, the rise in R_d as the energy decreases is not a characteristic of a Lorentz model.

Two explanations for the high pressure behaviour of the reflectivity of oxygen are possible. First, the appearance of high reflectance levels at ultra high pressure may be the result of "pressure-enhanced" high order infrared vibrational bands in oxygen. Or, secondly, solid oxygen could be promoted to a metallic state in the 100 GPa pressure range and consequently show appreciable near infrared reflectance. Extrapolation of the absorption edge to 0 eV indicates a band gap closure at 130 GPa. This supports the metallization hypothesis.

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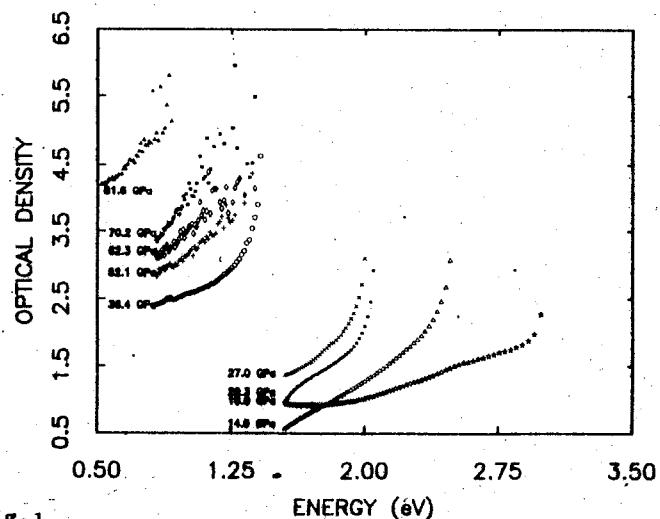


Fig. 1
Optical density of solid oxygen in the visible and the near infrared spectral range at different sample pressures. The three different groups of curves correspond to three different combinations of gratings and detectors set to cover the spectral range. Due to signal weakness data points at high optical densities are scattered.

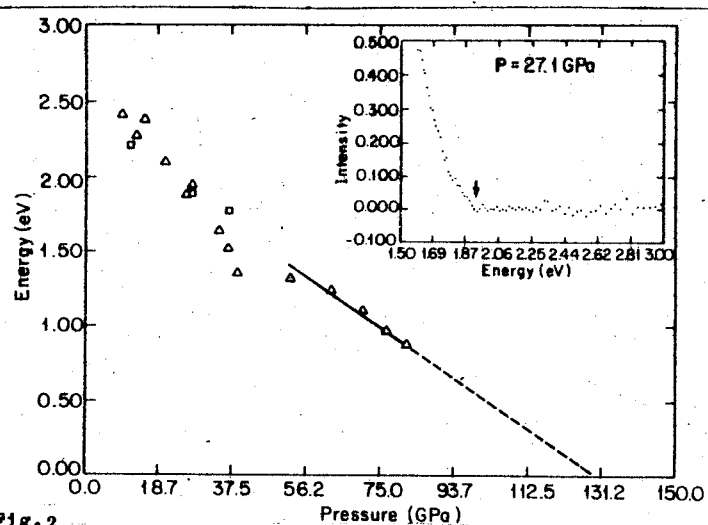


Fig. 2
Absorption edge as a function of pressure (Δ) as defined by transmission data (arrow on inset). Data points marked by $\square$ are absorption edges deduced by the authors from optical density curves in Nicol and Syassen [15].

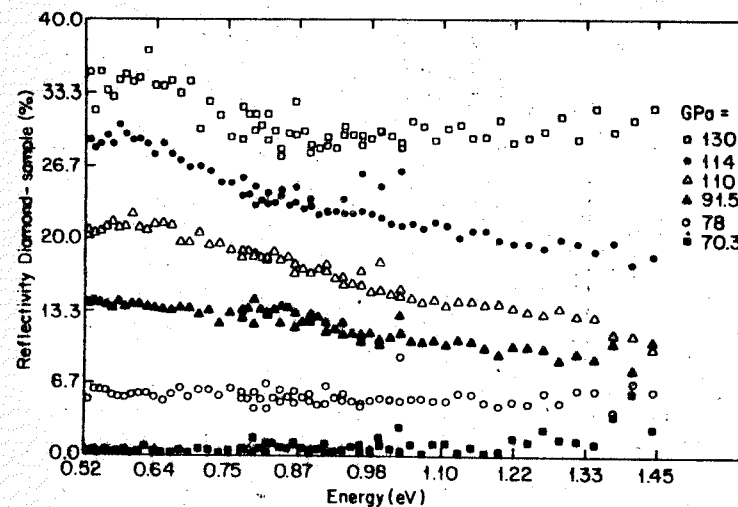


Fig. 3
Near-infrared reflectivity from the diamond-solid oxygen interface at different pressures. Small corrections have been applied to get a good match between data obtained on two different gratings (blazed at 1 and 2 μm) and to compensate for slight diamond absorption below .65 eV. Note the overlap of data from the two gratings between 1.0 eV and 1.3 eV.

EFFECT OF HYDROSTATIC PRESSURE ON THE OPTICAL SPECTRA OF EXCITONS AND V_K CENTRES IN IONIC CRYSTALS

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1. Introduction. Spectroscopic studies of solids under pressure, especially at low temperatures, give valuable information on various properties of crystals that are dependent on interatomic distances. For such studies we have developed a system of high-pressure equipment enabling a good-accuracy recording of the optical spectra of crystals under hydrostatic pressure of gaseous or solidified helium up to 13 kbar in the temperature range 300 - 4.2 K /1,2/.

With this equipment we have studied, in particular, the effect of pressure on the exciton spectra of Cu_2O crystals /3/ and LiH and LiD crystals /4/. In this paper, a brief review of our recent spectroscopic studies of excitons and V_K centres under pressure at low temperatures is given.

2. Reflection spectra of free excitons in alkali halide crystals. We have studied the effect of pressure, up to 12.5 kbar at 77 K, on the reflection spectra of free excitons (FE) in CsI , RbI and KI crystals /5/. Especially interesting results were obtained for CsI , that has a peculiar band structure. Calculations have shown /6/ that the uppermost valence band of CsI arises from 5p states of I^- ion and has a maximum at Γ point (Γ_8^- state). The lowest conduction band is formed by s-like states, and somewhat higher there is a d-like conduction band. Both bands have a minimum at Γ point (Γ_6^+ and Γ_8^+ states, respectively).

The first three peaks observed in the reflection spectrum of CsI at the energies 5.76, 5.90 and 5.97 eV correspond to the exciton transitions associated with the direct interband transitions $\Gamma_8^- \rightarrow \Gamma_6^+$ (1st peak) and $\Gamma_8^- \rightarrow \Gamma_8^+$ (2nd and 3rd peaks) from p-like (Γ_8^-) valence band to s-like (Γ_6^+) and d-like (Γ_8^+) conduction bands, all these FE states having the same symmetry, Γ_{15} .

The circles in Fig.1 (curves 4, 5 and 6) show the pressure dependence of these three exciton transition energies. It can be divided into three regions: 0-3.5 kbar, the region of the convergence of exciton bands (the line S is related to the s-like

conduction band, and the lines D and T are related to the d-like band); 3.5 - 6 kbar, the region of strong interaction of excitons of the same symmetry; more than 6 kbar, the region of the divergence of bands (the lines S', D' and T'). The initial pressure shifts dE/dP for S, T and D bands are respectively 21, -8.5 and -19 meV/kbar.

The behaviour of the exciton levels established by us points to their strong interaction and is explained by the known non-crossing rule for the levels of identical symmetry. Thus, we succeeded in observing an exciton analogue of the pressure-scanned Fermi resonance for three energy levels simultaneously.

The behaviour of the exciton bands under pressure agrees well with the proposed three-level model which takes into account the coupling (mixing) of the FE levels, along with their pressure shifts /5/. Computer-calculated positions of FE levels versus pressure are shown in Fig. 1 by solid curves.

Knowing the values of dE/dP for the reflection bands of FE in CsI and estimating the compressibility of the crystal χ_T at 77 K, we determined the deformation potential $E_d = dE/d\ln V = -(1/\chi_T) (dE/dP)$ for the three exciton transitions (S, T and D bands): -2.9, 1.2 and 2.7 eV. The first and the third values are close to the computed values /7/ for the interband transitions $\Gamma_8^- \rightarrow \Gamma_6^+$ (-2.36 eV) and $\Gamma_8^- \rightarrow \Gamma_8^+$ (2.74 eV) in CsI . This allows one to suggest that exciton levels and band edges shift under pressure roughly at the same rate. Hence, somewhere not very far from the region of the closest approach of exciton levels (~5.5 kbar) the inversion of s-like (Γ_6^+) and d-like (Γ_8^+) conduction bands must occur, since these bands have different symmetries and may therefore intersect on their pressure "scanning". Such band crossing is confirmed by theoretical calculations /6/.

In RbI and KI , the first reflection band of FE is associated with s-like conduction band. The values of dE/dP and E_d for this band are respectively 21 and 18 meV/kbar and -2.7 and -2.3 eV.

3. Luminescence spectra of self-trapped excitons. Earlier /8/ we studied the effect of pressure, up to 11 kbar at 77 K, on the photoluminescence (PL) of self-trapped excitons (STE) in CsI and RbI crystals by using excitation in the absorption bands of FE. Later we started to use X-ray excitation through a beryllium window instead of a sapphire window.

Recently we obtained the first data on the effect of pressure up to 12.5 kbar upon the X-ray luminescence (XRL) bands of

STE at 77 K in the following crystals: CsI (3.67; 42), CsI (4.66 at $P > 7.8$ kbar; 6), RbI (3.09; 75), RbI (3.88; 40), KI (3.31; 28), NaI (4.24; 41), CsBr (3.55; 55), NaCl (3.47; 31), BaF_2 (4.00; 10), CaF_2 (4.45; 5), Y_2O_3 (3.45; 5), Sc_2O_3 (3.55; 3). The numbers in brackets denote the peak position of the XRL band of STE in eV and the rate of the short-wavelength pressure shift of the band in meV/kbar. Alkali halides are characterized by very large shifts of the XRL bands of STE within 30-75 meV/kbar which coincide with those of the PL bands of STE for the alkali iodides studied. In other crystals with a different structure of STE and with a more rigid lattice the shifts are much smaller (3-10 meV/kbar).

The most interesting results have been obtained for CsI (Fig. 1). Under photoexcitation as well as X-ray excitation at 77 K the STE emission band peaking at 3.67 eV (curve 1) shifts at the rate 42 meV/kbar and in the range 7-9 kbar it gradually disappears. Instead, in the same pressure range, a new band of about the same intensity and half-width appears at a higher energy, 4.66 eV (curve 3). Its pressure shift is much smaller, about 6 meV/kbar.

The vanishing of the 3.67 eV band and the emergence of a new band at 4.66 eV indicates that at ~ 8 kbar a rearrangement of the energy structure of STE in CsI takes place. Perhaps it is connected with an inversion (crossing) of s and d conduction bands near 8 kbar. Indeed, such inversion may occur at a pressure markedly higher than 5.5 kbar - the region of the closest approach of FE levels, if the exciton binding energy for d band is larger than that for s band, because then the energy separation between s and d band edges will exceed the distance between the respective FE levels.

What is the origin of the new 4.66 eV band? We determined that it is excited in the region of the exciton absorption bands like the earlier known PL bands of STE at 3.67 and 4.27 eV. This points to the excitonic nature of the new band. One might suppose, that it is somehow related to the PL band of STE at 4.27 eV, seen only at liquid helium temperatures. We examined, at 4.2 K, the effect of pressure up to 7.5 kbar on both PL bands of STE at 4.27 and 3.67 eV and found them to exhibit a parallel shift (see curves 2 and 1 in Fig. 1) at the same rate, 43 meV/kbar, as the 3.67 eV band at 77 K.

Figure 1 shows that near 8 kbar the peaks of the 4.27 eV band (at 4.2 K) and of the 4.66 eV band (at 77 K) practically coincide. However, it is hard to admit that these bands are of the sa-

me origin. Several facts speak against it: (1) drastically different pressure shifts of the bands; (2) dissimilar thermal stability (the 4.27 eV band starts quenching already from ~ 4 K ($P = 1$ atm) /9/, but the 4.66 eV band, according to our measurements under pressure, only from ~ 120 K ($P = 12$ kbar); (3) different emission decay times τ (for the 4.66 eV band $\tau \approx 200$ ns as preliminarily measured by us at 77 K and 12 kbar, whereas for the 4.27 eV band $\tau \approx 100$ ns at 4.2 K and 1 atm and it drops rapidly with the increase of temperature /9/). Thus, pressure induces in CsI a new, hitherto unknown emission band of STE at 4.66 eV.

4. Luminescence spectra of free excitons in LiH. In /4/, we studied the effect of pressure up to 13 kbar on the reflection spectra of FE in LiH and LiD crystals at 77 K. It was shown that the E_1 exciton line of LiH shifts at the rate $-(0.30 \pm 0.03)$ meV/kbar (Fig. 2, curve 2). Now we examined the behaviour of the 2LO phonon-assisted line in the PL spectrum of FE in LiH up to 13 kbar at 77 K, i.e. we determined the pressure dependence of the line corresponding to the radiative annihilation of an exciton with the creation of two LO phonons. In Fig. 2 (curve 1), it is seen that this emission line, $E_1 - 2\hbar\omega_{LO}$, shifts at the rate $-(0.55 \pm 0.03)$ meV/kbar. From the energy difference between the lines E_1 and $E_1 - 2\hbar\omega_{LO}$ we estimated the LO phonon energy $\hbar\omega_{LO} = 137$ meV and also its pressure change $d\hbar\omega_{LO}/dP = 0.13$ meV/kbar. Knowing the quantities $\hbar\omega_{LO}$ and $d\hbar\omega_{LO}/dP$ as well as the compressibility χ_T /4/, one can estimate the mode Grüneisen parameter for LO phonons in LiH. A calculation by the formula $\gamma_1 = -(d\ln\omega_1/d\ln V) = (1/\chi_T\omega_1) (d\omega_1/dP)$ gives a value $\gamma_{LO} = 0.3$.

5. Absorption spectra of V_K centres in KCl. In /10/, theoretical calculations were made of how the energy of electronic transitions in the absorption spectrum of V_K centres (self-trapped holes) in a KCl crystal is changed by varying the lattice constant a_0 . It was predicted that the energy of optical transitions does not practically change until a_0 is reduced up to a certain threshold value corresponding to the pressure of 10-15 kbar and after that it begins to grow rapidly. We measured the 3.40 eV absorption band of V_K centres in KCl:Pb (the transition $2\sum_u^+ \rightarrow 2\sum_g^+$ in the pressure range 0 - 12.8 kbar at 77 K. Indeed, this band was found to exhibit only rather a small pressure shift of $-(2.5 \pm 0.5)$ meV/kbar (Fig. 3), its half-width increasing a lit-

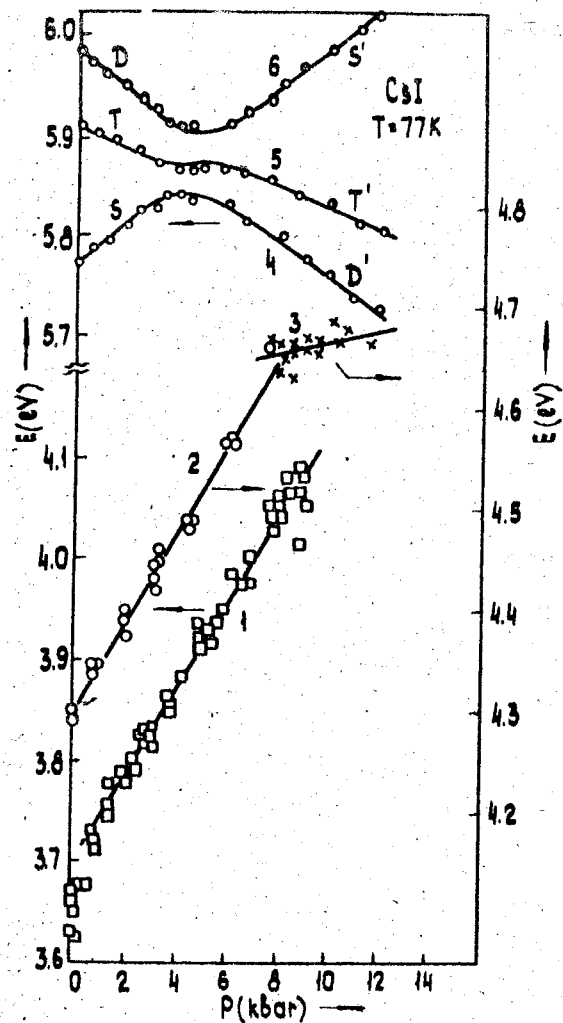


Fig.1. Pressure shifts of various exciton bands in CsI crystal:
 1 - the PL and XRL band of STE at 77 K and the PL band of STE at 4.2 K; 2 - the other PL band of STE at 4.2 K; 3 - the pressure-induced new PL and XRL band of STE at 77 K; 4, 5, 6 - experimental (circles) and computed (solid lines) positions of the three reflection bands of FE at 77 K.

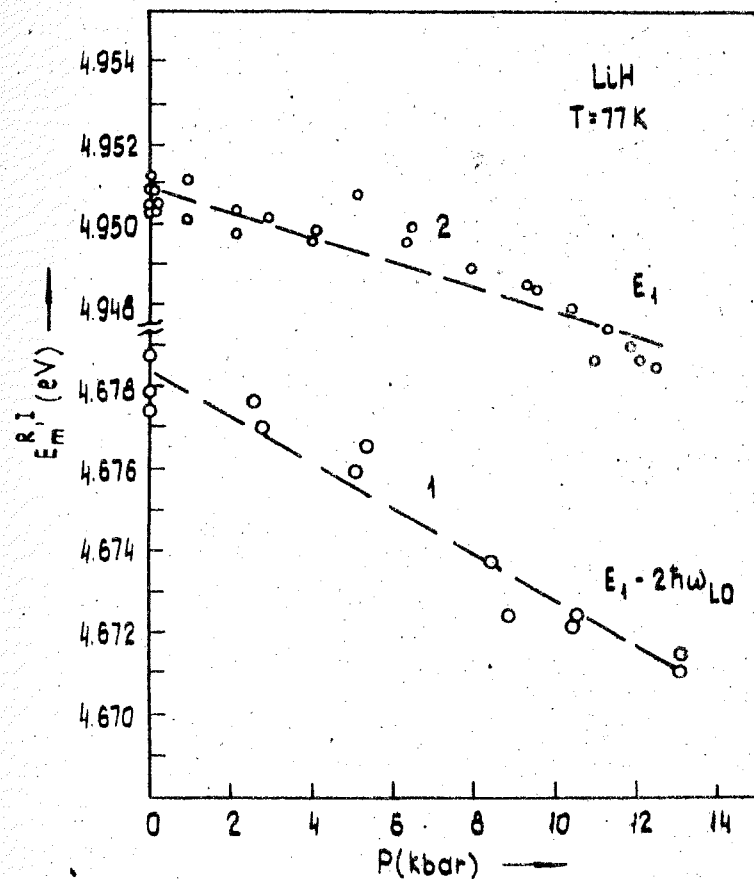


Fig.2. Pressure shifts of exciton lines in LiH crystal at 77 K:
 1 - 2LO phonon-assisted line in the PL spectrum of FE;
 2 - E_1 line in the reflection spectrum of FE.

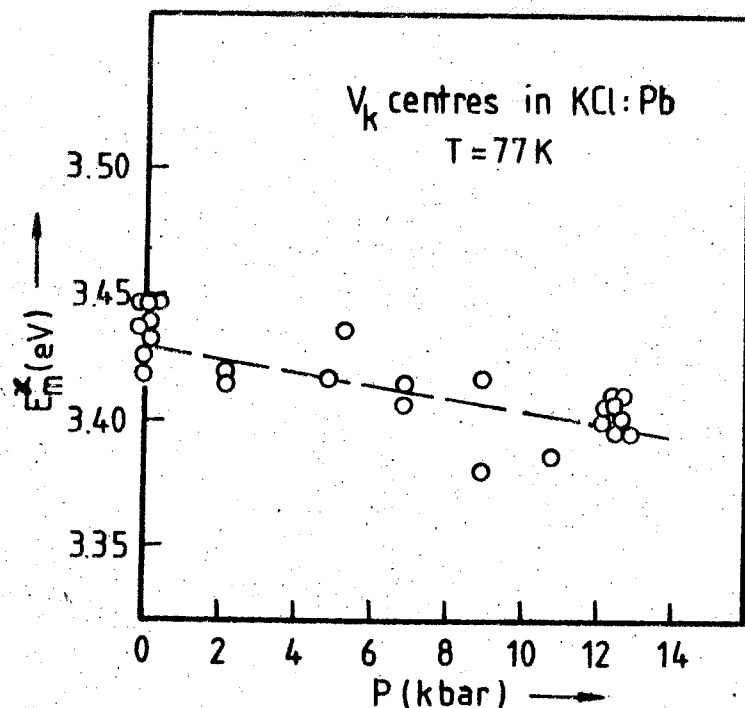


Fig.3. Pressure shift of the absorption band peak of V_K centres in KCl:Pb crystal at 77 K.

the under pressure. However, we could not detect up to 12.6 kbar that this slow shift started to turn into a rapid short-wave-length shift, as predicted by theory.

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NEUTRON SCATTERING INVESTIGATIONS OF SOLID HYDROGEN EXCITATIONS SPECTRA UNDER PRESSURES UP TO 11 KBAR.

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The abnormally great compressibility of solid molecular hydrogen results in the pronounced variation of the phonon density and the decrease of the molecular root-mean-square displacement on the equilibrium position already at relatively low pressures. At low the value of $\langle u^2 \rangle = 0.46 \text{ \AA}^2$ for parahydrogen at 5 K and P=0 is determined reliably, and the phonon density function is calculated under same conditions from the experimental phonon dispersion curves [1]. The finding of the complete picture for the real hydrogen phonon density function with inherent significant anharmonicity atures is faced with difficulties even at zero pressure [2].

We have carried out neutron incoherent inelastic scattering measurements on polycrystal specimens under pressures up to 11 kbar. The experiments were run on the high pressure facility based on the "Skel" Accelerator [3]. Three pressure cells were used: 1) specimen volume 14 cc, P=0-2 kbar; 2) 15 cc, 0.4-5 kbar; 3) 2 cc, 1-11 kbar, respectively. The last one had an internal cell which was pressed into the support made of powder aluminium alloy. This internal cell was from aluminium alloy crystallized under pressure, with enhanced strength.

One narrow peak related to the hydrogen molecule excitation to

the ortho-state is observed in inelastic scattering spectra at the energy transfer value $\Delta E = 14.6 \text{ meV}$. At greater energy transfers this process is accompanied by the creation of phonons. Neutron scattering cross-section corresponding to the peak involves the Debye-Waller factor, thus allowing the direct determination of the $\langle u^2 \rangle$ -value from its scattering angle dependence. The phonon density function was computed by iteration [4] after the multiple scattering contribution had been withdrawn. Transmission measurements were carried out to take account of specimen geometry corrections.

The preliminary analysis shows that the average magnitude of the Grüneisen parameter $\bar{\chi} \approx 2$ presents good enough the molar volume (V) dependence of $\langle u^2 \rangle$ over entire pressure range investigated (Fig. 1). The ratio of $\sqrt{\langle u^2 \rangle}$ to the nearest neighbour distance a is close to that calculated theoretically [5] and constitutes even at P=10.6 kbar a considerable value (~ 0.12). Hence zero vibrations play a significant role in parahydrogen lattice dynamics still.

The parahydrogen phonon density functions (without due account of the spectrometer resolution) for three pressure values are presented on Fig. 2. While increasing the pressure the role of multiple scattering processes grows; this makes necessary some additional calculations. The zero pressure phonon density function has one maximum at $E_{\text{max}} = 5.4 \text{ meV}$; the distinct maximum in the region of $E > 10 \text{ meV}$ (comp. e.g., with [2]) is essentially absent; the spectrum has also no pronounced boundary, instead an elongated "tail" exist. Such an appearance of the phonon density function is due to the joint influence of the spectrometer resolution function and of the finite life-times of interacting phonons. In the low phonon energy region it is the resolution function that has the main effect on the appearance of the experimental phonon density. But for energies exceeding the phonon density maximum energy the anharmonic phonon decay value starts to rise abruptly, thus affecting the phonon density more and more definitely.

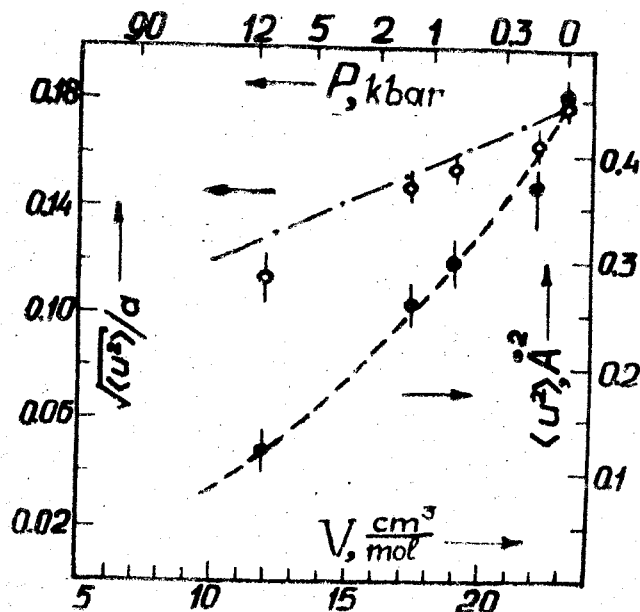


Fig. 1. Pressure effect on the hydrogen molecule root-mean-square displacement in the hcp-lattice. ϕ, ϕ - experiment and --- - curve of our's; - - - - - theoretical curve [5].

ly, ending in smearing the spectrum boundary completely and in forming a "tail" at high energies [6]. It was shown in [7] where no account was taken of phonon decay effects that pseudoharmonic phonon densities for different molar volumes can be reduced to the sole profile by the energy scaling with a factor $(V_i/V_0)^{1/3}$. By us, i.e., in the case of actual phonon densities such a scaling results in the coincidence of the curves for energies $\epsilon \leq \epsilon_{max}$, strong differences arising up for higher energies.

