# Structure transition of Sc to 300 GPa

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#### Summary

X-ray diffraction experiments were carried out at 297 K in order to study structural phase transitions of the trivalent rare-earth metal scandium (Sc) at pressures of up to 297 GPa. Four stages of structural transition were observed around 23, 104, 140 and 240 GPa. The crystal structure of the highest-pressure phase, Sc-V, was found to be a hexagonal lattice (S.G.: $P6_{1}22$  or  $P6_{5}22$ ) consisting of 6-screw helical chains. The lattice can be derived from modulations of the inter-plane stacking of the (111) planes in an fcc arrangement. The occurrence of an anisotropic structure suggests the importance of interactions between 3*d* orbitals with their nearest neighbor atoms.

### I. Introduction

Studies of the 3*d* transition metals at high pressures have attracted special interest for a variety of reasons, including structural phase transitions induced by electronic-transitions, their natural magnetic character and because they are major components of the Earth's core. The phenomenon of electron transfer from the *s*-band to the *d*-band under pressure (the so-called *s*-*d* transition) is a common feature of many band structure calculations involving these metals (Duthie, 1977 and Skirver, 1985). It is expected that the increase in the number of electrons that occur in the *d*-band with increasing pressure will not only affect the electronic properties, but also the stability of the crystal structure, and this often induces characteristic phase transitions. From these viewpoints, x-ray structural studies of these metals have recently been extended to multi-megabar pressures.

Scandium (Sc) is the first of the 3*d*-transition elements, and is often grouped with the rare-earth metals because of the close similarity its chemical properties to those of the rare-earths. The rare-earth metals (including Y, La, Pr, Nd and so on) exhibit successive phase transitions under high pressure due to *s*-*d* transitions. The structures follow to a systematic sequence, from hcp - Sm type - dhcp - fcc (Jayaraman, 1978, Vohra, 1981&1984, Porsch, 1993 and Hamaya, 1993). By analogy with the properties of Y, metallic Sc, which has the hcp structure under ambient conditions, is also believed to follow this systematic series. Previous x-ray diffraction studies reported that the hcp-Sc phase (Sc-I) showed a phase transition around 23 GPa (Vohra, 1982 and Zhao, 1996). Electrical resistance measurements at low temperature also suggest a transition at around 17 GPa (Wittig, 1979). However, the crystal structure of the high-pressure phase (Sc-II) did not correspond to any of the structures in the sequence as mentioned above, but rather could be explained as a complex structure consisting of distorted icosahedral clusters, and furthermore, Sc-II was stable up to 76 GPa (Zhao, 1996). Therefore, it has been suggested that Sc follows a special structural sequence that is different to the systematic sequence described previously.

On the other hand, transition metals (except for the rare-earth metals) also exhibit structural phase transitions under pressure due to the *s*-*d* transition. The structural sequence is commonly known to be hcp - bcc - hcp - fcc. However, our recent x-ray diffraction study covering the 3*d* transition metal titanium found that its structural sequence is different from the canonical sequence, in that anisotropic structures consisting of zigzag chains occur in the high-pressure phases that occur above 100 GPa (Vohra, 2001 and Akahama, 2001). This result suggests that the close-packed model of rigid spheres for atoms does not apply in the case of the earlier members of the 3*d* transition metals under extremely high-pressure conditions.

Our interest is concentrated on the structural behavior of the Sc metal under extremely high-pressure conditions, at which the electron transfer from the *s* band to the *d* band is almost complete. In this paper, high-pressure x-ray diffraction experiments are presented over a wide range of pressures, extending to 300 GPa, and four structural phase transitions of Sc are reported. The structure of the highest-pressure phase (Sc-V), which occurs at 240 GPa, is found to belong to a primitive hexagonal lattice consisting of a  $6_1$  or  $6_5$  screw chain, which shows anisotropy in its compressibility.

### **II. Experimental**

The present x-ray diffraction experiments were carried out using a monochromatic synchrotron radiation source on the BL10XU station at SPring-8, Hyogo. Powder diffraction patterns of the samples were collected by an angle-dispersive method with a diamond anvil cell (DAC) and an Image Plate detector. An Sc sheet of 99.9 % purity (Koch