All the data have been treated mathematically on the basis of a harmonic theory of crystal lattice. The consistency of the results obtained evidences that the harmonic phonon theory may be used to describe the dynamic properties of solid parahydrogen molecular crystal.

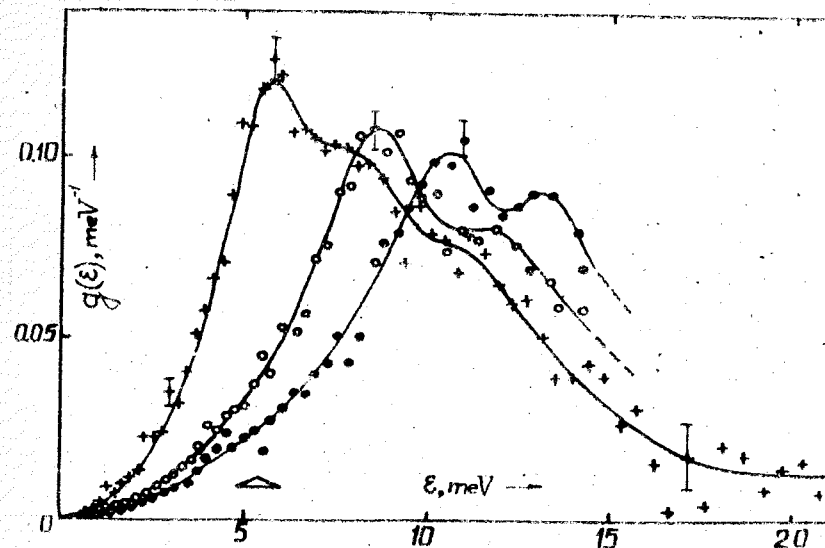


Fig. 2. Pressure effect on the phonon density function $g(\epsilon)$ of hcp-solid parahydrogen at 4.2 K: $+++ - P=0$, $ooo - P=0.3$ kbar, $... - P=1.5$ kbar.

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PIEZOSPECTROSCOPIC STUDY OF DEEP LEVEL ACCEPTOR ELECTRON STRUCTURE IN SEMICONDUCTORS

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The influence of the intra-center interactions (electron-phonon; exchange, etc.) on defect's wavefunctions in semiconductors is comparably with the influence of a uniaxial pressure P with a magnitude 0.1-1 GPa. The usefulness of this fact for quantitative characterization of deep center is demonstrated in this paper on the example of two deep-level acceptors produced by Cu- and Mn- atoms substituting Ga in the cubic lattice of GaAs.

We investigated the effect of uniaxial stress on relatively narrow bands of photoluminescence (PL) arising from the recombination of free electrons with holes bound on these acceptors (the photon energy range 1.3-1.45 eV).

The qualitative piezospectroscopic and magnetooptic investigations of this PL in the case of Cu_{Ga} have shown that in the light emitting state the complex Cu_{Ga} + four nearest neighbours (i.e. As) binds two holes and has D_2^- or D_{2d}^- symmetry with a preferred axis along one of the $\langle 100 \rangle$ crystal axes (Fig. 1, a). Such symmetry is caused by the Jahn-Teller (JT) effect attributed to the interaction of a hole having a full angular momentum $3/2$ with the quasilocal E-phonons. The Hamiltonian describing the interaction of bound holes with the applied stress and E-phonons consists of the sum of H_1 and H_2 operators related to the first and the second holes respectively and the hole exchange interaction Hamiltonian $\mathcal{H}_{1,2}$. In the case of the stress along the $[111]$ axis we have:

$$\mathcal{H}_{1(2)} = \frac{b'}{2} \{ (3J_z^2 - J^2) a_2 + \sqrt{3} (J_x^2 - J_y^2) a_3 \} - \frac{2d\varepsilon'}{3\sqrt{3}} \{ [J_x J_y] + [J_y J_z] + [J_z J_x] \} + a \text{Tr} \varepsilon$$

where J , J_x , J_y , J_z - are operators of the angular momentum and its projections on the x , y , z axes respectively for one hole; $[J_x J_y]$ - anticommutator of J_x and J_y ; b' - the interaction con-

stant of one hole with the E-vibrations (described in Q_2 and Q_3 coordinates); a and d - deformation potential constants of one bound hole in the case of hydrostatic compression (a) and pressure along the $[111]$ axis (d); ε' - relative deformation, $\text{Tr } \varepsilon$ - the sum of the diagonal elements of the deformation tensor.

The adiabatic potentials (AP) of the $\text{Cu} + \text{two holes}$ system (Fig. 1, b) are obtained by the addition of the elastic energy of the atoms forming the defect complex to the eigen-values of the $\mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_{1,2}$ Hamiltonian [1].

The analysis of the PL band form in the case of electron-phonon interaction described by these AP predicts that at $P \approx P_0$: 1) the width of the PL band decreases; 2) the position of the PL maximum sharply shifts; 3) the PL is strongly polarized along the stress axis. All these characteristic peculiarities are observed experimentally [2] (Fig. 2). The value of the sharp peak shift, as shown by the analysis in [1, 2], is close to stabilization energy E_{JT} . From Fig. 2 it is reasonable to conclude that $E_{JT} \approx 10$ meV.

In comparison with other acceptors the piezospectroscopic measurements [3, 4] of the Mn_{Ga} centers showed a weak increase of PL polarization and a significant nonlinearity in PL peak position shift ($\Delta \hbar \omega_m$) with an increase of the uniaxial pressure. These peculiarities are explained by the model of a neutral Mn_{Ga} acceptor which supposes that a hole (h) bound to a Mn_{Ga} center differs from a hole bound to a usual shallow acceptor only by the exchange interaction with the electrons from the not completely filled d-shell of Mn with a total spin $S_d = 5/2$. As a consequence of this interaction the states of the $\text{Mn}_{\text{Ga}} + h$ system are characterized not by the individual momenta of the 3d-electrons (5/2) and the hole (3/2), but by their total momentum F which may take values of 1, 2, 3 and 4. The ground state corresponds to $F=1$.

If the uniaxial pressure acts only on a bound hole then the state of the system in the case of a uniaxial pressure along the $[100]$ or $[111]$ axes may be described by the Hamiltonian:

$$\mathcal{H} = -A (\vec{J} \vec{S}_d) + a \text{Tr } \varepsilon - (f_1 \varepsilon')^2 / 4 + (J_{z_1}^2 - 5/4) r_1 \varepsilon'$$

$$(1 + r_1 \varepsilon' / A)$$

where A - is the exchange interaction constant; $f_1 = ad/\sqrt{3}$ for $P \parallel [111]$ and $f_1 = b$ for $P \parallel [100]$ where b - is the deformation potential constant for a stress along the $[100]$ axis; J_{z_1} - the operator of

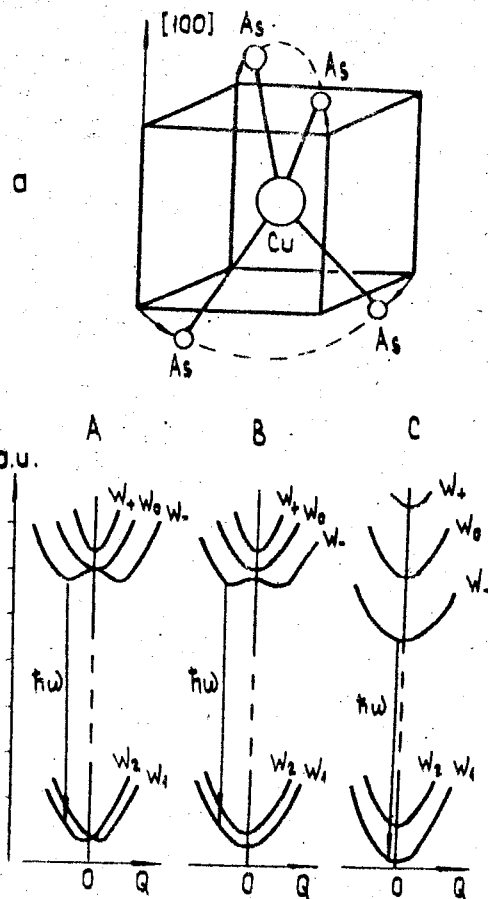


Fig. 1. A model of a Jahn-Teller center $\text{Cu}_{\text{Ga}} + 4 \text{As}$ (a) and a schematic view of the adiabatic potentials in the initial (W_+ , W_0 , W_-) and final (W_1 , W_2) states (b). A - $P=0$; B - $P \parallel [111]$, $P < P_0$; C - $P \parallel [111]$, $P > P_0$.

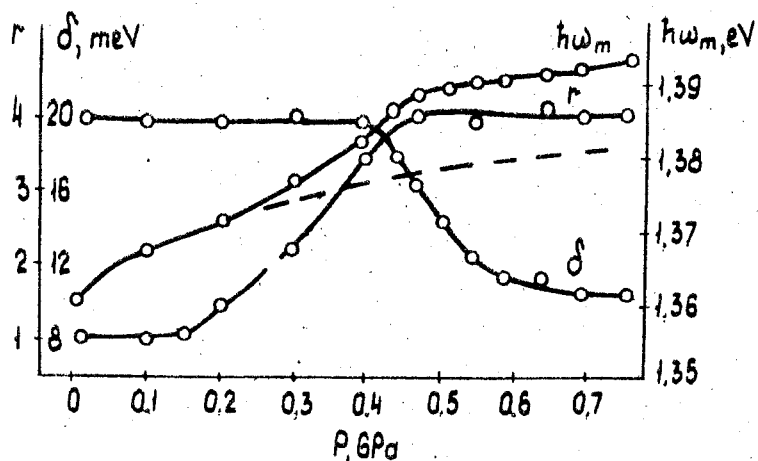


Fig. 2. The dependence of the polarization ratio (r), the photoluminescence peak position ($\hbar\omega_m$) and the half-width of the main PL line (δ) for Cu_{Ga} in GaAs as a function of the uniaxial stress $P \parallel [111]$. $T = 2\text{K}$.

projection of momentum J on the stress axis. The parameter Δ takes into account the intermixing of the ground and excited states.

The dependence of the state energy for $F=1, 2, 3$ on uniaxial stress is shown on Fig. 3. Same figure shows the uniaxial stress dependence of the polarization ratio (r) of PL due to electron capture by the neutral Mn_{Ga} center being in one of the first three energy states. Taking only ground state into account one may use the values of constants A , f_1 and Δ in such a way as to describe the results of PL measurements at $T=2\text{K}$. In such a process the value of α was chosen equal to its value for the v-band GaAs in accordance with the commonly accepted concept. Such approximation of the four experimental dependencies: $\Delta\hbar\omega_m(P)$, $r(P)$ for $P \parallel [111]$ and $P \parallel [100]$ gave us the possibility to determine that $A = -(4 \pm 1) \text{ meV}$. The other parameters occurred to have values close to the ones for the valence band ($b = -(2.2 \pm 0.6) \text{ eV}$; $-(5.5 \pm 1.5) \text{ eV}$; $\Delta = 50 \pm 1000 \text{ meV}$) which presents a quite reasonable result.

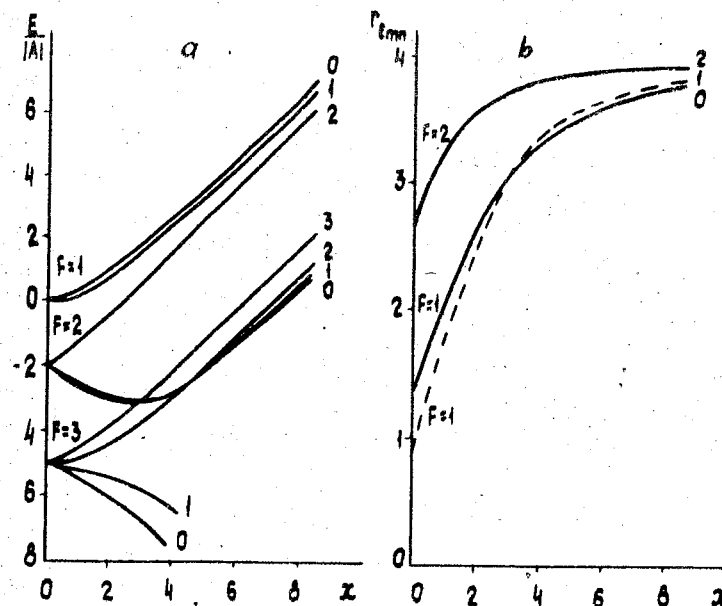


Fig. 3. The energy position of the first few states of the $\text{Mn}_{\text{Ga}}+h$ system (a) and the polarization ratio of photoluminescence in the case of electron capture from the c-band onto one of the low energy states of this system (b) as a

function of uniaxial stress: $X = \frac{f_1 \epsilon'}{A} (1 + \frac{f_1 \epsilon'}{\Delta})$. The num-

bers near the curves represent the absolute values of the total momentum F projection on the stress axis for given state.

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EFFECT OF HYDROSTATIC PRESSURE ON EMISSION PROPERTIES OF GaSb/AlGaSb DH DIODE LASERS

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At about 1.05 GPa the inversion of the Γ and L conduction band (CB) minima of GaSb occurs [1] and GaSb transforms into an indirect gap material. Hence, the high-pressure technique can serve as a tool for studying the effect of the L indirect CB on the efficiency of DH lasers with a GaSb active layer. This paper communicates the investigation of stripe lasers fabricated from a double p-Al_{0.4}Ga_{0.6}Sb - p-GaSb - n-Al_{0.4}Ga_{0.6}Sb heterostructure [2] in spontaneous and laser mode at 77 K and pressures up to 1.41 GPa. The obtained pressure dependences of laser characteristics are compared with the results of the calculations performed.

The energy of the prevailing longitudinal mode, E, (Fig. 1) increases linearly with pressure at the rate of about 140 meV/GPa, which is nearly equal to the pressure coefficient of the direct energy gap in GaSb [1]. Up to the pressure of P $\approx$ 0.7 GPa the change of the threshold current density J_{th} is proportional to E²(P). A more rapid increase of J_{th} starts at about 1.0 GPa (Fig. 1) when the L indirect CB population is already considerable. It is followed by the ceasing of the stimulated emission at about 1.28 GPa when J_{th} exceeds the normal pressure value by about 20 times and the L indirect CB is by 5 kT lower than the direct one.

The effective electron lifetime at the threshold, τ_{eff} , was evaluated by using the dependence of J_{th} on the duration of the injection current pulse as suggested by Gorbylev et al. [3]. At the normal pressure and 77 K $\tau_{eff} = (3 \pm 1)$ ns. This value is nearly equal to the calculated radiative lifetime of electrons at the threshold in the direct CB, τ_r . Starting from the pressure 0.7 GPa τ_{eff} first increases, then passes through its maximum (18 $\pm$ 2) ns at 1.15 GPa, and thereafter decreases rapidly (Fig. 2). The total electron concentration at the threshold, n, defined by the relation $n = J_{th} \tau_{eff} / ed$, where e is the electron charge, and d is the active layer thickness, grows with pressure by more than one order of magnitude.

For an analysis of the pressure dependence of J_{th} it was assumed that

$$J_{th} = ed \left(\int_0^\infty r_{sp}(E) dE + \frac{n}{\tau_N} \right) = J_R + J_N$$

where $r_{sp}(E)$ is the rate of spontaneous recombination at the threshold, and τ_N is the lifetime of electrons that determines the component J_N. The first component J_R was calculated according to the model proposed by Stern [4], taking into account the features of the GaSb band structure [5]. In particular, it was supposed that ΔE_{FL} (meV) = 89 - 85 P, where P is expressed in GPa. The pressure effect on the density of states was neglected. For calculating $r_{sp}(E)$, the hole concentration in the valence band, p, and the electron concentration in the Γ CB, n_Γ , were found from the oscillation condition taken in the form $g_{max} = \alpha + \alpha_{fc}$. The constant part of the optical losses in the laser, α , was evaluated from the optical gain spectra g(E) at normal pressure to be 220 cm⁻¹. The pressure-dependent losses caused by the free carrier absorption were approximated by α_{fc} (cm⁻¹) = $3 \cdot 10^{-12} n + 7 \cdot 10^{-12} p$, where the unit of measure for concentrations is m⁻³.

As it can be seen from Figs. 1 and 2, the theoretical dependences agree with the experimental ones in a wide pressure range in case $\tau_N = (2 \text{ to } 3) \cdot 10^{-8}$ s. Since the main part of injected electrons populates the L CB at P > 0.8 GPa, it seems to be reasonable to attribute the τ_N value to the recombination process in which namely these electrons take part.

Under pressures in excess of 1.15 GPa a drop of τ_{eff} and a very rapid increase of J_{th} with pressure take place, which is not explainable by the model considered. Besides, in this region the internal optical losses were evaluated after the measured differential quantum efficiency. It appears that the losses also increase before the oscillation ceases. The changes observable at high concentrations of non-equilibrium carriers are most likely caused by the Auger recombination and/or the intervalence band absorption.

The spontaneous luminescence spectra of the lasers were also measured. On increasing pressure in the range from 0.99 to 1.41 GPa, i.e. when $\Delta E_{FL} < 0$, the emission intensity at constant current decreases by two orders of magnitude and the maximum of

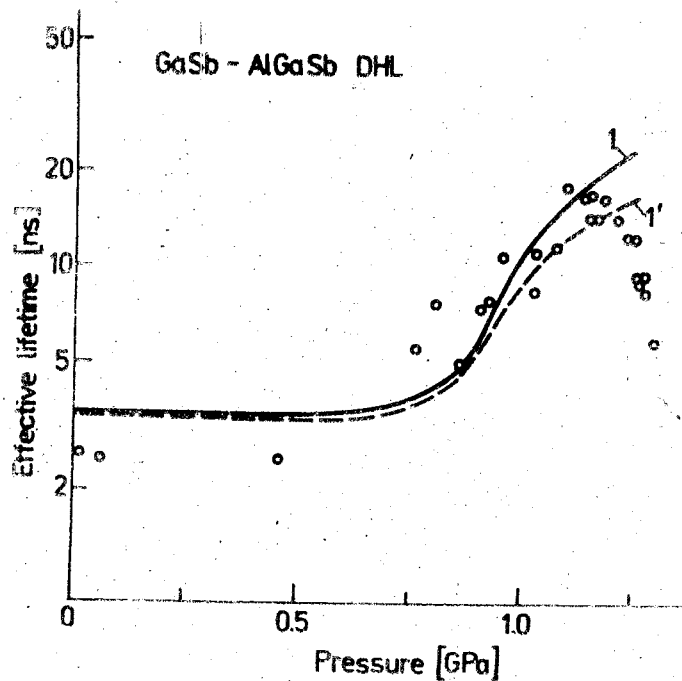


Fig.1. The pressure dependence of the prevailing longitudinal mode energy (I) and threshold current (filled circles and curves 2, 2') for the stripe GaSb/AlGaSb laser. Curves 2 and 2' have been calculated for $\tau_N = 30$ and 20 ns, respectively.

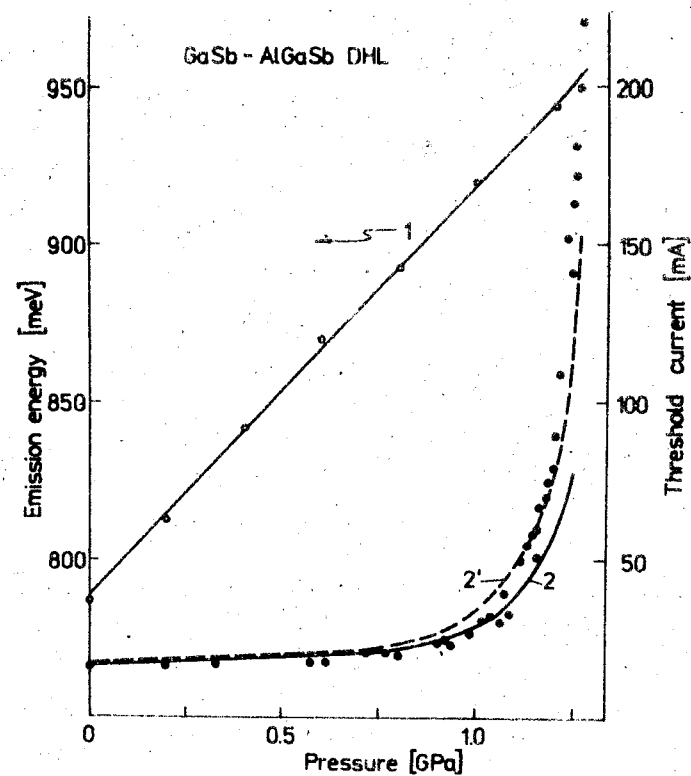


Fig.2. The pressure dependence of effective electron lifetime at the threshold for the GaSb/AlGaSb laser. Curves 1 and 1' have been calculated for $\tau_N = 30$ and 20 ns, respectively.

the spectrum shifts towards the shorter wavelengths with the rate of 120 meV/GPa. At the same time a low-energy tail appears in the emission spectrum, which most probably is caused by the radiative transitions of the electrons associated with the L indirect CB of GaSb.

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HIGH PRESSURE INFLUENCE ON CATHODOLUMINESCENCE OF CUBIC BORON NITRIDE

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In the luminescent spectra of cubic boron nitride (BN_{sph}) broad zero-phonon lines of optically active GC center as well as the lines of RC centers of radiation origin have been observed /1-3/. The GC-1 and GC-2 centers, sensitive to elastic microstress and the perfection of the BN_{sph} structure, are assumed /3/ to be impurity-vacancy complexes based on nitrogen and boron vacancies.

The influence of pressure on the cathodoluminescent (CL) spectra of BN_{sph} polycrystals has been investigated in this paper for elucidating the nature of the broad luminescent bands.

Polycrystals with different structure perfection served as samples: cubic boron nitride BN_{sph}^{1p} and BN_{sph}^{2p}, synthesized from high purity pyrolytic boron nitride at different parameters by direct phase transition $BN_n^p \rightarrow BN_{sph}^p$ and BN_{sph}^c ceramics, obtained by sintering BN_{sph} single crystals grown in the system with nitrogen excess at high pressures and temperatures.

Pressure treatment of the samples placed in graphite-like boron nitride container was performed at 9.5 GPa at room temperature. The pressure increased up to the given values at a step of 3 MPa/s, with the exposure under pressure being 1 h. After the complete cycle of the pressure treatment (up to 9.5 GPa) of the samples some insignificant changes in the parameters of the lattice and those of thin crystal structure of the material have been observed.

The CL spectra of the initial and the pressure treated samples were recorded at 80 and 300 K. The energy of the exciting electrons was 15 keV at a current density of 6 $\mu A/mm^2$.

The CL spectra of the initial BN_{sph}^{1p} and BN_{sph}^{2p} revealed the broad bands A and B with the maxima at 2.4 and 2.8 eV and a more narrow band C in the range 1.55-1.85 eV as well as the zero-phonon lines of the GC-1 center interacting with the phonons 49 and 64 meV and the GC-2 center with a weak phonon replica. A

structure (at 2.84, 2.95, 3.13 eV) was noted in the high energy section of the band B. The microhardness (63.5 GPa) of $\text{BN}_{\text{sph}}^{2p}$ with the band C of greater intensity in the CL spectra was higher than that (48.5 GPa) of the $\text{BN}_{\text{sph}}^{\text{IP}}$ samples.

In the CL spectra of the initial $\text{BN}_{\text{sph}}^{\text{C}}$ the broad band A being dominant in intensity was observed. The pressure treatment of the BN_{sph} samples leads to drastic change in the intensity of the bands A, B, C, in the widths and intensities of the zero-phonon lines (Figs. 1, 3). In this case the centers RC-1 and RC-2, observed earlier [2] only after the radiation treatment, have been recorded in the $\text{BN}_{\text{sph}}^{\text{IP}}$ spectra, while in the spectra of $\text{BN}_{\text{sph}}^{\text{C}}$ the PC-1 (at 2.84 eV) and PC-2 (at 2.325 eV) centers, followed by the phonon at 100 meV and the PC-3 (at 1.79 eV) center equidistantly located in it at a step of 0.53 eV (Fig. 2). A narrow zero-phonon line splitted into a doublet of the PC-3 center has been observed after the pressure treatment of the $\text{BN}_{\text{sph}}^{\text{C}}$ samples at 9.5 GPa. The PC centers have been first recorded in this investigation.

In the CL spectra of the investigated samples the G-band ($\text{BN}_{\text{sph}}^{\text{IP}}$) is dominant with respect to intensity, and the zero-phonon lines of the GC and PC-1 centers (Figs. 1, c, 2, a).

From the dependences of the intensities of the A, B and C bands (Fig. 3, a) and half-widths of zero-phonon lines of the GC-1, GC-2 and RC-2 centers (Fig. 3, b, c) on the values of the pressure applied to BN it is seen that the most pronounced change in the parameters of the bands and the lines has been noted at pressure 3.5 GPa, where, from the data given in [4], plastic deformation of cubic boron nitride (BN_{sph}) at room temperature takes place. Up to 3.5 GPa the intensity growth of the C band has been observed, and at $P=3.5$ GPa (Figs. 1, a, b; 3, a) it attains a maximum, the intensity of the bands A and B drops and the zero-phonon lines disappear. Then the intensity of the band C decreases rapidly up to zero and zero-phonon lines, though somewhat later, reappear. Further enhancement of pressure up to 9.5 GPa results in increasing intensity of the A, B bands and the zero-phonon lines of the GC and RC centers, in the splitting of the zero-phonon lines of the GC-2 center (Figs. 1, c; 2, b, c).

The dependence of the intensities of the A and B bands in the CL spectra of $\text{BN}_{\text{sph}}^{\text{C}}$ on the pressure treatment is about the same as that for $\text{BN}_{\text{sph}}^{\text{IP}}$. However, the intensity minimum has been recorded at higher pressure (4.5 GPa). The parameters of the zero-

zero-phonon lines of the PC-1 and PC-2 centers at pressure above 4.5 GPa are less sensitive to the change of pressure and plastic deformation of the samples than those of the GC and RC-centers. At pressure above 8 GPa the zero-phonon lines of the PC-1 center have not been noted.

The sensitivity of the band C to the change of dislocation density (microhardness) in the sample of initial $\text{BN}_{\text{sph}}^{\text{IP}}$ and $\text{BN}_{\text{sph}}^{2p}$ the growth in its intensity in the range of plastic deformation at room temperature allows one to make two assumptions. First, the radiative recombination of cubic boron nitride BN_{sph} in the range 1.55 to 1.85 eV can be associated with the electronic states in the band gap of BN_{sph} which form the dislocation band. Second, it is possible that the dislocations due to the plastic deformation distort the GC centers to a great extent to produce inhomogeneous broadening, while the appearance of the substantial background (C band) may be connected with that of strong interaction with long-wave lattice acoustic vibrations, the possibility of the interaction with which increases when the distortion of the structure of the defect occurs and the temperature increases, which manifests itself in the increase of intensity of the general background of the GC spectra and the emergence of a pronounced anti-Stokes wing.

It is worthwhile to notice (Fig. 3, a, b) that the change in the intensity of the bands A and B, the lines of the GC and RC centers when $\text{BN}_{\text{sph}}^{\text{IP}}$ is subjected to pressure is of general character. According to [3] one can assume that the appearance of the bands A and B in the CL spectra of cubic boron nitride is connected with the presence of multivacancy defects in it sensitive to elastic microstress. High stability of the bands allows one to suppose that the impurity atoms, connecting the vacancies into the stable complexes are included into their composition. On the other hand from the correspondence observed between the growth of the intensity of the band B (Fig. 3, a) and the zero-phonon line of the GC-1 center (Fig. 3, b), dominant with respect to the band A and the zero-phonon line of the GC-2 center in $\text{BN}_{\text{sph}}^{\text{IP}}$ subjected to pressure above 5.0 GPa one can assume that the vacancies due to boron and nitrogen, respectively, form the part of the complexes which give rise to the appearance of the bands A and B and that the formation of the vacancies due to nitrogen and its complexes mainly takes place when the cubic boron nitride is subjected to pressure.

The continuity of the bands A and B bands in the range from

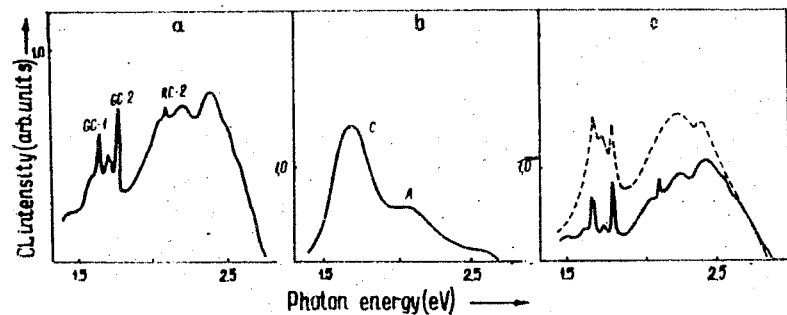


Fig. 1. CL spectra of BN^{Ip} polycrystal at 70 K (solid lines) and 300 K (dashed line) $^{\text{sph}}$ subjected to various pressures (GPa): a - 2.5; b - 3.5; c - 9.5.

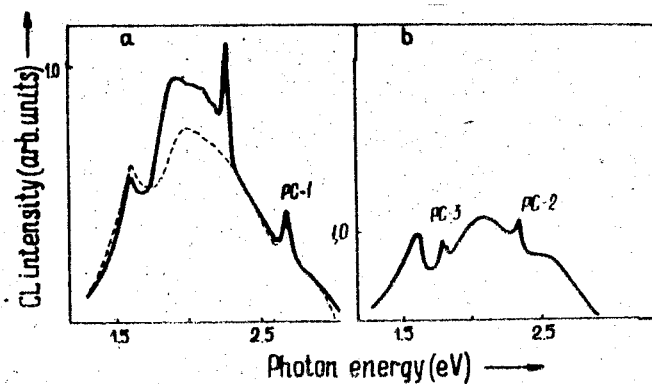


Fig. 2. CL spectra of BN^{C} ceramics at 70 K (solid lines) and 300 K (dashed line) $^{\text{sph}}$ subjected to various pressures (GPa): a - 2.5; b - 9.5.

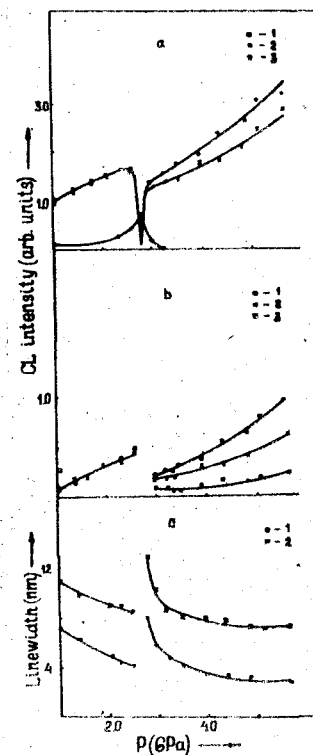


Fig. 3. Intensities, half-widths of lines A, B, C and zero-phonon lines of GC and RC centers of BN^{Ip} against pressure treatment: a) 1 - B; 2 - A; 3 - C; b) 1 - GC-1; 2 - GC-2; 3 - RC-2; c) 1 - GC-2; 2 - GC - 1.

1.85 to 3.25 eV and their sensitivity to temperature make it possible to assume the presence of a rather broad band with a quasi-continuous set of levels in the band gap of BN_{sph} . For these levels the thermoactive and recombination processes depending on the life-time of nonequilibrium carriers, are characteristic.

The enhancement of the intensity of the zero-phonon lines of the GC centers and their narrowing during the pressure treatment of polycrystals above 4.5 GPa testify to the decrease of microstress in the BN_{sph} samples in proportion to the pressure applied. The decrease of microstresses are likely to be due to the processes of annihilation of dislocations.

The behaviour of the parameters of zero-phonon lines of the C-I and PC-2 centers in the CL spectra of BN_{sph} after the pressure treatment of the polycrystals and the energy of their interaction with quasilocal oscillations (100 meV) which exceeds greatly that of similar oscillations of the defects of the vacancy-type (56.64 meV) allow to assume that the composition of the above mentioned centers does not include vacancies but most likely interstitial atoms.

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HIGH PRESSURE EPR MEASUREMENTS ON DIAMOND AND OTHER HARD MATERIALS

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One of the key problems at the optimized application of hard materials is the characterization of their brittle strength. The aim of this paper is to show, how the properties of paramagnetic centres (pc) in hard and superhard materials depend on uniaxial pressure and how one can relate this behaviour to the mechanic properties of materials. The objects investigated are at first synthetic diamonds of different origins: AC 65T, SDA 100, SDA 85 and MDAS. At second, for comparison crystals of Al_2O_3 and SiO_2 with a diameter from 0.1 to 1 mm were investigated under pressure. Use was made of an experimental arrangement, which allows to observe EPR-spectra of single crystals under the influence of uniaxial pressure in the GPa-range in situ. For this purpose a special device for the cavity of a Varian E₄ spectrometer was constructed and adapted for different orientations of the crystals (fig.1).

Both the anisotropic fine and hyperfine structure of pc (lattice defects, impurities like ^{14}N , Fe^{3+} , Cr^{3+} , Ti^{3+} ---) and their relaxation behaviour depend in different ways on the pressure applied. These magnetic properties are sensitive to mechanic tensions induced in the crystals and can contribute to a measure of the brittle strength of materials.

An example for pressure effect of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ is given in fig.2 with the variation of intensity from a Cr^{3+} -zfs-line. The variations at first run to 30% and decrease a little by repetition. In comparison to the diamond (see fig.3) the relaxation of $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ -crystals takes place in the range of 300 K in significantly shorter time and the degree of irreversibility of the pressure-induced process is essentially smaller.

EPR-spectroscopically detectable pressure effect ($\vec{p} \parallel [100]$; $\vec{H} \parallel [100]$) on diamond crystals could be investigated till now only after external load by 77 K and transportation in the EPR-appara-

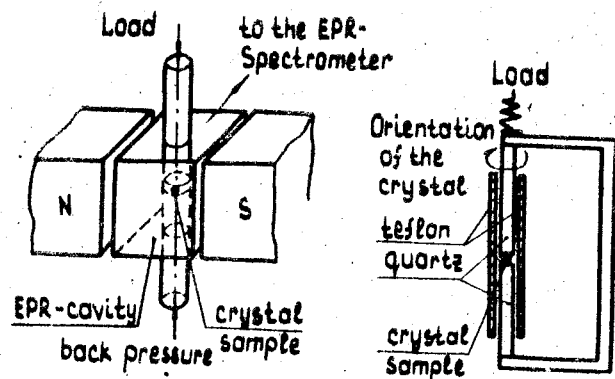


Fig. 1: Scheme of pressure apparatus in combination with the EPR-spectrometer.

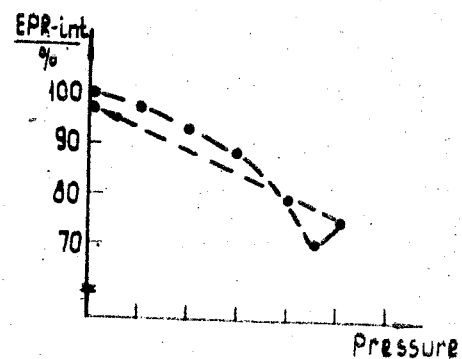


Fig. 2: Relative variation of EPR-intensity of a Cr^{3+} -zfs-line in $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$, measured in situ under pressure resp. after relaxation of pressure.

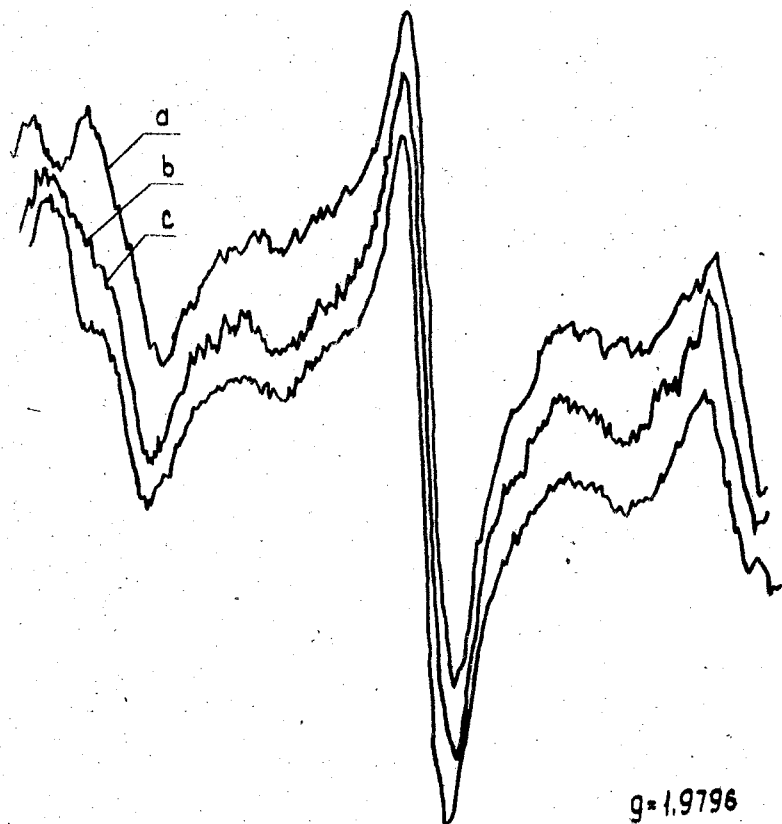


Fig. 3: EPR-spectra on diamonds under uniaxial pressure (p): a) EPR-spectrum of a crystal AC 65T (c. 200 μm diameter) at 77 K, $p = 0$; b) see a) after 20 min. under pressure (c. 5 GPa, external at 77 K); c) see b) after relaxation time of 30 min. at 300 K.

tus at this temperature and p=0. Variations are given in the limits of anisotropic ^{14}N -hfs of the paramagnetic nitrogen atoms in the diamond-lattice. The following experiments furthermore showed, that at low temperatures the pressureinduced effects slowly relax and consequently an observation in the pressureless state is possible (fig. 3b).

Processes of partial crystalregeneration after intervallic increasing of temperature up to 300 K is to see in fig. 3c.

It is very important to remark, that only in very few cases these effects are to observe, because the most investigated crystals in consequence of their imperfections are destroyed during the carryout of in situ-experiments.

EFFECT OF PRESSURE ON THE HYPERFINE INTERACTIONS FOR ^{119}Sn IMPURITY ATOMS IN LAVES PHASES GdT_2 (T = Mn, Fe, Co, Ni)

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To study influence of high pressure on the electron structure of alloys a comparative measurement of magnetic hyperfine fields (MHF) for ^{119}Sn impurity atoms in Laves phases GdT_2 (T = Mn, Fe, Co, Ni) prepared at normal (samples A) and 7.7 GPa (samples B) pressures have been carried out by Mossbauer technique. In these compounds the atoms of tin replace as the Gd-atoms as the 3d-metal atoms.

It has been found that MHF and their temperature dependences for two types of samples are quite different. The parameters of the hyperfine interactions for the ^{119}Sn measured at 5 K are listed in Table. The ^{119}Sn Mossbauer spectra at 5 K are plotted for - and B-types GdFe_2 in Fig.1, a,b.

Magnetic hyperfine fields B_1 and B_2 , isomeric shifts IS for ^{119}Sn impurity atoms in compounds CdT_2 prepared at normal (samples A) and pressure 7.7 GPa (samples B). Hyperfine interaction parameters have been measured at 5 K. IS is given relatively CaSnO_3 at 293 K

Compound		Sn in Gd-site		Sn in 3d-metal site	
		B_1 , T	IS, mm/s	B_2 , T	IS, mm/s
GdMn_2	A	-36.7(4)	1.93(3)	(-) 7.2(2)	1.76(5)
	B	- 9.3(3)	1.96(4)	- 7.3(3)	1.84(4)
GdFe_2	A	-36.1(2)	2.10(6)	-27.4 (3)	1.88(4)
	B	-52.6(5)	2.08(10)	-16.5 (5)	2.00(8)
GdCo_2	A	-28.1(4)	1.93(4)	-25.8 (4)	1.80(6)
	B	-51.4(3)	2.08(8)	-16.6 (5)	1.94(6)
GdNi_2	A	-	-	-32.4 (3)	2.00(4)
	B	(-)14.5(3)	2.07(6)	(-)2.2 (3)	1.96(4)

The MHF for GdFe_2 and GdCo_2 prepared normal pressure are caused by the interaction of the 4f- and 5d-electrons of Gd, and the MHF temperature dependences are different from that of the summary magnetizations. The values of MHF decrease continuously with increasing temperature and at $T \approx 95$ (2) K are equal to zero. The diminishing of the MHF at $T > 95$ K may be connected with the depolarization of the 5d-electrons. The depolarization temperature is equal to the energy of the magnetic interaction of 4f- and 5d-electrons.

In the samples GdFe_2 and GdCo_2 prepared at the high pressure the MHF at the ^{119}Sn nuclei are connected with the moments as of Gd and as of Fe and Co-atoms. For these samples the temperature dependences of MHF for ^{119}Sn - atoms are existed up to Curie temperature of the compounds.

The differences of spin densities at the impurity nuclei and the temperature dependences of MHF show that the electronic structure of the samples of the A- and B-type are different. But it is known from X-ray study that crystalline structure and the lattice parameters are not changed.

The heating of GdFe_2 (sample B) up to $T > 650$ K leads to return of the electronic state of sample A. It is shown by study of spectra at ^{119}Sn at 5 K after each step of annealing that the change of metastable electronic state goes through the intermediate state, which is characterized by only 3d-3d interaction for atoms Sn in Fe sites, then through the coexistence of the intermediate state with the normal state to the normal state.

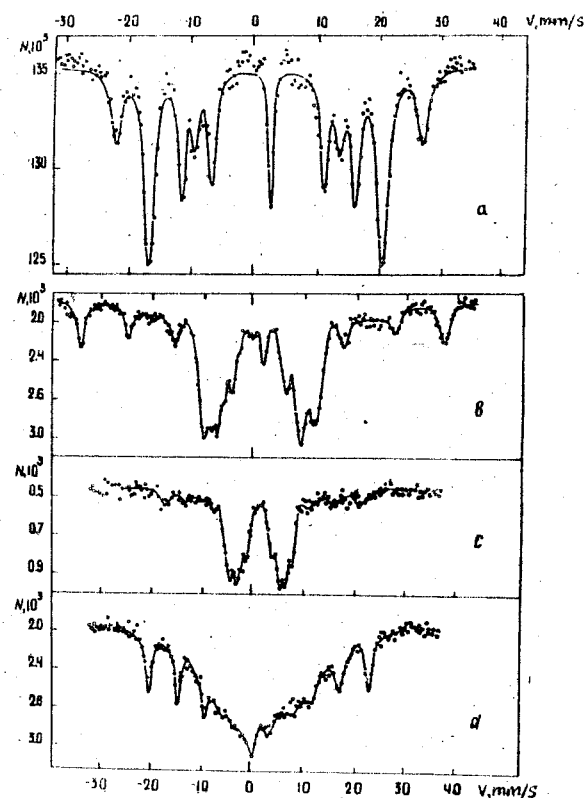
The results of our investigation may be summarized as follows.

1. The band structure of the compounds GdFe_2 , GdCo_2 , GdNi_2 crystallized at normal pressure have the gap between 5d- and 3d-energy levels.

2. In the GdFe_2 , GdCo_2 , GdNi_2 (C15-type) crystallized under high pressure arise the band structure in which energy levels of 5d-electrons hybridize with the levels of 3d-transition metal electrons. This effect is also observed in the compounds of the heavy rare earth metals prepared at ambient pressure (for example, LuFe_2). Electronic states created at high pressure remain unaltered after lowering the pressure.

3. The variation of the GdMn_2 electron structure leads to the variation of the crystalline structure from C15 to C14.

4. The values and temperature dependencies of the MHF at the ^{119}Sn non-magnetic nuclei are determined by the spin density polarization of the valent electrons of the compound so that their wave functions are becoming hybridized with the that of the impurity electrons.



Mossbauer spectra for ^{119}Sn impurity atoms measured at 5 K in samples of compound GdFe_2 prepared:

- a) at normal pressure; b) at pressure 7.7 GPa;
- c) at pressure 7.7 GPa with annealing at 673 K in during 12 h; d) at pressure 7.7 GPa with annealing at 773 K in during 12 h.

DIAMOND AND CUBIC BORON NITRIDE UNDER HIGH PRESSURE: RAMAN SCATTERING, EQUATION OF STATE AND HIGH PRESSURE SCALE

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The development of the diamond-anvil cell has stimulated Raman-scattering investigation of vibrational modes in covalent crystals. The linear pressure coefficient reported for diamond by M.Hanfland et al. /1/ ($2.90 \pm 0.05 \text{ cm}^{-1}/\text{GPa}$) agrees to within mutual experimental error with the result of H.Boppard et al./2/ ($2.87 \pm 0.01 \text{ cm}^{-1}/\text{GPa}$). As to cubic boron nitride, the only work by J.A.Sanjurjo et al. /3/ reports $3.45 \pm 0.07 \text{ cm}^{-1}/\text{GPa}$ for LO- and $3.39 \pm 0.08 \text{ cm}^{-1}/\text{GPa}$ for TO-modes. Since no compressibility data are available /1,2,3/, the mode Grüneisen parameter $\gamma = -\partial \ln \nu / \partial \ln V$ is defined as $\gamma = \frac{K}{V} \cdot \frac{\partial V}{\partial P}$ and depends on the bulk modulus K and the calibration of the ruby scale. The above papers report $\gamma = 0.96$ and $\gamma = 0.95 \pm 0.03$ for diamond and $\gamma_{\text{LO}} = 1.21$, $\gamma_{\text{TO}} = 1.51$ for BN.

In the present experiment we perform the first-order Raman scattering investigation simultaneously with the X-ray density determination. This direct determination of V versus P permits us to compute the mode Grüneisen parameter as a function of V . Moreover, P - V data yield the bulk modulus K and its pressure derivative $K' = (\partial K / \partial P)_T$. We compared these values with available experimental results and made some conclusions about the calibration of the ruby scale.

The first-order Raman modes and [440] X-ray-diffraction peak were observed at pressures up to 40 GPa. A gasketed diamond anvil cell with helium as a pressure medium was used. Measurements were performed on (110) cleaved plates of about 60 μm in diameter and 15 μm in thickness. The Raman spectra were excited with the 488.0 and 514.5 nm lines of an Ar⁺-ion gas laser and analyzed in backscattering geometry by double grating spectrometer DFS-24. The angular position of [440] diffraction peaks was determined by two-circle diffractometer simultaneously with Raman measurements. All measurements were carried out at room temperature.

We present our results in the form of the relationship between measured quantities:

$$\frac{\rho}{\rho_0} - 1 = a_1 \left(\frac{\lambda}{\lambda_0} - 1 \right) + a_2 \left(\frac{\lambda}{\lambda_0} - 1 \right)^2, \quad (I)$$

$$\frac{\nu}{\nu_0} - 1 = b_1 \left(\frac{\lambda}{\lambda_0} - 1 \right) + b_2 \left(\frac{\lambda}{\lambda_0} - 1 \right)^2, \quad (I')$$

were ρ , ν , λ - current density, Raman frequency and wavelength of the R_1 luminescence line of ruby; ρ_0 , ν_0 , λ_0 - the same values at $P=0$. The least-squares method gives $a_1 = 4.28 \pm 0.03$, $a_2 = 0$, $b_1 = 4.09 \pm 0.02$, $b_2 = 3.2 \pm 1.2$ for diamond and $a_1 = 4.95 \pm 0.03$, $a_2 = -5.7 \pm 2.3$, $b_1(\text{TO}) = 5.93 \pm 0.04$, $b_2(\text{TO}) = -8.4 \pm 2.7$, $b_1(\text{LO}) = 4.54 \pm 0.04$, $b_2(\text{LO}) = 0$ for BN.

Figure 1 displays the plot of Raman frequency versus density. This relationship allows us to compute the Grüneisen parameter as a function of density. Within experimental accuracy γ is found to be constant both for diamond and BN, when helium is soft enough to be nearly hydrostatic medium ($P \approx 30 \text{ GPa}$). Experimental values are listed in the Table.

Grüneisen parameters of LTO(TO)-modes, bulk moduli K_0 and their pressure derivatives K'_0 for diamond and boron nitride

	γ	K_0 , GPa	K'_0
Diamond	0.965 ± 0.005^a	$444 \pm 3^b (442^{c,d})$	$1.9 \pm 0.3^b (4.0 \pm 0.7^c)$
Boron	$1.20 \pm 0.01(\text{TO})^a$	385 ± 3^b	2.35 ± 0.21^b
nitride	$0.91 \pm 0.01(\text{LO})^a$	381 ± 3^e	4.46 ± 0.15^e

a-present work; b-present work, scale /4/; c-ref./5/; d-ref./6/; e-present work, "diamond" scale.

So, the Grüneisen law $\rho/\rho_0 = V_0^\gamma / V^\gamma$ is valid for diamond and boron nitride; what permits them to be treated as ideal Grüneisen bodies. This result allows to conclude that longwavelength optical modes do not destabilize diamond lattice up to high pressures.

Figure 2 shows compression isotherms of diamond and boron nitride (pressure is calibrated according to the sublinear pressure scale suggested by Mao et al./4/). Since the value of relative density change $(\rho - \rho_0)/\rho_0 = \Delta\rho/\rho_0$ is small, we may expand pressure in a power series of $\Delta\rho/\rho_0$ and take only two first terms:

$$P/K_0 = \frac{4\rho}{\rho_0} + \frac{1}{2} (K'_0 - 1) \left(\frac{4\rho}{\rho_0} \right)^2, \quad (2)$$

where K_0 and K'_0 are the bulk modulus and its pressure derivative at $P=0$. The values of K_0 and K'_0 found from Eq.(2) by least squares method are given in the Table. K_0 for diamond is in excellent agreement with very reliable ultrasonic /5/ and Brillouin scattering /6/ data. This fact indicates that the initial slope of $P(\Delta\lambda)$ in /4/ is correct and, at the same time, the accuracy of our results is sufficiently high. On the other hand, our value for K'_0 remarkably differs from one in /5/.

Eqs.(1) and (2) suggest us to construct a new high pressure scale based on an "a priori" equation of state for diamond. Unfortunately, the error of the known value K'_0 /5/ is too large for this procedure to be faultless. Nevertheless the estimation $K'_0=4$ for diamond is believed /7/ to be accurate within several percents.

Eqs.(1) and (2) with $K'_0=4$ for diamond yield a new calibration function $P(\Delta\lambda)$ which differs from calibration suggested by Mao et al./4/ at high pressure:

$$P(\Delta\lambda) = A \left[\frac{\Delta\lambda}{\lambda_0} + m \left(\frac{\Delta\lambda}{\lambda_0} \right)^2 \right], \quad (3)$$

where $A=(1892 \pm 25)$ GPa, $m=6.4 \pm 0.5$,

or

$$P(\lambda) = \frac{A}{n} \left[\left(\frac{\lambda}{\lambda_0} \right)^n - 1 \right], \quad (3')$$

where $A=(1918 \pm 25)$ GPa, $n=11.7 \pm 0.5$.

This calibration gives higher pressure, than /4/: near 30 GPa the pressure according to the new "diamond" scale is about 7% higher. The values of K_0 and K'_0 for boron nitride obtained from new calibration function are listed in the Table.

In conclusion, Raman frequencies of diamond and boron nitride may be used as a pressure sensor (see also Ref.1). Expanding pressure in a power series of $\Delta V/V_0$ we obtain in the second order for diamond (using the condition $(\partial^2 V/\partial P^2)_0=0$):

$$\frac{P}{K_0} = \frac{1}{\gamma_0} \cdot \frac{\Delta V}{V_0} + \frac{1}{2} \left(\frac{K'_0}{\gamma_0^2} - \frac{1}{\gamma_0} \right) \left(\frac{\Delta V}{V_0} \right)^2 \quad (4)$$

We would like to thank Dr.I.S.Gladkaja for generously supplied boron nitride single crystals.

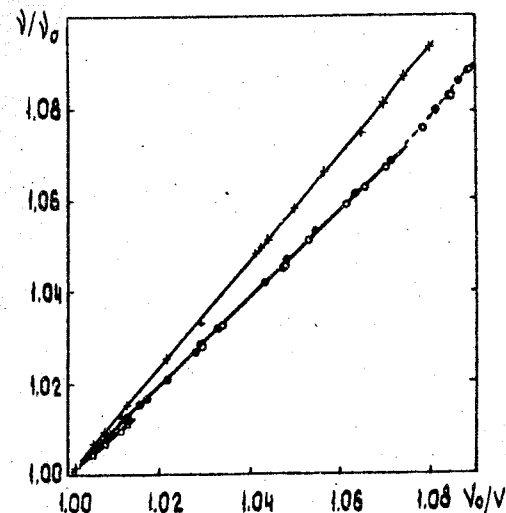


Fig.1. Relative Raman frequencies versus relative density: o - diamond; + - boron nitride, TO-mode; □ - boron nitride, LO-mode.

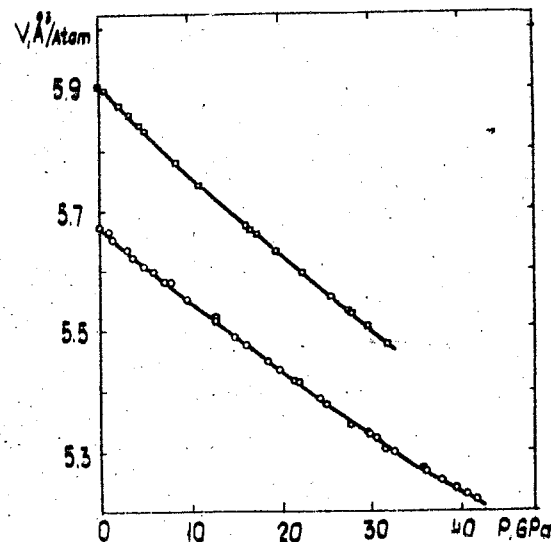


Fig.2. Compression isotherms: o - diamond; □ - boron nitride.

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X-RAY ABSORPTION SPECTROSCOPY AT HIGH PRESSURE

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I. Introduction

In this paper we review some of our work involving the absorption spectroscopy of synchrotron radiation by materials under high pressure. The studies were performed at the Stanford Synchrotron Radiation Laboratory at pressures ranging from 1 bar to approximately 220 kbar.

Like X-ray diffraction, synchrotron X-ray absorption spectroscopy /1,2/, which probes materials at the microscopic level, is well suited to high pressure studies. Moreover, since this new technique is still in a developmental stage, the ability to alter the microstructure of a material by means of high pressure aids our understanding of the theory underlying the X-ray absorption spectra. This applies to the XANES (X-ray absorption near-edge structure) as well as to the EXAFS (extended X-ray absorption fine structure). As the studies reported here will emphasize, this technique is especially sensitive to valence states, electronic structure, atomic vibrations, bond lengths and their mean square disorder σ^2 , coordination numbers, and atomic rearrangement during phase transitions.

Our high pressure method employs pressure cells containing the sample between opposed anvils, with the X-rays or γ -rays on axis /3/. Although diamond anvils are generally preferred and have led to pressures as high as 5 megabars, they tend to produce Bragg peaks that disturb the EXAFS (but not always the XANES). Therefore, our workhorse for X-ray absorption experiments is the boron carbide anvil, which permits larger samples but certainly limits our pressure range. The latter is, so far, not a major drawback, since we have reached pressures of over 200 kbar and have yet to reach our limit. As we shall see, there are many exciting experiments to do in this pressure range. Moreover, since there is still a great scarcity of synchrotron radiation beam ti-

me, it will be many years, if ever, before experiments in this pressure range are exhausted.

In addition to the alkali halides, we have found metallic copper (and gold) to be excellent high pressure calibrants /4/. Although these materials are less compressible than the alkali halides, their spectrum extends to higher energy (wave vector), enabling one to extract changes in bond length small enough to observe pressure changes of ~ 3 kbar. The XANES of copper, to our knowledge, is the only system that has been calculated theoretically from first principles as a function of pressure /5/. Our experimental results are in accord with the predicted $v^{-2/3}$ dependence of the spectral shift.

II. Samarium Compounds

Systems that exhibit valence fluctuations continue to fascinate researchers. One class of such materials is typified by the samarium chalcogenides. We have studied both SmS and SmSe, which exhibit pressure-induced transitions from the insulating state to the metallic, mixed valent state /6/. Our Sm-L₃-XANES measurements nicely show the effective samarium valence changing from +2 to +3, accompanying an EXAFS-determined volume decrease /7/. In addition, the disorder parameter, σ^2 , has been measured. In the case of SmSe this work has been extended to 77 K, by means of a new high pressure cryostat, so that the thermal disorder may be separated from the static disorder.

Although these results are still under final analysis and interpretation, the results so far are intriguing. The apparent valence change, determined from the XANES, occurs at higher pressures than the main volume decrease. Although the XANES shifts by about 7 eV through the transition, the EXAFS does not appear to be a superposition of two shifted spectra. Moreover, the EXAFS yields a single near-neighbor bond length, although a small increase in σ^2 is observed through the main volume decrease. Such observations appear to be consistent with a dynamic fluctuation between the 4f⁶ and 4f⁵ Sm configuration. An interpretation perhaps similar to that for Mössbauer or magnetic resonance spectra combined with relaxation processes is under consideration.

III. Systems Exhibiting Rotation of Atomic Polyhedral Units

We have measured the X-ray spectrum of α -quartz GeO₂ as a

function of pressure /8/. This work extends earlier neutron diffraction work at lower pressures /9/. What is observed is a compression of the Ge-Ge bond but not of the Ge-O bond because of rotation of the GeO₄ tetrahedral units.

Similar behavior occurs in some perovskite structures. The most dramatic is perhaps the "compressibility collapse" in ReO₃, /10/, where the octahedral units first compress and then abruptly rotate in a manner that preserves the cubic symmetry (M-type distortion). As we have reported /11/, such a rotation is very apparent in the EXAFS radial distribution function (RDF), where the multiple scattering affect along the Re-O-Re path is very sensitive to deviations from the 180° bond angle. Measurements at 77 K are still required to separate thermal and static disorder. In addition, some theoretical work in collaboration with J.Rehr of our department is required to refine our understanding of the multiple scattering effect. Since good neutron diffraction data exist for ReO₃, this is an excellent system for comparison. Other related systems under study are RbFeF₃, Na₂WO₃, K(Ta,Nb)O₃, and the newly discovered high T_c superconductors, La-(Ba,Sr)-Cu-O and Y-Ba-Cu-O /12/.

IV. Other Systems

We are currently analyzing data on amorphous germanium, a-Ge. Our sample was obtained from Bouldin and Stern of our department, who had earlier performed a temperature-dependent study /13/. There have been reports of a phase change to the metallic state at about 60 kbar. Our sample exhibits no dramatic changes up to approximately 100 kbar, although higher shells, not apparent at low pressure, become barely discernible. However, we have determined the bond compressibility and its mean square disorder, as well as the pressure dependence of the coordination number; these parameters are not readily determined by other techniques.

We recently have succeeded in extending our pressure range sufficiently to observe the bcc-fcc 120 kbar transition in metallic iron. The original goal of this work was only to measure the XANES change at the transition. Our past experience indicated that obtaining good EXAFS data for low X-ray energies (~ 7 keV) was very demanding. However, as with copper, the EXAFS range was spectacular and the quality of the data surprisingly good, despite the considerable attenuation of the X-rays by the pressure cell (Fig.I). The RDF so obtained exhibits a continued change with pressure af-

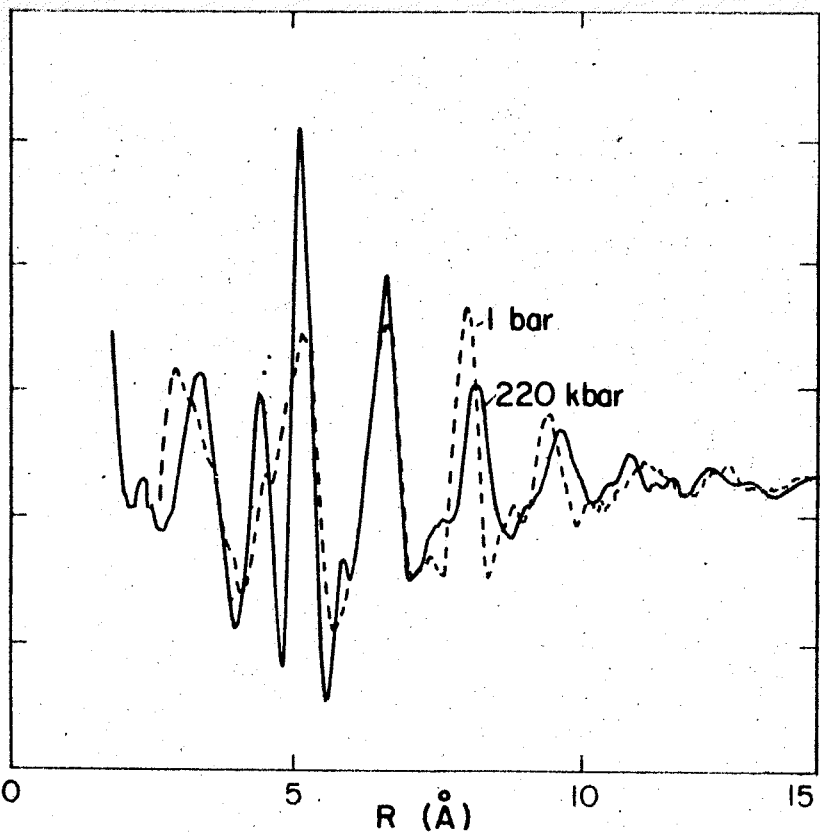


Fig.1. EXAFS interference function for metallic iron at several pressures.

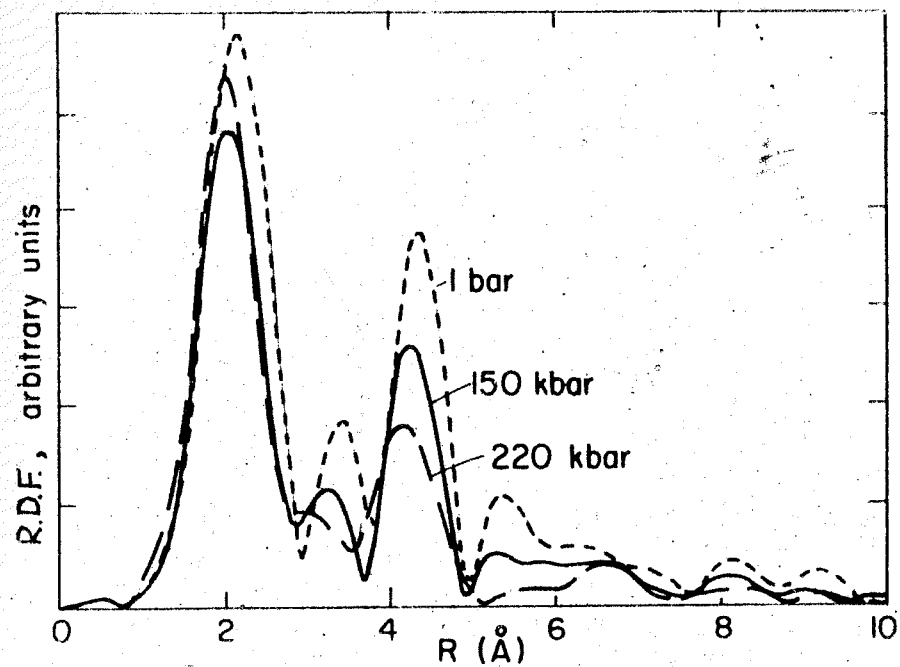


Fig.2. Radial distribution function (RDF) of metallic iron at several pressures.

ter the onset of the transition (Fig.2). Changes in many coordination shells are seen. An analysis of the data at the highest pressure is consistent with the hcp structure and a pressure of about 220 kbar. No pressure calibrant was used in this first attempt as it could have attenuated the signal. However, since good X-ray data exist for this system the pressure can be obtained from the EXAFS-determined near-neighbor spacing. Our method is more sensitive to local atomic displacements than the X-ray measurements. Development of techniques to unravel the overlapping data from the many coordination shells is being pursued.

Acknowledgements

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THE SPECTRA OF NH_4I UNDER HIGH PRESSURE

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Abstract

Careful infrared and Raman spectroscopic measurements on crystals of NH_4I as functions of temperature and pressure suggest the presence of a previously unreported phase transition. There is some evidence to suggest that this is of the commensurate-incommensurate type. If the Pippard relationships are obeyed throughout the transition region, then a sizeable thermal anomaly can be predicted from the spectroscopic data.

Introduction

There are at least five different crystallographic phases of NH_4I , see fig.1. Phase I is disordered NaCl type, II is disordered CsCl type, III is a tetragonally distorted CsCl type structure with anti-parallel order, IV is a fully ordered CsCl type structure and the structure of V has not yet been determined [1]. The order (or disorder) referred to above, relates to the orientations of the NH_4^+ ions. A tetrahedron can be orientated in two different ways within a cube, and a random distribution of NH_4^+ tetrahedra between the two alternative orientations is referred to above as a disordered structure.

A transition from order to disorder (III - II, IV - II, see fig.1) is often called a λ -transition, because of the characteristic shape of the specific heat anomaly. These transitions, and the III - IV transition, involve changes in the NH_4^+ orientations, and quite a lot of interesting information has been obtained [2,3,4] about the orientations within the

different stable structures. However, surprisingly little information seems to be available about the part played by torsional oscillations (or hindered rotations) in the mechanisms responsible for the phase transitions. There is some indication [5] that the form of the rotational type motion is geometrically quite complicated. Spectroscopically, the torsional oscillation of the NH_4^+ ion has usually been labelled ν_6 , and we have been studying ν_6 , $2\nu_6$ and $3\nu_6$ as functions of temperature and pressure, in an effort to reach a clearer understanding of the part played by this motion during phase transitions.

Recently [6] we found some evidence from this study to suggest that there was a previously unreported phase transition in the phase III region of fig.1 at about 110K. Here we report further data on this new transition.

Experimental

Single crystals of NH_4I were grown from aqueous solution. Variable temperature work at zero pressure was performed using an Oxford Instruments continuous flow cryostat. High pressure results were obtained using purpose-built high pressure cells which employ helium gas as the pressure transmitter. Purpose-built cryostats allowed the temperature of the high pressure cells to be varied in the range 77 to 500K with a stability of about $\pm 0.5\text{K}$ over the time required to record a spectrum. Raman spectra were excited by the 488 nm line of a Spectra Physics argon ion laser and were recorded with a Spex Ramalog 5M spectrophotometer. Infrared spectra were recorded using a Perkin-Elmer 580B spectrometer.

Results

Preliminary Raman data were recorded over the range 10 to 4000 cm^{-1} for each of the phases I, II, III and IV for various temperatures and pressures in the ranges $77\text{K} < T < 300\text{K}$ and $0 < P < 10\text{ kbar}$. Neither the gas compressor nor the three-window high pressure cell was capable

of working up to the pressures required to produce phase V [1]. Similarly, infrared spectra in the range 180 to 4000 cm^{-1} were recorded for a range of different crystal thicknesses.

From earlier work [7] on NH_4Br we suspected that the orientational order might break down in two stages. The λ -transition, at relatively high temperature, being the break-down of the short-range order, we suspected that a lower temperature transition might be found at the onset of some long-range disorder. Thus we took special note of the spectra below 220K, and paid special attention to the bands related to the torsional oscillation ν_6 .

Fig.2 shows the Raman spectrum observed in the ν_6 and $2\nu_6$ region at the various indicated temperatures between 71 and 129K under zero pressure. Probably the most obvious change is in the band shape of the $2\nu_6$ bands at about 110K. However, plotting the main peak frequencies as in fig.3 also brings out the fact that something happens at about 110K. The infrared spectra do not show quite the same effect.

Fig.4 shows the infrared absorption in the vicinity of $2\nu_6$ and here the major effect is in the intensity changes in the side bands that are located about 20 to 30 cm^{-1} either side of the main band. Notice how, as the temperature rises, the high frequency side band decreases in intensity and becomes lost by about 120K, whereas the low frequency band is too weak to record at temperatures below 50K but increases to a maximum for temperatures in the 110 to 120K range.

Similar results were obtained under modest pressures which kept the samples within the nominal stability range of phase III, as given in fig.1, although slightly higher temperatures were required at higher pressures to obtain the equivalent spectra. For example, if we interpreted the data of figs. 2 - 4 as showing a phase transition at 110K,

then under 1.6 kbar pressure the similar transition would be found at 122K.

Discussion

Raman data (figs.2 and 3) certainly suggest the possibility of a phase transition at about 110K. Equivalent infrared data, fig.4, are at first sight less convincing. The high frequency side band at about 598 cm^{-1} could be assigned as $295 + 170 + 133$ (all Raman active modes) and its apparent disappearance as the temperature rises above about 120K could simply reflect the rapid broadening of this band. Lower frequency side bands (about 537 cm^{-1} , see fig.4 and 502 cm^{-1}) are less easily explained. There could be contributions from "hot bands" of the form $3\nu_2 - \nu_2$ and $4\nu_2 - 2\nu_2$ for the broad higher temperature features and the small sharp band at 502 cm^{-1} at low temperatures could be a $3 \times 170\text{ cm}^{-1}$ overtone. However, in view of the Raman data, it also seems that a progressive transition centred at about 110K may be causing some subtle change in transition probabilities for these side bands on the infrared $2\nu_6$ band.

If we concentrate on the Raman frequency shift data, and if we assume that the Pippard relationships [8] hold over this region, then we may use the formalism developed in an earlier paper [9] to assess the probable size of the associated thermal anomaly. This gives the expression:-

$$C_p = - \frac{TV}{\gamma_p} \left(\frac{dP}{dT} \right)_\lambda \cdot \frac{1}{v} \cdot \left(\frac{dv}{dT} \right)_p + \text{constant}$$

where $(dP/dT)_\lambda$ is the slope of the transition line (0.13 kbar/K in this case, see earlier), γ_p is the isobaric mode Grüneisen parameter (given by $\gamma_p = -(1/\alpha) (1/v) (dv/dT)_p$) and the other symbols have their usual meaning. The usual form of this relationship is obtained by cancelling the $(1/v) (dv/dT)_p$ term with the same term within γ_p .

However, the form given above is useful because it allows spectroscopic data to be used to predict C_p and its critical exponents [3,9].

Fig.5 shows a plot of $1/v dv/dT$ versus T (i.e. the varying part of the expression for the specific heat C_p). Without good data for the thermal expansion of NH_4I we can not get a good value for γ_p and hence a proper scale for the anomaly in C_p . However, the form of fig.5 is certainly suggestive of a λ -type anomaly and the magnitude of the $1/v(dv/dT)_p$ term is about 0.1 times that found for ν_5 NH_4Cl in reference [9] which would suggest that the thermal anomaly should be easily observed.

It has been reported [10] that quick or repeated cooling and warming of crystals containing NH_4^+ ions can lead to samples with traces of a previous phase trapped as metastable inclusions. This would cause anomalous spectra to be observed and we therefore used several different samples mounted in different ways in experiments with different heating and cooling rates. The reproducibility of the effects reported here leads us to believe that there is a genuine transition at about 110K at zero pressure and about 122K under 1.6 kbar.

A break-down in the long-range order of the orientations of the NH_4^+ ions seems to be involved in this transition. Whether it is simply the onset of random long-range disorder or whether it represents a transition to an incommensurate phase is not yet clear. Our initial efforts to investigate these effects using X-ray diffraction have run into a problem that is hinted at in some of the earlier literature where some doubts were raised about the phase III structure.

Conclusions

Minor changes in the spectra associated with the torsional oscillations of the NH_4^+ ions (ν_6 , $2\nu_6$, $3\nu_6$) in NH_4I have been interpreted in terms

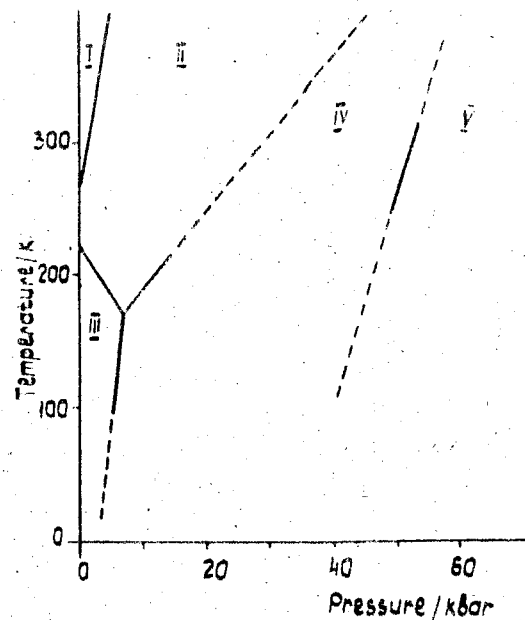


Fig. 1.

Phase diagram for NH_4I . Phase I is a disordered NaCl structure, II is disordered CsCl, III is tetragonal (slightly distorted from a CsCl structure) with anti-parallel ordering, IV is parallel-ordered CsCl and V is as yet unknown. The IV - V boundary is not yet properly defined.

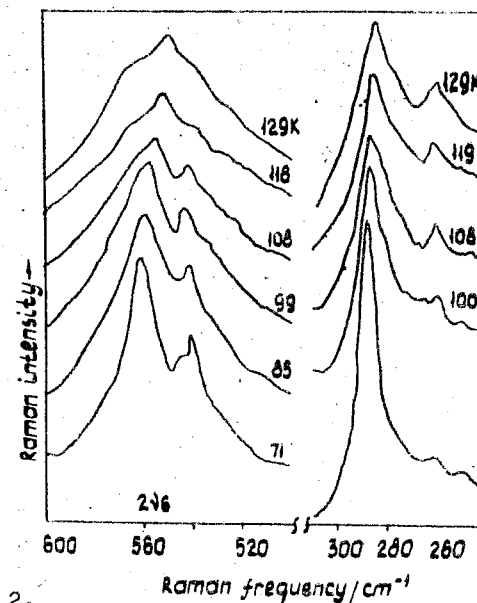


Fig. 2.

Raman spectra of NH_4I in the v_6 and $2v_6$ region recorded under zero pressure at the various indicated temperatures between 71 and 129K.

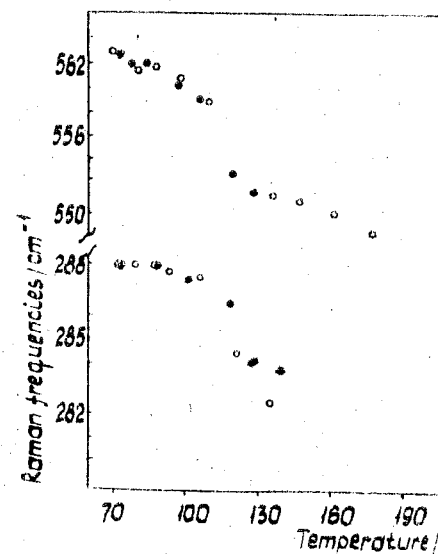


Fig. 3.

Raman peak intensity frequencies in the v_6 and $2v_6$ regions plotted as functions of temperature. (See fig.2 for corresponding spectra.)

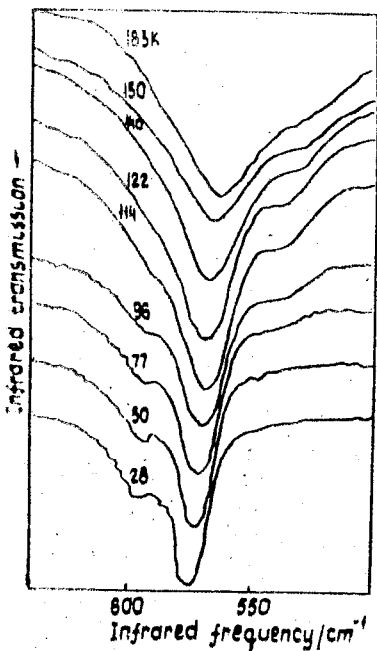
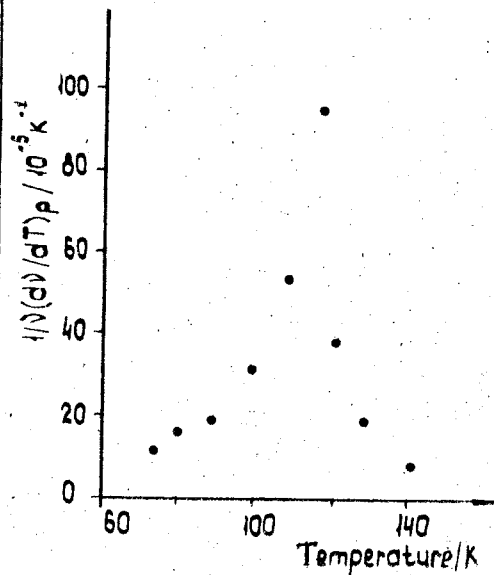


Fig. 4.

Infrared absorption spectra of NH_4I in the vicinity of $2\nu_6$ as a function of the indicated temperatures between 28 and 163K.

Fig. 5.

Plot of $(1/\nu) (d\nu/dT)_p$ versus temperature for $2\nu_6$ of NH_4I .



of a structural change in the crystal at about 110K at zero pressure rising to about 122K at 1.6 kbar. It is believed that this change is essentially a break-down in the long-range order of the orientations of the NH_4^+ ions.

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THE VARIABLE PRESSURE-FIXED TEMPERATURE RAMAN FREQUENCY DATA FOR NH_4Cl

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Abstract

As reported in our previous work, the Raman frequency shifts have been correlated to volume change for the NH_4Cl crystal. We report in this study the Raman frequency data obtained at variable pressures and fixed temperatures close to phase transitions in NH_4Cl . By determining the isothermal mode Grüneisen parameter γ_T for the ν_2 (1708 cm^{-1}) and ν_5 (174 cm^{-1}) modes of NH_4Cl , the Raman frequencies were calculated at various pressures for several fixed temperatures between 250K and 273K for this crystal. Close to phase transitions temperatures, variations of the Raman frequencies of these modes with the pressure indicate the second order (2.8kbar, ~267K) and the tricritical (1.6 kbar, ~257K) type of phase transitions in NH_4Cl . The order-disorder contribution in addition to the volume contribution to the Raman frequency shift has been considered to interpret the phase transitions occurring in this crystal. For comparison purposes, our Raman data requires the frequency measurements performed as a function of pressure at fixed temperatures close to phase transitions in NH_4Cl . When this data is available, in the presence of this work some details in the nature of the phase transitions in this crystal system may become better understood.

Introduction

Ammonium halides which exhibit λ type of phase transitions have been the subject of many investigations. The λ transition of NH_4Cl , is particularly attractive to study since it is weakly first order transition near (~0 kbar), tricritical ~1.6 kbar and is clearly a second order ~2.8 kbar.

In our previous work /1a,b/ we have discussed the conditions under which the frequency shifts can be related to the volume changes across the phase transitions in ammonium halides. By defining the isothermal mode Grüneisen parameter γ_T as

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$$\gamma_T = \frac{1}{\beta} \frac{1}{\nu} \left(\frac{\partial \nu}{\partial P} \right)_T \dots \dots \dots (1)$$

and postulating /1 a,b/ that this remains constant across the transition, one can predict the frequency shifts from the volume change data across the phase. Here $\beta = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$ is the isothermal compressibility.

In this study we have applied this formalism to the NH_4Cl system to investigate its weakly first order, tricritical and second order phase transitions. Some details in our calculations are given below.

Calculations and results

We first correlated volume changes to the frequency shifts as functions of pressure at two fixed temperatures, 250.24K and 273.35K, for NH_4Cl . This data was deduced from observed frequencies which were obtained in our Raman experiments. We performed the experiments by varying temperatures for the fixed pressures of 0 kbar, ~1.6 kbar and ~2.8 kbar as reported previously /1/.

We were then able to predict the Raman frequencies for some other fixed temperatures for the 1st order, tricritical and the 2nd order regions. The variable pressure-fixed temperature frequency data which we obtained is for the ν_2 (1708 cm^{-1}) and ν_5 (174 cm^{-1}) Raman modes of NH_4Cl .

The expression which predicts the frequencies has been obtained from Eq.(1) and modified for the other fixed temperatures as given below:

$$\nu = \Delta_T + A(T) + \nu_I \exp \left[-\gamma_T \ln(V/V_I) \right] \dots \dots (2)$$

where

$$A(T) = a_0 + a_1 (T_I - T)$$

and, $\Delta_T \neq 0$ for $P \geq P_C$ and $\Delta_T = 0$ for $P < P_C$. In this expression, ν_I and V_I are the values of the frequency and volume at ambient conditions. Δ_T is the pressure driven order-disorder contribution to the mode frequency.

For the frequency predictions we determined the isothermal mode Grüneisen parameter γ_T using the extrapolated values of the

length-change data /2/ and of our observed frequencies at $T = 273.35\text{K}$ (well away from phase transitions). This gave us the slope values of $(\partial \ln \nu / \partial P) = 1.45 \times 10^{-7} \text{ bar}^{-1}$ and $\beta = 5.44 \times 10^{-6} \text{ bar}^{-1}$ from which we obtained $\gamma_T = 0.0266$ for the $\nu_2(1708 \text{ cm}^{-1})$ mode.

This value can be compared to $\gamma = 0.022 \pm 0.003$ at $T = 296\text{K}$ for the $\nu_2(1690 \pm 2 \text{ cm}^{-1})$ Raman mode of NH_4Br due to Ebisuzaki /3/.

For the $\nu_5(174 \text{ cm}^{-1})$ Raman mode of NH_4Cl we obtained $\gamma_T = 2.619$ using the same β value and slope value of $(\partial \ln \nu / \partial P)_T = 1.425 \times 10^{-5} \text{ bar}^{-1}$ for this mode. There is considerable scatter in the γ_T values reported in the literature for this mode. Ebisuzaki /4/ obtained 2.4 for the ordered phase and Heyns /5/, Ebisuzaki /4/ and Wang /6/ gave values of 2.1, 3.1 and 3.5 respectively for the disordered phase. We believe that for this mode a single γ_T value should apply for both phases, and that the true value must be close to 2.6.

In relation (2) the coefficients of the temperature dependent term $A(T)$ for both modes (ν_2 and ν_5) which we evaluated for the temperature region $250\text{K} \leq T \leq 275\text{K}$ at zero pressure are tabulated in Table 1.

Using the values given in Table 1, we calculated the frequencies by means of Eq.(2) as functions of pressure at fixed temperatures between $250.24\text{K} \leq T \leq 273.35\text{K}$. The calculated frequencies are given in Table 2.

At $T = 250.24\text{K}$ we were able to determine the order-disorder contribution $\Delta_T = 1.48 \text{ cm}^{-1}$ for the $\nu_5(174 \text{ cm}^{-1})$ mode. So, the frequencies of this mode were predicted for both phases ($P < P_C$ and $P \geq P_C$) at this temperature. In our analysis we did not determine Δ_T for the $\nu_2(1708 \text{ cm}^{-1})$ mode at $T = 250.24\text{K}$.

Discussion

Using a constant γ_T value across the phase change region, we predicted the frequencies as functions of pressure at fixed temperatures. These predictions were made for the disordered phases of the 1st order, tricritical and the 2nd order regions of NH_4Cl . For the ordered phases we were not able to predict the frequencies (except ν_5 at $T = 250.24\text{K}$). This is due to the Δ_T , pressure driven order-disorder contribution to the mode frequency since we could not determine its temperature dependency. To predict the frequencies for the ordered phases ($P \geq P_C$) would require the frequency measurements performed at various pressures for several fixed temperatures.

Table 2. Calculated frequencies for the $\nu_5(174 \text{ cm}^{-1})$ and $\nu_2(1708 \text{ cm}^{-1})$ Raman bands of NH_4Cl . The length-change data were used through the relation (2)

T(K)	250.24	(251.6)	254.31	255.95	257.14	(257.85)	(260.2)	(266.6)	270.13	273.35
P _C (bars)	833.0	989.0	1302.5	1491.8	1633.0	1715.5	2022.0	2836.0	3335.0	...
$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$	$\nu(\text{cm}^{-1})$
P=1	170.45	170.36	170.19	170.09	170.01	169.97	169.82	169.61	169.01	169.01
250	171.14	171.03	170.91	170.76	170.67	170.63	170.48	170.22	170.22	170.22
500	171.82	171.70	171.58	171.42	171.34	171.29	171.12	170.84	170.84	170.84
750	172.49	172.36	172.26	172.10	171.99	171.94	171.77	171.46	171.46	171.46
1000	176.22	172.94	172.66	172.75	172.66	172.58	172.42	172.07	172.07	172.07
1250	177.17	173.42	173.33	173.42	173.33	173.24	173.12	172.67	172.67	172.67
1500	177.96	173.99	173.99	173.99	173.99	173.88	173.75	173.89	173.89	173.89
1750	178.67	174.41	174.41	174.41	174.41	174.34	174.21	174.54	174.54	174.54
2000	179.38	175.14	175.14	175.14	175.14	175.02	174.89	175.14	175.14	175.14
2250	180.03	175.82	175.82	175.82	175.82	175.71	175.58	175.82	175.82	175.82
2500	180.67	176.51	176.51	176.51	176.51	176.40	176.27	176.51	176.51	176.51
2750	181.29	177.20	177.20	177.20	177.20	177.08	176.95	177.20	177.20	177.20
3000	181.91	177.89	177.89	177.89	177.89	177.77	177.64	177.89	177.89	177.89
3250	182.51	178.58	178.58	178.58	178.58	178.46	178.33	178.58	178.58	178.58
P=1	1709.59	1709.55	1709.46	1709.40	1709.36	1709.34	1709.26	1708.82	1708.82	1708.82
250	1709.66	1709.61	1709.53	1709.47	1709.43	1709.40	1709.33	1708.88	1708.88	1708.88
500	1709.73	1709.68	1709.60	1709.54	1709.50	1709.47	1709.39	1708.94	1708.94	1708.94
750	1709.80	1709.75	1709.67	1709.60	1709.56	1709.54	1709.46	1709.01	1709.01	1709.01
1000	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.07	1709.07	1709.07
1250	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.13	1709.13	1709.13
1500	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.25	1709.25	1709.25
1750	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.31	1709.31	1709.31
2000	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.38	1709.38	1709.38
2250	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.44	1709.44	1709.44
2500	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.61	1709.61	1709.61
2750	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.68	1709.68	1709.68
3000	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.75	1709.75	1709.75
3250	1709.80	1709.75	1709.74	1709.67	1709.63	1709.60	1709.52	1709.75	1709.75	1709.75

Table 1. γ_T , Δ_T , a_0 and a_1 values calculated from Eq.(2)

Mode	P, kbar	T,K	γ_T	Δ_T, cm^{-1}	$(\partial \ln \nu / \partial P)_T$ bar^{-1}	a_0	a_1
$\nu_2(1708 \text{ cm}^{-1})$	0	273.35	0.0266	-	1.45×10^{-7}	0.05600	0.02684
$\nu_5(174 \text{ cm}^{-1})$	0	273.35	2.619	1.48 (at 1.425 250.24K)	-8.5885×10^{-5}	-2.3257×10^{-3}	-2.3257×10^{-3}

Our results show that the volume contribution to the mode frequency is associated with the ordering effect, Δ_T , at and below the transition point. This effect can provide a satisfactory explanation for the changes in the character of the phase transitions in the NH_4Cl system. So that we can assume for a second order phase transition that changes in frequency are due to the volume contributions only. When the order-disorder effect appears to contribute to the mode frequency, a 2 nd order phase transition may then be expected to change, i.e. it becomes a nearly 2 nd order, tricritical or a weakly 1 st order.

Conclusions

As we have given for the example of NH_4Cl in the present work, the frequency shifts can be correlated to the volume changes also for some other systems which exhibit nearly 2 nd, multicritical or weakly 1 st order phase transitions.

Such an analysis described in this work may then provide a better understanding for the nature of the phase transitions in those systems.

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PRESSURE AND TEMPERATURE DEPENDENCE OF THE RAMAN ACTIVE PHONONS IN THE LAYERED STRUCTURES $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$.

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Mixed crystals of the transition metal dichalcogenide layered structures $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$ have been grown by the vapour (iodine) transport method for $x = 0.0, 0.1, 0.25, 0.5, 0.75, 0.9$ and 1.0 . X-ray diffraction was used to verify their D_{3d}^3 space group symmetry. The Raman spectrum consists of two modes (E_g and A_{1g}) whose room-temperature frequencies, for HfS_2 , are 261 and 337 cm^{-1} respectively. Also present in the spectrum is a symmetry forbidden mode, observed at 325 cm^{-1} for HfS_2 , which has been attributed to an interaction with a close-lying infra-red active mode. We have measured the change of phonon frequency with hydrostatic pressure (in a diamond anvil cell) for these three phonons, up to 45 kbars , where the crystals cracked. The Gruneisen parameter has been determined. We have also determined the temperature dependence of the phonon frequencies (10 K to 300 K) at $p = 0 \text{ kbars}$. From the combined temperature and pressure variations of the frequencies, we have determined the intrinsic (volume) and extrinsic (interaction) contributions to the frequency shifts. These results and their relevance, to the symmetry forbidden mode, will be discussed.

INTRODUCTION

Mixed crystals are being studied recently for a number of reasons. From a practical point of view, one hopes to "tune in" to a desired physical property simply by changing the chemical composition. At a more abstract level, they offer the possibility of studying order-disorder. These are just two examples. We have chosen to study the systems $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$ because they are fairly simple. First of all, they are layered structures; secondly, the unit cell at the two limits $x = 0$ and $x = 1$ spans one layer and contains one formula unit (1). In this work, we report on the pressure (for the first time) and temperature dependence of the Raman spectrum. In mixed crystals, the phonons are described as "single mode" in which case the frequency varies linearly with the composition, or as "two mode" in which

case there is a discontinuity (2). It is of interest to see how pressure and temperature affect this behaviour. In the case of HfS_2 and ZrS_2 , one has observed in the Raman, an infra-red active mode whose presence has been attributed to long range Coulomb forces (3). Combined studies of pressure and temperature allows one to separate the role played by volume and that played by interactions. Thus, in this instance, the relationship among Coulomb forces, phonon-phonon interaction and chemical composition, if any, can be determined.

EXPERIMENTAL

The crystals were grown by the iodine transport method (1). X-ray diffraction patterns of the samples were obtained, from which the space group of the structure was confirmed.

The Raman spectrum was obtained with the use of an argon ion laser and a Jobin Yvon double monochromator equipped with proper electronics. The high pressure spectra were obtained in a diamond anvil cell (3), in which the compressing fluid was ethanol-methanol. The ruby fluorescence was used to calibrate the pressure. We found that the samples cracked at about 40 kbars , which limited our high pressure limit. The temperature measurements were made in a CTI Cryogenics refrigerator, capable of reaching about 10 K .

GROUP THEORY ANALYSIS

The layered structures HfS_2 and ZrS_2 belong to the space group D_{3d}^3 . The unit cell spans across one layer only and contains one formula unit. The irreducible representations at the Γ points are (4)

$$\Gamma = A_{1g} + 2E_u + E_g + 2A_{2u}$$

of which $1E_u$ and $1A_{2u}$ are acoustic. The Raman spectrum should thus consist of just two peaks. The group theory analysis does not consider long range

Coulomb forces present when the atoms are charged. In this case, the infra-red active LO-TO modes can appear in Raman. For the structures studied here, the A_{2u} (LO) mode has been observed in the Raman spectrum, and it has been called a "hybrid" mode (5). Its strong Raman signal has been attributed to a resonance with the A_{1g} mode. We have also observed, for ZrS_2 , the E_u (LO) mode in the Raman, but it is superposed with the A_{1g} mode, and could not be studied as a function of temperature and pressure.

RESULTS

A typical Raman spectrum of HfS_2 at 18K, using the 5145 Å excitation is shown in Fig. 1. Clearly shown are the E_g and A_{1g} modes and also the hybrid mode, which is known, by polarization experiments to be an A_{2u} (LO) mode. The evolution of the Raman spectrum as a function of x shows that, as one approaches ZrS_2 , the hybrid mode increases in intensity, and at the same time, a second hybrid mode, or a fourth peak, has appeared. By comparison with infra-red data, the fourth peak is E_u (LO).

The frequency dependence of the modes as a function of x is given in Fig. 2. We have followed the pressure dependence of the modes, but show only the case of $x = 0.25$ in Fig. 3. However, all the quantities measured are given in Table.

The temperature dependence of the modes is presented in Fig. 4. The phonon frequencies are temperature independent for $x < 0.5$, but at $x = 1$, the frequencies are measurably different than those at $x = 0$. The temperature parameters are added to Table.

DISCUSSION

a) The dependence of the frequencies on concentration

The Raman frequencies of HfS_2 are in general higher than those of ZrS_2 . The variation with x is quite linear. Since the reduced mass in the

PRESSURE AND TEMPERATURE DEPENDENCE OF THE PHONONS IN THE MIXED CRYSTALS $Hf_{1-x}Zr_xS_2$

x		ν (cm^{-1})	γ	$(\frac{d\nu}{dT})$ ($\text{cm}^{-1} \text{K}^{-1}$)	$(\frac{\partial \nu}{\partial P})_T$ $\text{cm}^{-1} \text{kbar}^{-1}$	$-\frac{\alpha}{\beta} (\frac{\partial \nu}{\partial P})_T$	$(\frac{\partial \nu}{\partial T})_P$
0.0	A_{1g}	337	0.54	~ 0	+ 0.45	- 0.02	+ 0.02
	A_{2u}	325	—	~ 0	—	—	—
	E_g	261	0.37	~ 0	+ 0.24	- 0.01	+ 0.02
0.1	A_{1g}	336	0.58	~ 0	+ 0.48	- 0.02	+ 0.02
	E_{2u}	324	0.41	~ 0	+ 0.33	- 0.02	+ 0.02
	E_g	260	0.28	~ 0	+ 0.18	- 0.01	+ 0.01
0.25	A_{1g}	335	0.61	~ 0	+ 0.50	- 0.02	+ 0.01
	A_{2u}	323	0.52	~ 0	+ 0.41	- 0.02	+ 0.02
	E_g	258	0.49	~ 0	+ 0.31	- 0.01	+ 0.01
0.5	A_{1g}	335	0.61	+ 0.008	+ 0.50	- 0.02	+ 0.03
	A_{2u}	322	0.50	~ 0	+ 0.40	- 0.02	+ 0.02
	E_g	256	—	~ 0.013	—	—	—
0.75	A_{1g}	334	0.56	+ 0.01	+ 0.40	- 0.02	+ 0.03
	E_{2u}	321	0.57	~ 0	+ 0.45	- 0.02	+ 0.02
	E_g	254	—	~ 0	—	—	—
0.9	A_{1g}	334	0.54	+ 0.01	+ 0.44	- 0.02	+ 0.03
	E_{2u}	321	0.54	0	+ 0.43	- 0.02	+ 0.03
	E_g	252	—	~ 0.01	—	—	—
1.0	A_{1g}	333	0.54	+ 0.03	+ 0.44	- 0.02	+ 0.05
	A_{2u}	320	0.55	0	+ 0.43	- 0.02	+ 0.02
	E_g	250	—	~ 0.01	—	—	—

halfnium compound is larger than that of zirconium, our results indicate that the restoring force is larger in the former compound. This conclusion is plausible from the following considerations: (i) X-ray data indicate that the unit cell in both substances is practically the same (6); for example the distance between the sulfur atom and the metallic atom is 2.56 Å in ZrS_2 but only 2.57 Å in HfS_2 (6). (ii) We know that halfnium has 28 electrons more than zirconium. In other words, by varying the composition from Zr to Hf, one is adding more electrons in practically the same volume, thus increasing the bond strength.

Mixed crystals are characterized by single mode or two mode behaviour. Let us remark that we observe single mode phonons throughout the pressure and temperature ranges studied. We would like to suggest the following explanation as to why single mode behaviour was observed. In transition metals, d electrons form part of inner atomic core. Moreover, the atomic size is not affected that much, which explains why the interatomic distances are practically the same in ZrS_2 and HfS_2 . Thus, with the electronic structure at the periphery of the metal atom hardly x sensitive, and with the interatomic distance also hardly x sensitive, averaging processes are expected to be smooth.

We wish to add that in the eigenvectors of the Raman active modes, the metal atoms are stationary (4).

b) The intensity of the hybrid mode

The Raman spectrum of these compounds is predicted to have just two peaks, the E_g and the A_{1g} modes. Yet, the A_{2u} (LO) mode is weakly observed in HfS_2 and it increases in strength to the point that it is almost as intense as the A_{1g} mode in ZrS_2 . The intensity of this phonon, which should appear only in the infra-red, depends on the coupling to the close-lying A_{1g} mode. Our results indicate that the coupling between these two phonons varies in a smooth way from HfS_2 to ZrS_2 , with the coupling strongest in the latter compound.

We have observed the hybrid A_{2u} (LO) mode for all values of x studied, which confirms the interpretation of the peak as an intrinsic mode, and not one due to impurities, nor faults.

c) Pressure dependence of the Raman spectrum

The pressure dependence of a phonon is best expressed by the Gruneisen parameter

$$\gamma = \frac{1}{\beta} \frac{1}{\omega} \frac{d\omega}{dP}$$

where β is the compressibility. Flack (7) has measured, for HfS_2 , $\beta_{\perp}$ to the layers to be $2.8 \times 10^{-4} \text{ kbar}^{-1}$ and $\beta_{\parallel}$ to be $19 \times 10^{-4} \text{ kbar}^{-1}$. Thus γ is quite accurately known for HfS_2 . However β is unknown for the other values of x. Assuming that β is x independent, we give the various γ_i in Table I. In general, β is inversely proportional to the density, and since HfS_2 is denser than ZrS_2 , we expect that a more realistic value of γ for ZrS_2 is smaller than that given in Table.

d) Temperature dependence of the Raman spectrum

It is well known that temperature variations affect the volume and the interactions. Writing $w = w(T, V)$, then

$$\frac{d\omega}{dT} = \left(\frac{\partial \omega}{\partial T} \right)_V - \frac{\alpha}{\beta} \left(\frac{\partial \omega}{\partial P} \right)_T$$

The first term gives the contributions due to the interactions while the second, due to the volume. We remark that $\frac{d\omega}{dT} = 0$ for all frequencies and for $x < 0.5$ (Fig. 4). We interpret this to mean that the two effects have opposite sign and that they cancel in the HfS_2 limit. However, as x tends to 1, i.e. the ZrS_2 limit, $\frac{d\omega}{dT}$ is not negligible. One clearly sees that in ZrS_2 , the A_{2u} (LO) and A_{1g} modes are almost identical at $T = 0$, but they repel each other at high temperatures. Since the pressure does not change their relative energy difference (Table), then it is the phonon-phonon interaction which increases more significantly than the volume contribution, as x tends to 1.

This argument can be quantified somewhat by calculating the two contributions, and this is done in Table. For β , we have used the measured HfS_2 value. α is unknown, not even for HfS_2 , but we have used the value of $114 \times 10^{-6} \text{ K}^{-1}$ which has been measured for MoS_2 (7). We see from Table that the volume contribution is hardly dependent on x , but that the phonon-phonon interaction increases as x increases.

We have remarked that the bands are weaker in ZrS_2 compared to HfS_2 . We now find that the anharmonic terms are larger in ZrS_2 compared to HfS_2 .

SUMMARY AND CONCLUSIONS

The phonon frequencies in the mixed layered structures $\text{Hf}_{1-x}\text{Zr}_x\text{S}_2$ follow the single mode behaviour. The restoring force is largest in the $x = 0$ limit. The intensity of the A_{2u} (LO) mode observed in Raman, also increases smoothly as a function of x .

From the combined study of the pressure and temperature dependence of the phonon frequencies, we deduce that the volume effect and the interaction effect cancel in the $x = 0$ limit, but that the interaction effect takes over in a smooth way from $x = 0$ to $x = 1$.

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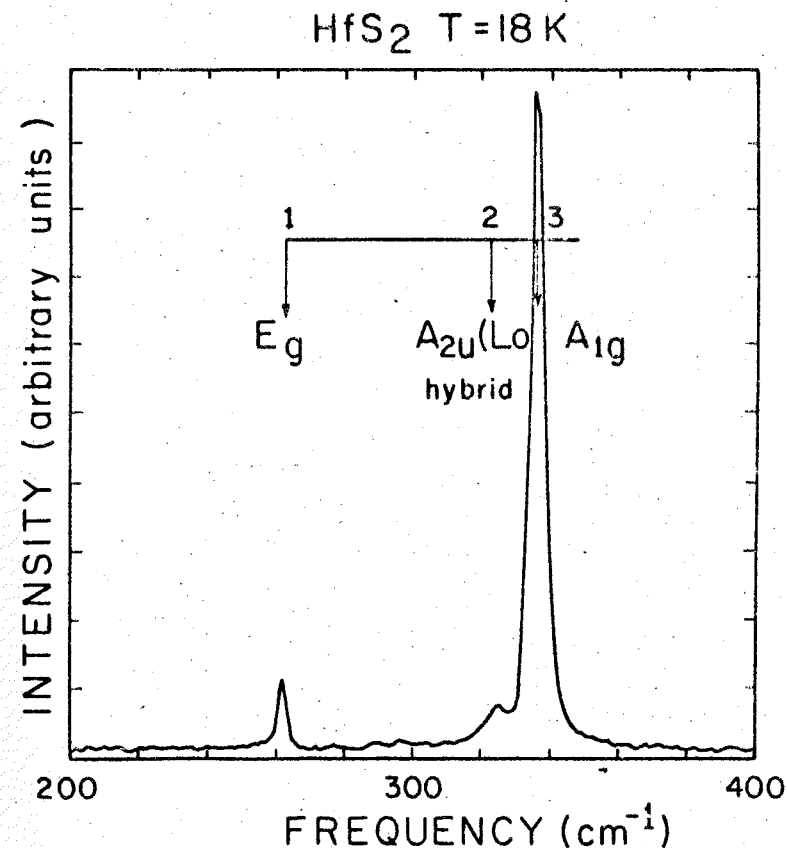


Fig.1,a.

Fig. 1. The Raman spectrum at 18K of HfS_2 (a), $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{S}_2$ (b), ZrS_2 (c), excited with the 5145 Å line. The parameters associated with the peaks labelled 1, 2, 3 and 4 are given in Table. (см. продолжения рис.1 на с. 356,357).

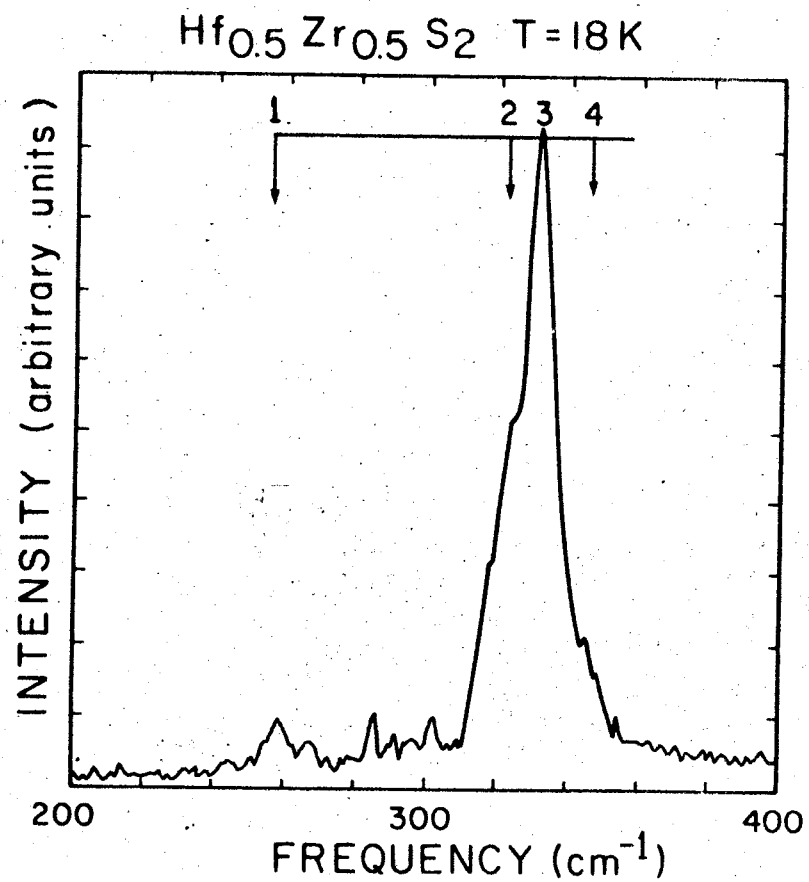


Fig.1,b.

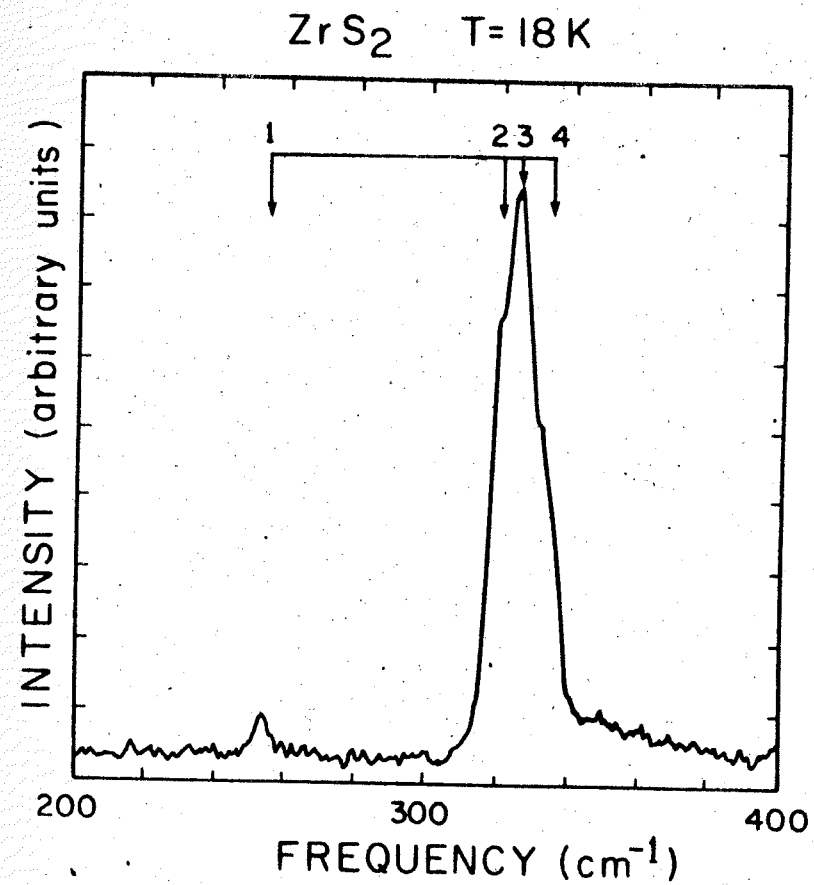


Fig.1,c.

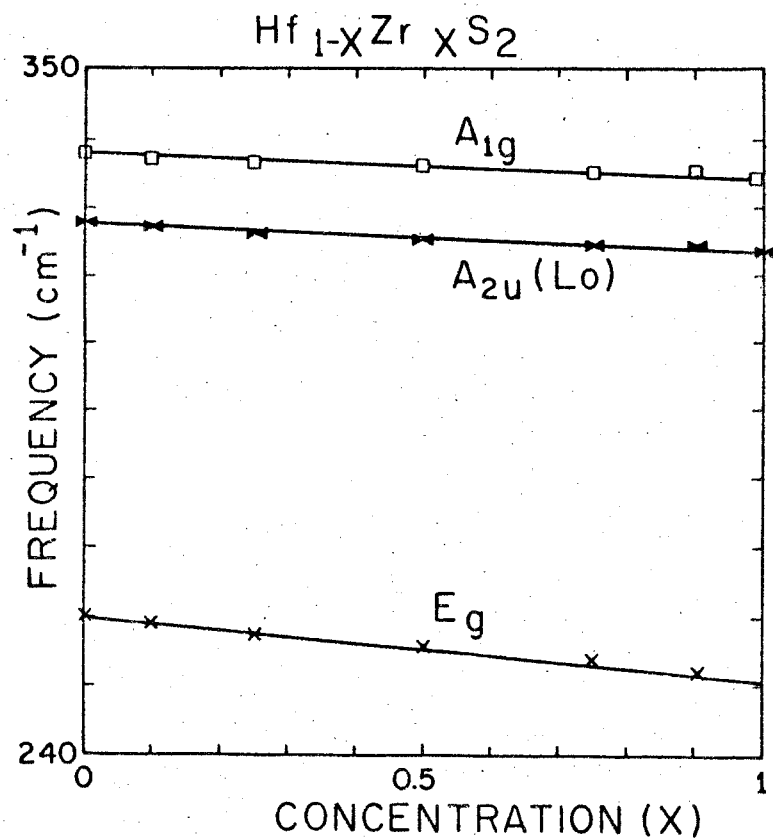


Fig. 2. The dependence of the phonon frequencies on the composition x .

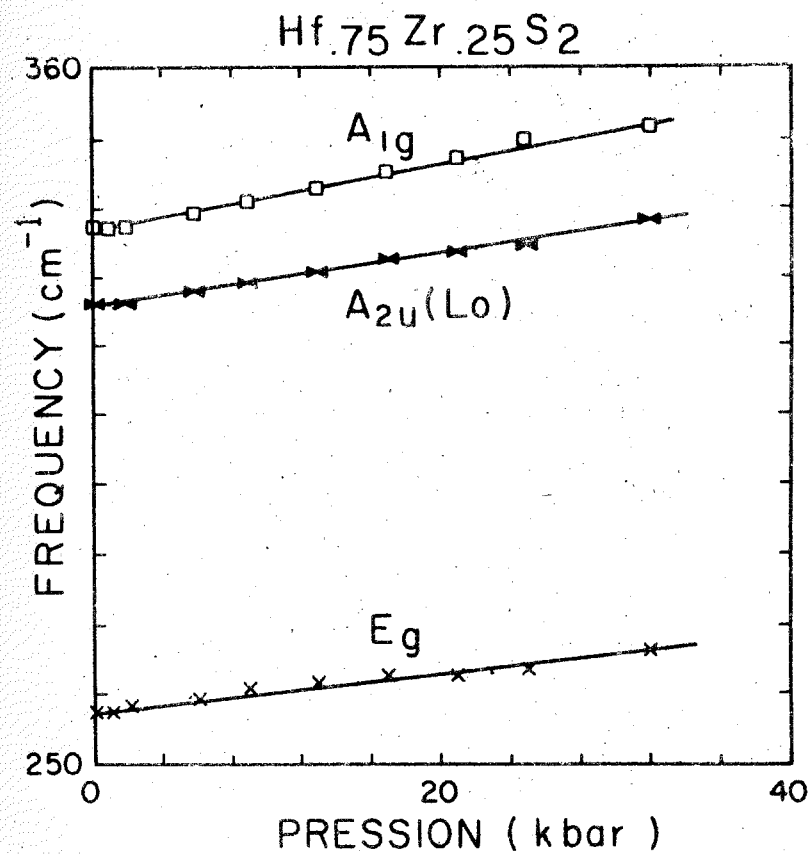


Fig. 3. The pressure dependence of the compound $\text{Hf}_{0.75}\text{Zr}_{0.25}\text{S}_2$.

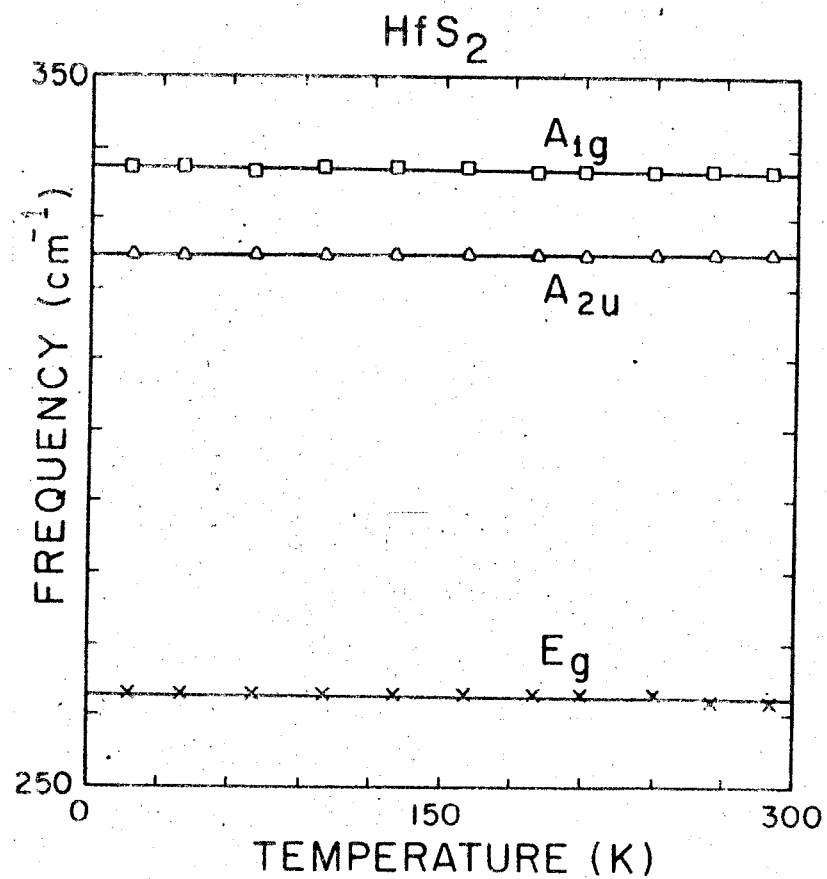


Fig. 4, a.

Fig. 4. The temperature dependence of the HfS_2 (a), $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{S}_2$ (b) and ZrS_2 (c) phonons. (см. продолжения рис. 4 на с. 361, 362).

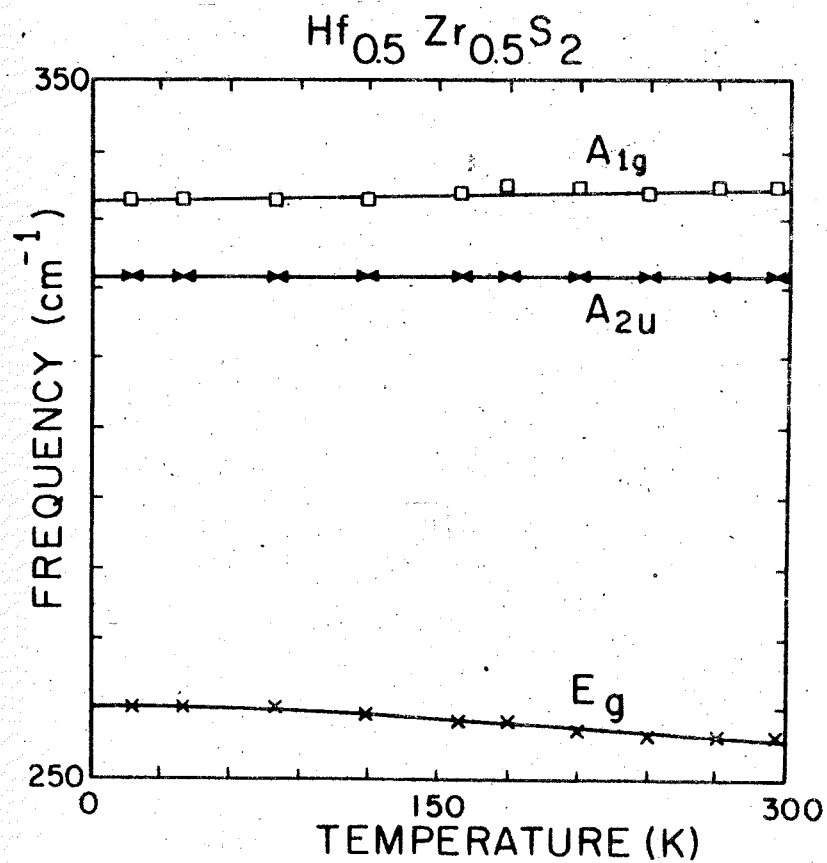


Fig. 4, b.

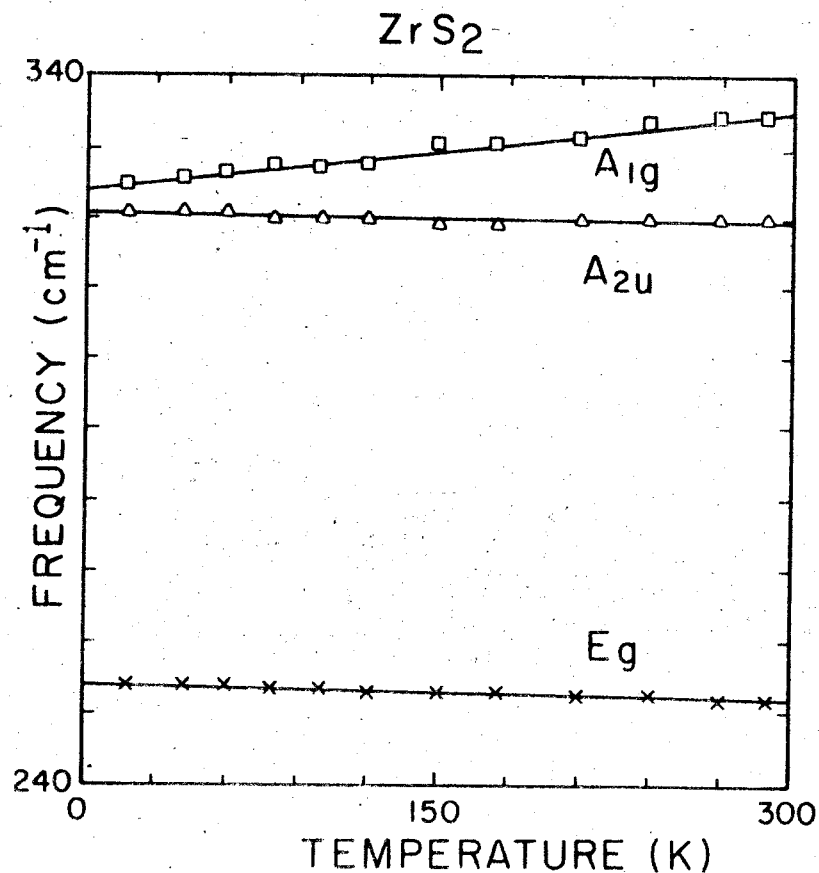


Fig.4,c.

POSSIBILITIES OF EPR SPECTROSCOPY UNDER HIGH PRESSURES

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A combination of extremal experiment conditions carried out in a wide range of temperatures and pressures with informative and fine method of investigation, which is the electron paramagnetic resonance, allows to obtain the unique information on interactions in solids.

The EPR is conventionally used for investigation of such objects as dielectric crystals containing paramagnetic ions as impurities. The study of their energy spectrum, dynamic characteristics and especially spin-spin interactions is of great interest for the solid state physics.

Though the EPR is a very popular method the investigations at high pressure have not been widely recognized up to now. This is due to the fear of technical difficulties. But we think they can be overcome by any laboratory provided with equipment for material treatment.

Not going into details of the experimental technique we present new data obtained in the high pressure experiments made on some rare-earth ions introduced into ethylsulphate (ETS). What was to be expected in this kind of experiments? Uniform compression leads to the decrease of interionic separations in a solid which changes crystal field magnitude. This results in the change of the energy spectrum consisting in increase or decrease of energy separations and ground state magnetic moment.

For example, in Ce^{3+} ion in EuETS and YETS there is big increase of energy gap between two lower doublets at a rate of $\partial\Delta/\partial P = 12 \text{ cm}^{-1}/\text{GPa}$ [1]. In LaETS at $P \sim 80 \text{ MPa}$ in the same ion there is an intersection of Stark sublevels of multiplet $^2F_{5/2}$ and the ground state is $|\pm 5/2\rangle$ rather than the initial one $|\pm 1/2\rangle$ which results in an increase of the magnetic moment of the ground state by a factor of 4.

Investigations of the EPR spectrum under high pressures make it possible to establish some relationships between crystal field parameters. Increase of $Q_{||}$ under pressure with simultaneous decrease of $Q_{\perp}$ of Nd^{3+} ion allows us to estimate change in the ratio of the crystal field parameters B_6^b/B_6^0 [2]. It was shown that the crystal field theory cannot explain changes in the EPR spectrum of non-Kramers Tb^{3+} ion.

Experiments performed on Gd^{3+} ions in LaETS and $LaCl_3 \cdot 6H_2O$ showed that application of high pressures is very perspective for understanding mechanisms of ground state splitting of S-ions.

Measurements of spin-lattice relaxation times at high pressures performed for the first time showed that changes are of four orders of magnitude /1/. This is most vividly manifested in the Orbach processes where the excited level energy changes at a rate of $10-20 \text{ cm}^{-1}/\text{GPa}$. So principally new possibilities for investigation of relaxation processes appear which differ from conventional ones taking only temperature and field dependences into account.

Since at pressure increase the excited level seems to move along the phonon spectrum of the crystal it is possible to estimate applicability of the Debye model to the description of the Orbach processes. Experimental Δ^{-3} -dependence (Δ - is the excited state energy) of Ce^{3+} ion relaxation rate in LaETS confirms applicability of the Debye model. Different power dependence of Ce^{3+} ion relaxation rate in lanthanum-magnesium nitrate on the magnitude of Δ gives evidence of different distribution of phonon density.

It is shown that using external pressure for changing energy level systems of two different ions in the same lattice one can enhance cross-relaxation processes /5/. Similar effects were observed for the spin systems of Co^{2+} ions transmitting energy to quickly relaxing Ni^{2+} ions and for Nd^{3+} ions connected with Ce^{3+} and Pr^{3+} ions /2/. Moreover pressure considerably decreases anisotropy of relaxation times in combination process of Nd^{3+} ions revealed in LaETS /2/.

Uniform compression is a new tool for investigation of spin-spin interaction between paramagnetic ions. This method has positive advantage over the homological series method since it provides the possibility of smooth change of the distance between interacting ions and also due to the fact that it can be applied to the investigation of any crystals even those which do not form isomorphic series.

Investigation of interaction between Ce^{3+} ions in ethylsulphates yielded dependence of the interaction energy on the energetic distance from the excited level. This dependence showed the exchange through the field of phonons to be the main interaction mechanism /6/.

Different pressure dependences of competing mechanisms - magnetic dipole-dipole and exchange through the field of phonons

- changes the sign of anisotropic part of interaction between ion pairs at $P \sim 0.2 \text{ GPa}$.

Reconstructing the energy spectrum of excited states one can alter the nature of spin-spin interaction in $CeETS$ /7/ which, in its turn, leads to the change in the character of magnetic ordering of this crystal. If up to 0.5 GPa the ordering is antiferromagnetic then at higher pressure the crystal becomes ferromagnetic with the ordering temperature increasing at pressure increase.

Application of high pressure for the investigation of spin-spin interaction of Ce^{3+} ion pair in ethylsulphate lattice /8/ made it possible to solve the main experimental task, namely, to separate the contributions of various interaction mechanisms and to prove that the main contribution to non-dipole part is made by isotropic exchange and to determine dependence of Coulomb exchange on the distance between the rare-earth ions. Increase of the exchange in NdETS crystals leads to decrease of effective interaction which should reduce ferromagnetic ordering temperature.

It should be emphasized that obtaining these data for rare-earth ions is at present unique. It became possible only due to application of new extremal conditions caused by high pressure.

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DETERMINATION OF CHARGE STATE OF DEFECTS IN SEMICONDUCTORS BY STUDYING PHOTOLUMINESCENCE AT UNIAXIAL STRESS

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The photoluminescence (PL) resulting from the capture of a free carrier by a neutral defect which binds more than one carrier has some peculiarities. They are caused by the fact that in the final state there remains one or several carriers at the defect. For such a defect the shift of the position of the PL band maximum produced by the uniaxial pressure P depends on the deformation potential constants (DPC) of both states - the initial and the final - whereas for a defect binding one carrier this shift is related to DPC of the initial state only. On the other hand, some other characteristics of the impurity PL at uniaxial pressure (e.g. the polarization) usually are related exclusively to the splitting of the initial state energy level and therefore determined by its DPC.

Thus, it is possible to determine the charge state of the defect by comparing various characteristics of impurity PL at uniaxial pressure.

This is demonstrated for the acceptor center Cu_{Ga} in GaAs responsible for the PL band with a maximum at 1.36 eV. The results of the magneto-optic study suggest that before light emission Cu_{Ga} binds two holes /1/. However, some other investigations lead to the hypothesis of the presence of only one hole at the center /2/.

We measured DPC of the center in the initial state and the PL band maximum shift due to $P \parallel [100]$. The analysis of the experimental results was based on the pressure dependence of the center adiabatic potential (AP) evaluated in /3/.

The interaction of the holes bound at the center with the crystal deformation at $P \parallel [100]$ is determined by DPC A_T and B_T /3/.

B_T which is responsible for the splitting of the orientationally degenerate energy level of the light-emitting center due to $P \parallel [100]$ was determined from the pressure dependence of the integral PL polarization ratio $r_0 = I_{\parallel} / I_{\perp}$ ($I_{\parallel}, I_{\perp}$ are the intensities of light integrated over the PL band for orientations of the electric vector of the light wave parallel and perpendicular to P). The interaction of the holes at Cu_{Ga} can be neglected /3/ and then

if the contribution of quadratic terms to AP is essential,

$$r_0 = [4 \exp(\frac{3}{2}x) + 2] / [\exp(\frac{3}{2}x) + 5] \quad (1)$$

Here, $x = B_T \epsilon_i / kT$, $\epsilon_i = -P / (C_{II} - C_{I2})$, $C_{II} = 12.26 \cdot 10^{10}$, $C_{I2} = 5.71 \cdot 10^{10} \text{ N/m}^2$ are the elastic constants of GaAs.

As can be seen from Fig.1 Eq.(1) fits well to the experimental data in the whole range of r_0 values with the adjustable parameter $B_T = -(3.1 \pm 0.1) \text{ eV}$.

The constant related to A_T was determined from the temperature dependence of Hall constant R at the hydrostatic pressure P_H . For the center which can localize two holes it is necessary to consider two following situations: a) two holes are at the acceptor, b) a hole is at the acceptor and a hole in the v-zone. This consideration for the partially compensated p-semiconductor leads to the following expression /3/:

$$\partial [\ln(RT^{3/2})] / \partial P = -3(A_T - a_T^k - A_v) / (C_{II} + 2C_{I2}) \quad (2)$$

Here, a_T^k is DPC for the final state with one hole, A_v is DPC for v-band. From Eq.(2) and the experimental dependences $R(T)$ we found $A_T - a_T^k = -(8.6 \pm 0.1) \text{ eV}$. If the investigated center could bind only one hole it would be necessary to set $a_T^k = 0$ in Eq.(2) and in that case the value $-(8.6 \pm 0.1) \text{ eV}$ would relate to A_T .

At $P \parallel [100]$ the PL peak position for the center binding two holes before the light emission is determined by following expression, providing the splitting of the orientationally degenerate center level exceeds kT and is defined by equation from /3/:

$$\hbar\omega_m = \hbar\omega_m(0) - \frac{A_T - a_T^k}{C_{II} + 2C_{I2}} P + \frac{B_T - b_T^k}{C_{II} - C_{I2}} P \quad (3)$$

Here, b_T^k is DPC of the final state.

For Eq.(3) to fit well to the observed value $\partial(\hbar\omega_m) / \partial P = 0 - 2.5 \text{ meV/GPa}$ (Fig.2), it is necessary to set $b_T^k = -(0.3 \pm 0.2) \text{ eV}$ which seems reasonable. On the other hand, for the center binding one hole $a_T^k = b_T^k = 0$ and the substitution of the values of A_T and B_T into Eq.(3) yields $\partial(\hbar\omega_m) / \partial P = -(11 \pm 1) \text{ meV/GPa}$ which differs considerably from the measured value.

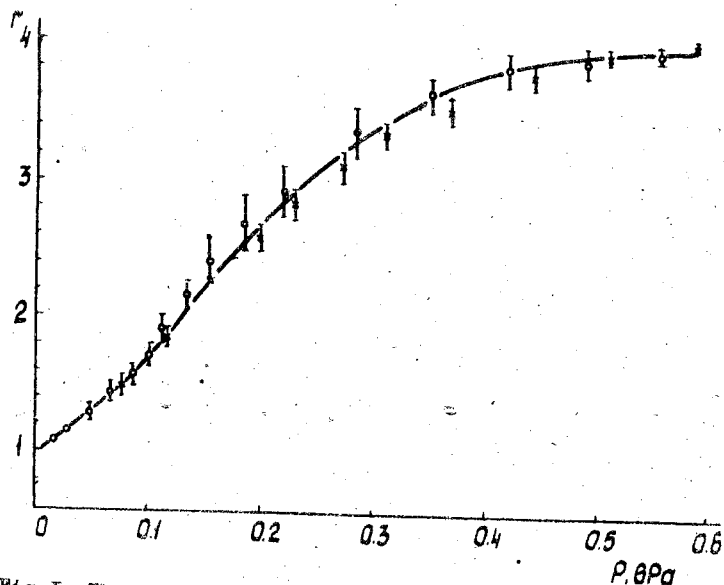


Fig. 1. The dependence of the integral polarization ratio on the pressure along the [100] axis; points - experimental data at 77 K; solid curves - results of evaluation (Eq. (1)).

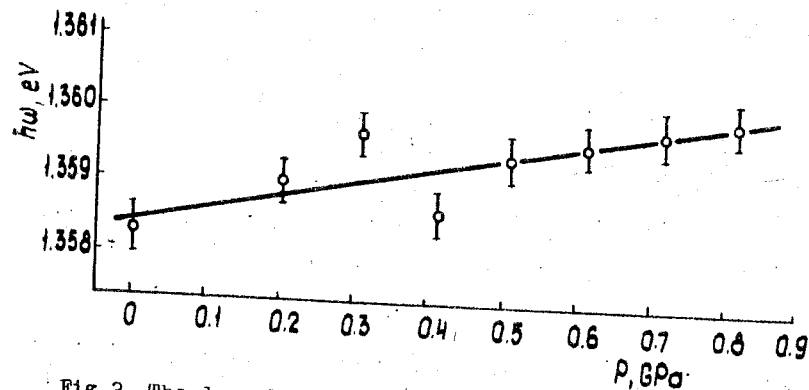


Fig. 2. The dependence of PL band maximum position on the value of the pressure along the [100] axis at ~2 K.

It follows from these results that Cu_{Ga} in GaAs binds two holes before the light emission and not one.

It should also be noted that DPC of this center exceed considerably the corresponding DPC for v-band and centers binding one hole. This supports in addition our conclusion of the center Cu_{Ga} in GaAs to bind two holes in the light-emitting state.

Thus, this work demonstrates that it is possible to determine the charge state of a light-emitting defect in a semiconductor from various characteristics of the impurity PL at uniaxial pressure.

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NUCLEAR MAGNETIC RESONANCE IN ALLOYS AND COMPOUNDS: PRESSURE AND TEMPERATURE EFFECT

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In alloys and compounds of magnetic atoms with nonmagnetic ones the electron system of the latter exerts considerable influence on the magnetic properties of solids. A good example is Fe-Y compounds. Y-content variation alters the magnetic moment of Fe-atoms in these alloys as much as 25%. This effect is well known, but the mechanism of it needs investigation. Two variants are possible: a) fill-in of localized 3-d states of Fe-atoms takes place; b) valence electrons of Y form a zone of itinerant electrons. To investigate it we propose NMR-methods and usage of high pressure. In fact, itinerant electrons external in position in relation to localized ones would be the first "to response" to all-side compression of a specimen by giving another pattern of change and spin density. Below we discuss application of these ideas to Y_xFe_y and other alloys, which are Fe-based.

Local magnetic fields at the nuclei of nonmagnetic Y-ions are due to influence of magnetic Fe-atoms. If external Y-electrons go over to localized 3d-states, then pressure load would result in identical change of local fields at the Y^{89} and Fe^{57} nuclei. But if these electrons are itinerant, then this change would be different. Studies of NMR spectra of Y-Fe shows that all-side compression results in decrease of the magnetic moment of Fe and increase of the local field at the Y^{89} nuclei, and thus we concluded that electrons inducing fields at the Y^{89} nuclei and forming the magnetic moment of Fe-atoms are itinerant ones. Comparison of these results with magnetic measurement data from literature for Y-compounds gives basis for the following pattern of spin electron density distribution in these solids: 1) Fe magnetic moment is difference of two contributions: $\mu_{Fe} = \mu^0 - \mu^I$, where μ^0 is the constant value for the whole series of compounds YFe_2 , YFe_3 , Y_6Fe_{23} , Y_2Fe_{17} , and μ^I is the moment connected with polarized itinerant electrons; 2) local field at the Y^{89} nuclei is proportional to the magnetic contribution μ^I .

NMR and pressure studies make possible quantitative estimations of μ^0 and μ^I contributions to the Fe magnetic moment. This is essential for comprehension of it in alloys.

Let us suppose that Fe magnetic moment in YFe_2 is a superposition of localized and itinerant contributions

$$\mu_{Fe} = \mu^{loc} + \mu^{it} \quad (1)$$

Let us assume that the field at the Fe^{57} nuclei is proportional to μ_{Fe} , and that at the Y^{89} nuclei to μ^{it} respectively, i.e.

$$H^{Fe} \sim A^{Fe} \mu_{Fe} \quad (2)$$

$$H^Y \sim A^Y \mu^{it} \quad (3)$$

Here A^{Fe} and A^Y are the hyperfine interaction (HFI) parameters for Fe^{57} and Y^{89} nuclei respectively. Since under all-side compression variation of fields H^{Fe} and H^Y is contrary, in (1) we must use the sign "-".

Below we write down expressions for variation of these values under pressure

$$\partial \ln \mu_{Fe} / \partial \ln Y = -(\mu^{it} / \mu_{Fe}) \partial \ln \mu^{it} / \partial \ln Y \quad (4)$$

$$\partial \ln H^{Fe} / \partial \ln Y = \partial \ln A^{Fe} / \partial \ln Y + \partial \ln \mu_{Fe} / \partial \ln Y \quad (5)$$

$$\partial \ln H^Y / \partial \ln Y = \partial \ln A^Y / \partial \ln Y + \partial \ln \mu^{it} / \partial \ln Y \quad (6)$$

We see that if we know variation of fields at the Fe and Y nuclei under pressure we can estimate the value of μ^{it} , if we know the corresponding variation of HFI-parameters A^{Fe} and A^Y .

Comparison of results from [1,2] indicates that the parameter A^{Fe} in YFe_2 within the experimental error does not vary at the lattice compression, i.e., $\partial \ln A^{Fe} / \partial \ln Y \approx 0$. On the contrary the HFI parameter for Y^{89} nuclei varies, and $\partial \ln A^Y / \partial \ln Y \approx +0.56/3\%$.

Using experimental data: $\partial \ln H^{Fe} / \partial \ln Y = +0.85 \pm 0.1$, $\partial \ln H^Y / \partial \ln Y = -1.1 \pm 0.1$, $\mu_{Fe} = 1.45 \mu_B$, from (4) one can find that $\mu^{it} = (0.75 \pm 0.2) \mu_B$. In accordance with (1) for the localized contribution of Fe magnetic moment we have $\mu^{loc} = (2.2 \pm 0.2) \mu_B$. This value is close to the magnetic moment $\mu^0 = 2 \mu_B$ found by comparison of magnetic parameters of Y_xFe_y compounds with different stoichiometry [4]. Quantitative agreement witnesses that model approximation used in the analysis is not too rough.

NMR and pressure studies permit also to consider temperature

effect. There are quite a few papers the authors of which obtained different temperature-dependent curves for local fields at the nuclei of nonmagnetic ions and at the nuclei of magnetic atoms of the matrix. In particular, such effect was stated for YFe_2 and for Fe-Al, Fe-Ga alloys. We showed that this difference can be removed by reduction the temperature-dependent curves to the constant volume.

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EFFECT OF FORMATION CONDITIONS ON SYNTHETIC DIAMOND LUMINESCENCE

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Experiments on diamond crystallization in metal-carbon systems at $P = 5 + 6$ GPa, $T = 1500 + 1700$ K have been carried out in a low gradient cubic cell on a high-pressure "split-sphere" apparatus. Using both the method of synthesis (1) and temperature drop (2) a wide range of growth rates from $V = 10^{-1}$ down 10^{-4} mm/min was realized, diamond crystallization time being changed from $t \approx 10$ to $6 \cdot 10^2$ min, correspondingly. The system Ni-Mn-C was used as a basic one, sometimes some amounts of B, Ti, Al were added into charge or proportion of components Ni and Mn was changed.

A wide set of methods such as ESR, optical spectroscopy (absorption in UV, visible, IR regions, photo and X-rays excited luminescence, thermoluminescence) as well as electrical conductivity were used to study the diamond crystals.

In all studied crystals the already known defect centers such as: single nitrogen atoms, exchange-coupled complexes of nitrogen atoms divided by several carbon atoms (ESR); D-centers (the suggested model of boron-nitrogen complex) in IR absorption were found. In some crystals paramagnetic nickel centers were observed at $T = 80$ K. Specially nonactivated crystals with the resistance more than 10^{10} Ohm were referred to the type Ib.

The main difference of the samples obtained by temperature drop in respect to synthesized ones is more than an order lower nitrogen and nickel impurity concentration /1/, which is due to a lower rate of crystallization.

Results

In photo and X-rays excited luminescence spectra for inactivated synthetic diamonds wide bands with the main maxima at 450, 530 nm with a number of superposed electron-vibrational systems (EVS) with zero phonon lines (ZPL) in the range of 478-491 nm at 503 nm and at 885 nm (a doublet of ZPL) are observed.

EVS of ZPL 503 nm is connected with the nitrogen-vacancy centre H3. The others have been obtained in the works made in

the Physical Institute of Acad.Sci.USSR (Moscow) after ion implantation of Ni^+ into the natural diamonds. Thus, corresponding defects may involve a metal catalyst ion.

At present, the bands with maxima 450, 530 nm are related by Sobolev to native defects namely edge dislocations of 60° and 90° type, respectively.

In specially nonactivated diamonds the main influence of formation conditions takes place via the diamond crystallization rate that defines the concentration of captured uncontrolled impurities (for example, Ni and N from ESR data).

It is possible to change the paramagnetic centre concentration in the range from 10^{17} to 10^{20} cm^{-1} in diamond by changing the formation method (synthesis, temperature drop) and the crystallization rate. The main influence of paramagnetic, disperse, nitrogen is the X-rays and photo excited luminescence quenching at nitrogen concentrations more than $2 \cdot 10^{19} \text{ cm}^{-3}$.

As to Ni centres, an increase in crystallization rate results in intensity increase in the corresponding luminescence systems in IR and in visible spectra range. In diamonds with the increased Ni content besides the common EVS there appears those with ZPL in the range of 493-496 nm at 80 K, connected with the exchange-coupled pairs Ni-Ni.

Activation of diamonds by boron in the process of synthesis allows the crystals of semiconductor character to be obtained with resistance $R=10^3 \text{ Ohm}$ in comparison with that for nonactivated ones, being more than 10^{10} Ohm . In these diamonds, the thermally stimulated luminescence curve (TLC) peak $T_M \sim 230 \text{ K}$ with $E_T \sim 0.37 \text{ eV}$, connected with the boron ion in the substituted position is dominated, but it is usually weak in TLC curves for nonactivated samples. In luminescence spectra of boron-activated crystals a band with maximum 480-500 nm, also referring to boron, rises at 200-250 K as the main peak TLC glowing /1/.

A new EVS with ZPL doublet at 417.2 and 418.7 nm appeared in luminescence spectra when activating by aluminium.

In luminescence spectra of the crystals produced from titanium-rich charge a band 450 nm relating to dislocations of 60° type, appears at 300 K; EVS of nickel centres are more than an order intensive. Titanium influence is rather referred to the effect of nitrogen bonding during the crystallization, paramagnetic nitrogen content decrease in diamond and, respectively, luminescence quenching weakening /2/.

In boron-activated crystals ($\sim 0.15 \text{ wt.}\%$) of distinctly increased content of Ni there appears to be EVS with ZPL doublet at 690 nm and at $T=80 \text{ K}$. It is possible to suggest the centre formation of donor-acceptor pairs of nickel and boron.

High-temperature annealing under conditions of stabilizing pressure provides additional possibilities to effect on diamond luminescence.

Thus, the exposure of the crystals obtained by the synthesis method to diamond crystallization conditions ($P \approx 5-6 \text{ GPa}$, $T \approx 1500-1700 \text{ K}$) for some hours as well as an increase in time of diamond growth by the temperature drop method result in the following changes in spectra of photo and X-ray luminescence of non-activated diamonds:

1. A band of 480-500 nm which is absent at 80 K appears at 200 K and rises to 300 K, this is very similar to the band observed in boron-activated diamonds. The luminescence maximum band shifts to 560-580 nm at 80 K.
2. The intensity of EVS on hand decreases as P-T treatment time increases, which is connected with the processes of defect migration, first of all, of vacancies, and formation of more complicated complexes.
3. In the diamonds obtained by the synthesis method, a new EVS appears with ZPL at 417.2 418.7 nm which is typical of the aluminium-activated crystals.

The points 1 and 3 seem to be explained by an additional activation from the high-pressure apparatus fittings.

The investigations carried out show that a change of synthesized diamond formation conditions, high-temperature annealing under diamond crystallization conditions and activation essentially effect via concentration and behaviour of defects on luminescent properties of synthetic diamond, which can be used to obtain crystals of certain parameters.

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Abstract

The effect of hydrostatic pressure at low temperature on potassium alum has been studied using Raman spectroscopy. Polarized spectra have been obtained over the range 8 to 4000 cm^{-1} . Two new phases of this material have been found, a third new phase is implied by the form of the emerging phase diagram, and the apparent termination of one of the transition lines is suggestive of a multi-critical effect.

Introduction

Alums are a large family of double salts with general formula $m_1^+ m_2^{3+}(\text{RO}_4)_3 \cdot 12 \text{H}_2\text{O}$. m_1^+ can be K, Rb, Cs, NH_4 , NH_3CH_3 , NH_3OH , Tl, and m_2^{3+} can be Al, Ga, Fe, Cr, Co, V, In, Ti, and R can be S, Se, and Te. The family belongs to T_h^6 (Pa3) space group, and there are $Z = 4$ molecules in a unit cell. X-ray diffraction has identified three different types of alums [1] which are distinguished by the size of the monovalent metal ion. A small metal ion leads to the formation of an alum of type γ , a large ion causes alums of type β . The third and most common type of alum is caused by an ion of intermediate size and is referred to as an α alum. In potassium aluminium alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, which is an α alum, the m_1^+ and m_2^{3+} metal ions are each surrounded by six water molecules in an almost regular octahedron.

The temperature dependence of the Raman spectrum at zero pressure shows no phase transitions, but indicates a distribution between two possible sulphate orientations which persist down to low temperatures [2,3]. It seems that there is a small energy difference between the

two possible sulphate orientations, amounting to about 2009 Jmol^{-1} , and at higher temperatures the relative populations of the two positions follow the expected thermal equilibrium, but at lower temperatures a fixed relative population becomes "frozen in" [4,5].

Experimental details

Crystals of potassium alum were grown from water solution. A four-sided face usually formed along the (011) direction and sometimes also along the (001) direction.

The crystal structure is centro-symmetric so that complete assignment of modes requires both infrared and Raman study. It is possible to observe all the Raman active modes by cutting two different crystals. This allows the Eg, Fg, and Ag + Eg modes to be recorded separately on appropriate polarizations and so the Ag, Eg and Fg modes can be unambiguously assigned by using Raman tensors.

The polarized spectra were recorded in a 90° scattering configuration. Hydrostatic pressures up to 9 Kbar were produced in a high pressure cell which used helium gas as the pressure transmitter at temperatures up to 500K and down to liquid nitrogen temperature [6,7].

The spectra were recorded using a Spectra Physics argon-ion laser operating at $\sim 1 \text{ W}$ at 488 nm. The spectra were recorded using a Spex-Ramalog 5 M Raman spectrometer. The spectral slit width was varied from 2 cm^{-1} to 4 cm^{-1} .

Results and Discussion

A very large number of Raman spectra have been recorded in the pressure range up to 9 kbar and a selection of them is presented in fig.1.

Precise measurements of the temperature and pressure have been used to improve our understanding of the properties of this material and determine its phase diagram.

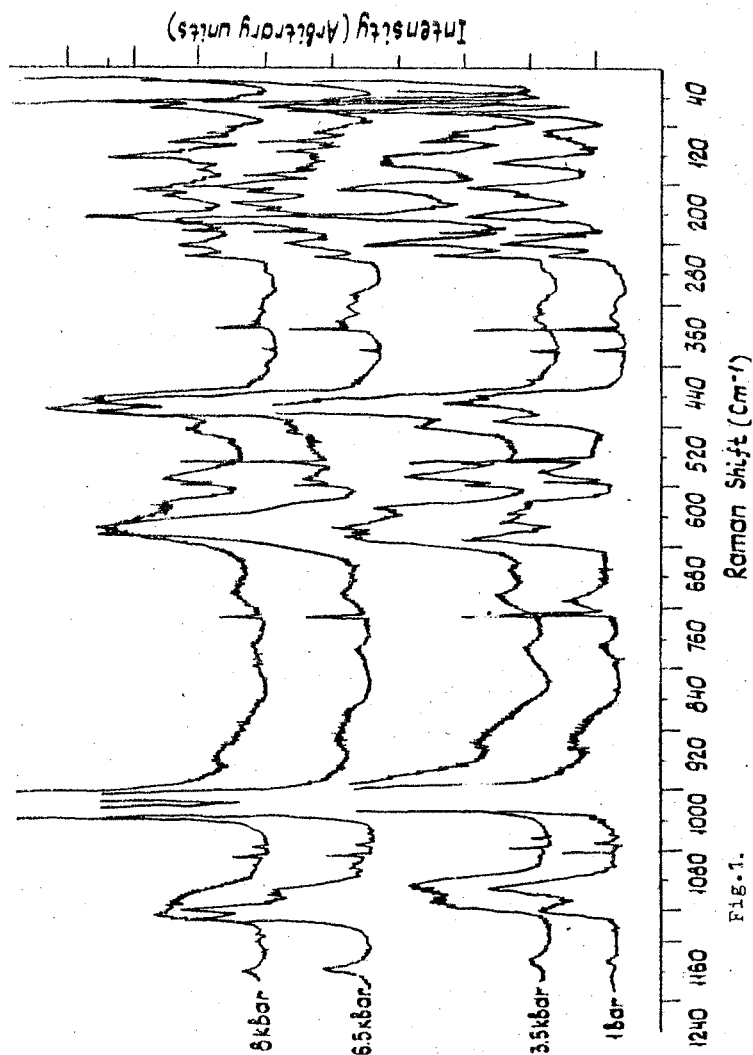


Fig. 1.

Raman spectra of Potassium Alum, polarized to record Ag + Eg modes only.

Samples all at 80K and under pressures of zero, 3.5 kbar, 6.5 kbar and

8 kbar as indicated.

In this paper we concentrate on the region of the spectrum between $980 - 1000 \text{ cm}^{-1}$ which belongs to the symmetric-stretching mode ν_1 of the sulphate ions.

In potassium alum the symmetric-stretching mode ν_1 splits into 1 Ag, 1 Au, 1 Fg and 1 Fu modes, and here we have concentrated on the Ag mode.

After the first phase transition, which is at 4 kbar and 80K, the crystal appears to go into an amorphous state which remains up to 7 kbar and 86K. In this state the polarization ratio becomes very low (~ 1) and the spectra show significant differences from the phase I spectra across the whole range, but particularly in the lattice region which is shown in fig.2. The most characteristic feature of this state is the decrease in the intensity of all the bands by a factor of about 3 or 4 times, due probably to the translucent form of this phase. The main ν_1 peak at around 990 cm^{-1} in this phase shows significant deviations from a Lorentzian bandshape, particularly on the high frequency side, as shown in fig.3.

After increasing the pressure to 7 kbar and for temperatures less than 86K, another state appears which has a spectrum that is generally more like that of phase I at liquid nitrogen temperature. However, an extra band appears between the two Ag ν_1 Raman lines which are associated with the two orientations of the sulphate ions, see fig.4. There is a clear decrease in intensity of this new feature when the temperature is increased and its intensity drops to zero at a well-defined temperature. Thus we have two well-defined transitions that are identified (i) phase I to phase II by the appearance of a third band in the ν_1 region, and (ii) phase I to phase III by the change from a transparent to a translucent solid accompanied by a dramatic drop in intensity of all Raman signals, a loss in polarization ratios and a marked asymmetry in the strongest Raman band. These two transition lines seem to meet at about 6.8 kbar

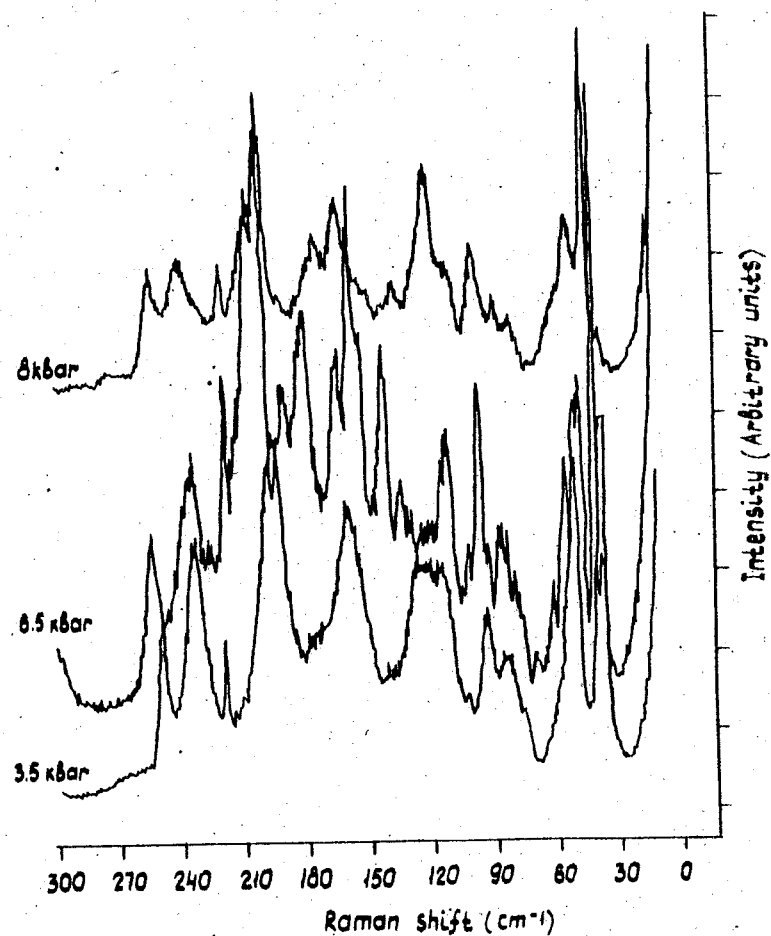


Fig. 2.

Raman spectra of Potassium Alum in lattice mode region, polarized to record A_g and E_g modes only. Samples all at 80K and under pressures of 3.5 kbar, 6.5 kbar and 8 kbar as indicated, these being for phase I, Phase III and phase II respectively.

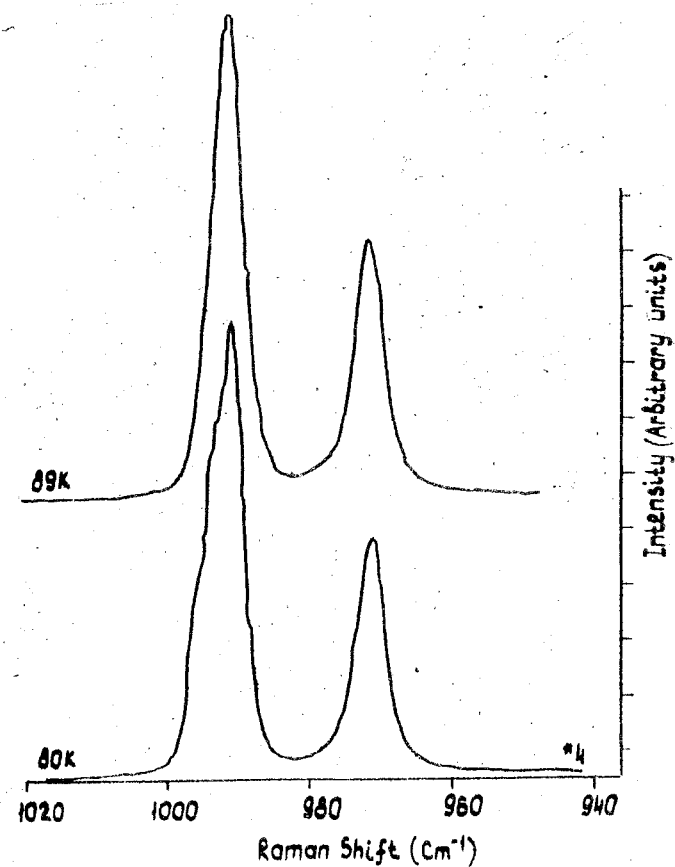


Fig. 3.

Raman spectra of Potassium Alum in $\nu_1 \text{SO}_4$ region under pressure of 6.5 kbar and temperatures of 80K and 89K as indicated showing phases III and I respectively. Gain for phase III spectrum is four times greater than for phase I, and note asymmetry of the strongest band in phase III.

and 82K and a third transition, phase II to phase III must exist, going down in temperature from the I, II, III triple point. A provisional phase diagram is shown in fig.5.

At pressures below 4 kbar there is no evidence of the phase I to phase III transition.

At 3.9 kbar there is no transition to be found in our experiments although at 4 kbar it could easily be detected. As the I to III transition line seems to rise in temperature slightly as the pressure is reduced, we do not think that our failure to detect this transition at 3.9 kbar has anything to do with our approach towards the low temperature limit of our apparatus. At zero pressure we have recorded data down to 20K without any sign of a phase transition. Thus there is some sort of anomaly with the low temperature part of the phase diagram. From the data currently available we are forced to consider the possibility of a critical point at about 4 kbar and 82K.

Most of our experiments were performed under various constant pressures using temperature as the continuously changing variable. Our thermocouples were about half-way radially into the pressure cell cylinder and we believe that the sample temperature was lagging behind our thermocouple by about 2K at the usual heating and cooling rates. We suspect that there is very little (if any) temperature hysteresis in the transitions themselves.

Conclusion

Our interest in $\text{KAl(SO}_4)_2 \cdot 12\text{H}_2\text{O}$ came as an extension of work on the various forms of ice. (Note that there are 7 phases of ice in the region covered by these experiments.) We therefore expected to see more transitions than we have so far observed in this material, which is largely composed of H_2O molecules. However, the transitions that we have observed are very interesting and we intend to make further studies on this family of crystals.

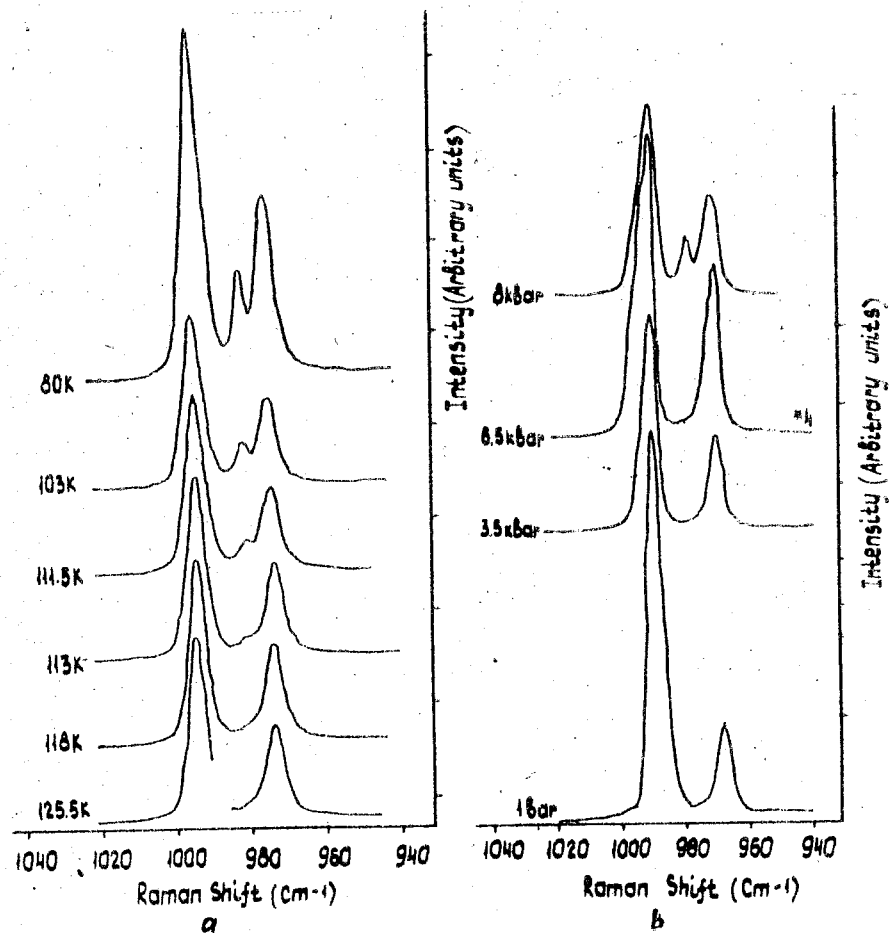


Fig. 4.

Sulphate ion symmetric-stretching region of Ag Raman spectrum of potassium alum (a) as a function of temperature at 8.5 kbar, (b) as a function of pressure at 80K.

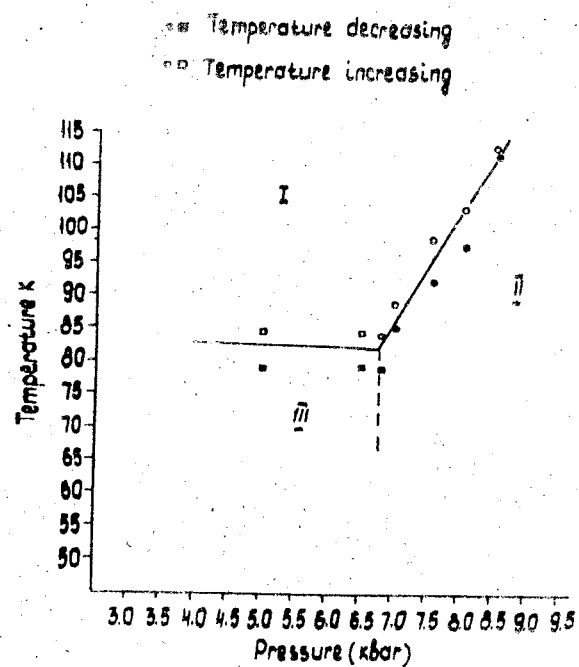


Fig. 5.

Proposed phase diagram for $\text{K Al(SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. Thermal hysteresis (indicated by solid and open symbols) is at least partially due to temperature lag of sample with respect to the thermocouple. Note the apparent critical point near 4 kbar 82K.

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Abstract

The transmission of diamond and other anvil apparatuses that contain absorbing samples has been calculated as a function of frequency for planar anvils that are inclined to one another and for anvils whose faces are distorted into concave parabolas of revolution. The inclination or the amount of parabolic distortion can be measured by the decrease in amplitude of interference fringes in transparent regions of the spectrum. In regions where the samples absorb, the effect of the distortion of the anvils on peak intensities, integrated areas, and time auto-correlation functions of the dipole moment, which have been obtained by Fourier transforming the adsorption bands, has been calculated. For concave parabolic faces that are each 10 μm deep, or for inclined planar faces whose maximum and minimum separations differ by 20 μm , the peak and integrated absorbances of a Lorentzian band having a peak transmission of 36% and a half-width of 10 cm^{-1} differ by at most 0.8% and 0.5% respectively from the corresponding quantities for plane anvil faces. These distortions are expected to occur only at about 500 kbar. Even for a strongly absorbing sample whose peak transmission is 0.7%, the peak and integrated absorbances differ from the true values by less than 3.2% and 1.8% respectively. The effect of the distortion on the line shape as determined from the apparent change of the time auto-correlation function of the dipole moment is only a few percent even for strongly absorbing samples. Integrated areas and shapes of infrared bands, and the related effective charges and auto-correlation function of the dipole moment, can, therefore, now be measured accurately up to a least 500 kbar.

Introduction

Diamond anvil cells are now standard tools for high-pressure spectroscopy, and the effect of pressure on vibrational frequencies has often been measured and shifts of force constants and changes of phase have often been identified [1]. The integrated intensity of adsorption bands tells us about the effective charge of the atoms and molecules and their shape tells us about the time auto-correlation function of the dipole moment. Although these are important properties that carry interesting information, they have rarely been measured under pressure [2] perhaps because the anvil faces often tilt so that they are no longer parallel to one another, and their faces often distort from planar under the large loads that must be applied to reach high pressures. These distortions change the apparent shapes and integrated areas of adsorption bands.

In this paper, the effects of distortions that are likely to occur up to about 500 kbar [3] on the apparent parameters of absorption bands are calculated in order to obtain the conditions needed to accurately measure the absorptivity, the integrated absorptivity, and the time auto-correlation function of the dipole moment.

Method of Analysis and Results

If the anvil faces are inclined to one another in the x direction, the thickness of the sample, whose cross-section along the axis of the faces is drawn in the lower part of Fig. 1, is

$$h(x) = h_0 + a_2 x, \quad (1)$$

where h_0 is the distance between the anvil faces at the center of the anvils, a_2 the tangent of the angle between the faces, and x , where $-r_0 < x < r_0$ and r_0 is the radius of the anvil face, is the distance from the center along the line of maximum slope. If the absorption band is Lorentzian, then the absorptivity $K(\nu)$ is

$$K(\nu) = \frac{a\beta\nu^2}{(\nu_0^2 - \nu^2)^2 + \nu^2\beta^2}, \quad (2)$$

where β is the damping constant, and a/β the peak absorptivity. The transmission through anvils inclined to one another is then

$$\frac{I(v)}{I_0(v)} = \frac{1}{2} \int_{-r_0}^{r_0} e^{-K(v)h(r)} 2(r_0^2 - x^2) dx, \quad (3)$$

when reflection is ignored. The effect of incidence at angles up to 15° on the transmission is $<10^{-3}$ [4].

If the anvil faces are distorted to parabolas of revolution, as drawn in section through the center of the faces in the upper part of Fig. 1, the thickness of the sample at radius r is

$$h(r) = h_0 + a_1 r^2, \quad (4)$$

where h_0 is the thickness at the center of the anvil faces and r the distance from the center of the faces. The transmission of the sample is then

$$\frac{I(v)}{I_0(v)} = \frac{1}{2} \int_0^{r_0} e^{-K(v)h(r)} 2\pi r dr. \quad (5)$$

The inclination of the anvil faces or the parabolic distortion can be measured by the height of the interference fringes at frequencies where the sample is transparent [5].

The effect of both wedge and parabolic distortions on the apparent integrated area A for samples whose peak absorptivity is 200 and 1000 cm^{-1} was calculated by numerically integrating the absorbance according to the equation

$$A = \int_{\nu_0 - 50 \text{ cm}^{-1}}^{\nu_0 + 50 \text{ cm}^{-1}} \log_{10} \frac{I_0(\nu)}{I(\nu)} d\nu,$$

where ν_0 is the frequency at the peak, using a band whose half-width was 10 cm^{-1} and a sample whose mean thickness was $50 \mu\text{m}$. The apparent area is plotted against the wedge height $2a_2 r_0$ in the lower frame of Fig. 1 and against the maximum parabolic distortion $a_1 r_0^2$ in the upper frame of Fig. 1. The distortions reduce the apparent area by a maximum of only about 1.8%.

The effect of the distortions on the shape of the absorption band was investigated by Fourier transforming the band. The resulting auto-correlation function $C(t)$ of the dipole moment [6] is plotted against the time in the lower and upper frames of Fig. 2, for wedged-shaped and parabolic samples respectively and for the parameters listed in the figure. The fractional difference Δ between the

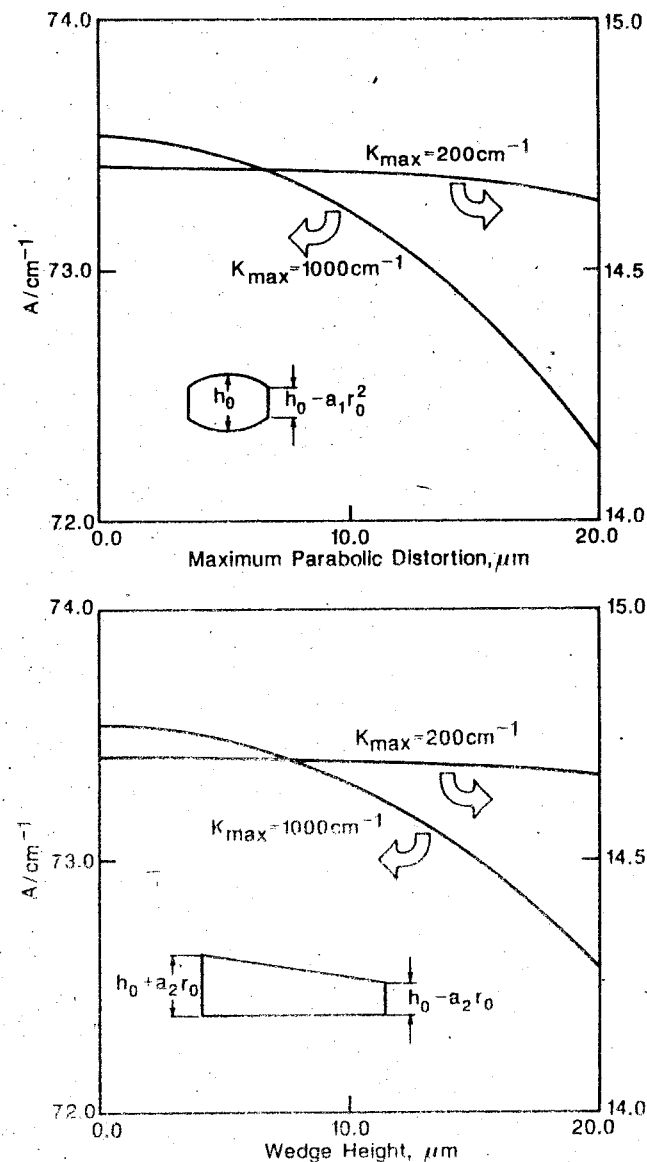


Fig. 1. Graph of integrated absorbance versus maximum parabolic distortion $a_1 r_0^2$ in the upper frame and wedge height $2a_2 r_0$ in the lower frame. The samples are held in diamond anvils having a circular aperture and a mean thickness of $50 \mu\text{m}$, half-width of 10 cm^{-1} , and maximum absorptivity K_{max} of 1000 and 200 cm^{-1} as indicated.

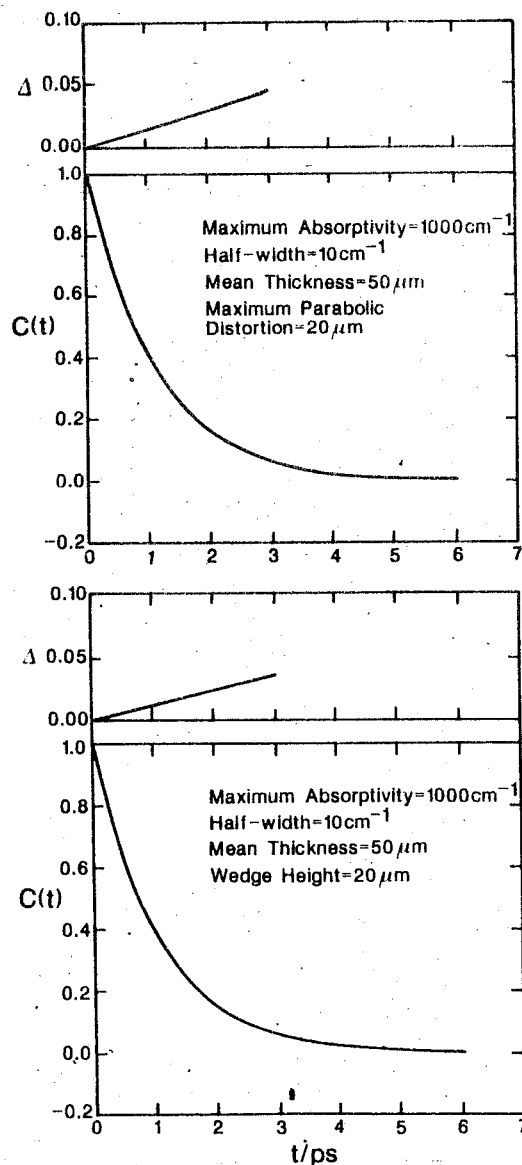


Fig. 2. Effect of parabolic distortion or nonparallel anvil faces on the time auto-correlation function $C(t)$ of the dipole moment. The fractional deviation Δ of the auto-correlation function from the true value is plotted on the upper part of each frame.

correlation function as measured between parallel and between parabolic and inclined faces is plotted against the time in the upper parts of the two frames in Fig. 2. It is less than 0.04 throughout the region where the correlation function is greater than 0.1.

In summary, it has been shown that accurate integrated absorption intensities and line shapes can be measured in diamond and other anvils even if the faces are distorted from plane parallel. Integrated absorptivities and the corresponding effective charges, and line shapes and their corresponding correlation functions, can now be measured accurately in diamond anvils at pressures up to at least 500 kbar.

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A device permitting to register ESR spectra directly in the resonator of a spectrometer in the process of shear deformation with high pressure, has been described by us in /1,2/.

The aim of this work is to establish basic regularities in the dynamics of radicals yield and decay, induced by shear deformation of a solid at high pressure and to determine the fundamental kinetic parameters of radicals recombination and their dependence on the magnitude of shear deformation, pressure, and chemical structure of compounds under investigation.

Arylinedandione dimers synthesized as described earlier were used as model compounds. They dissociate in solutions with the rupture of C₂ - C₂ bond (E = 17 kcal/mol) and the subsequent recombination and formation of the initial dimer. The maximal pressure of the apparatus was 30 kbar, the temperature range from 293 - 400 K, the accuracy of thermostatic control ± 1 K. The concentration of radicals was determined from the secondary calibrated reference DFPH, being in the order of magnitude 10^{18} spin/cm³.

The ESR spectra of radicals, induced by shear deformation under pressure, exhibit a singlet with the g-factor of ~ 2.00 and $\Delta H_{pp} = 12$ G. Pressure has no effect on either its position or width. The pressure discharge leads to an irreversible and drastic (by 8 to 10 times) decrease in concentration. Further increase in pressure (without any shear) leads to an increase in concentration (with the accuracy of 5%). At present one can give no clear explanation of such high recombination rates of radicals in solids after pressure discharge. They are probably caused by high local concentrations of radicals.

Fig.1 shows the dependence of radicals yield on the shear angle under pressure of 7 and 12 kbar. At low angles (10-12°) the radicals concentration sharply increases (by 15 times), the rate of increase being larger at 12 kbar than at 7 kbar while the maximal concentration for both pressures is the same. The pattern of

these dependencies then changes with pressure growth. At 12 kbar and shear angles larger than 10° one observes a sharp drop in concentration and its stabilization at a lower level. At 7 kbar there is a slow build-up to maximal concentration (at shear angle of approximately 20°) and a slow decline at larger angles. This dependence indicates that shear deformation induces two competing processes - generation of radicals and their decay. The former process predominates at low angles while at larger angles the process of forced mass-transfer promoting radicals diffusion and their subsequent recombination is favoured. The competition of these factors determines the extremum on the dependence of radical yield on shear angle. A decrease in pressure "washes out" the extremum, shifting it into the range of larger shear angles while the maximal concentration remains unchanged.

The kinetic curves of polychromatic kinetics are described by equation

$$\frac{n}{n_0} = \left[\ln \frac{k_{\max}}{k_{\min}} \right]^{-1} (-\ln k_{\min} - \ln n_0 t) \quad (I)$$

where n_0 and n are the initial and current concentrations of reacting species. The value of $\ln t$ is determined by x-coordinates of interception points of a kinetic curve in $n/n_0 - \ln t$ coordinates with straight lines at n/n_0 equal to 0 and 1, being characterized by distribution of rate constants with boundary values $k_{\max}$ and $k_{\min}$.

The figure shows that the kinetic curves depend on the angle of shear deformation while their expressions in the coordinates of the polychromatic kinetics equation (I) corresponds to this equation (Fig.2). A decrease in shear angle is accompanied by distribution narrowing; at shear angles from 5 to 40° and pressure of 7 kbar, $\lg (k_{\max}/k_{\min})$ decrease from 4.5 to 3.6, and at 12 kbar from 4.9 to 4.2.

One feature should be noted: $k_{\max}$ value for both dimers is weakly dependent on pressure and shear angle (thus with dimer I $k_{\max}$ varies from 20-40 l/mol s; with dimer II the constant retains the same order). On the contrary $k_{\min}$ is strongly dependent on shear angle and pressure. At constant pressure $k_{\min}$ shifts into the area of larger values as shear angle is increased. This tendency is typical of both dimers at 7 and 12 kbar. In other words shear deformation and pressure do not affect the rate of

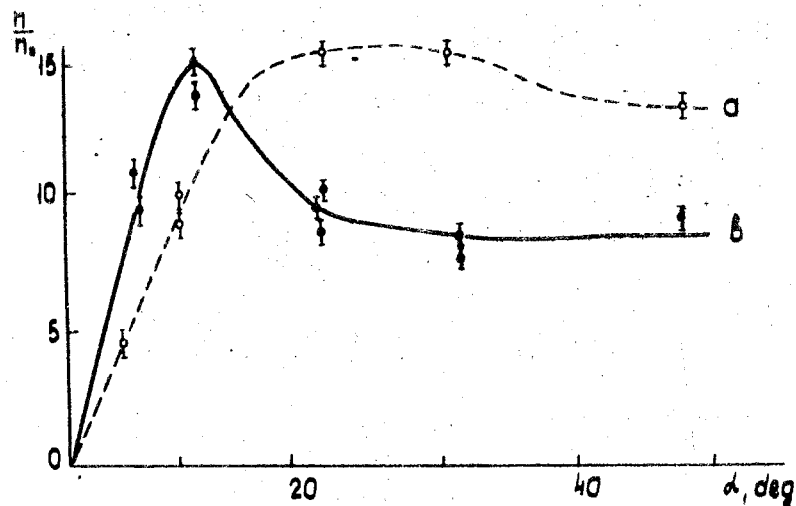


Fig. 1. Dependence of radical yield on shear angle;
a - 7 kbar; b - 12 kbar.

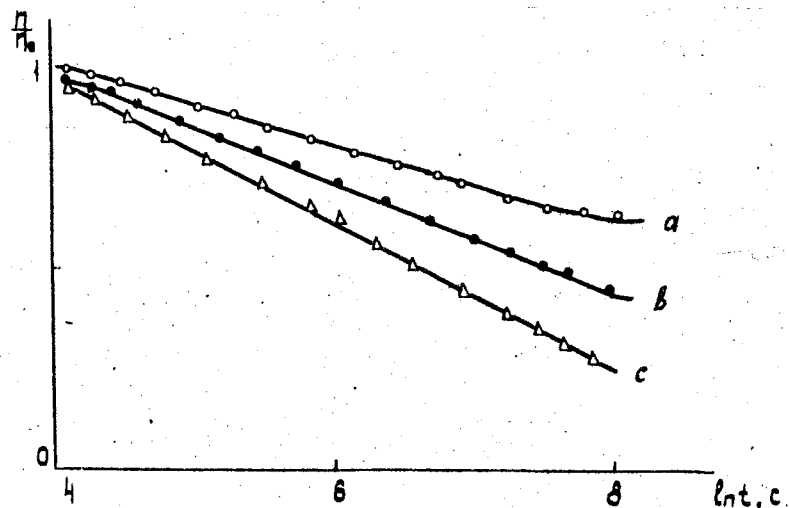


Fig. 2. Kinetics of recombination of radicals induced by shear deformation in dimer I at 12 kbar by angles;
a - 50°; b - 20°; c - 45°; anamorphosis of kinetic curves in equation 1 coordinates.

the fastest reactions while exerting strong influence on the slowest reactions: $k_{\min}$ shifts into the area of larger values which results in the distribution narrowing. Depending on pressure and shear angle the recombination activation energies are distributed over a wide range of values from 5 to 25 kcal/mol, the pre-exponential factor varies over the range of ten orders of magnitude.

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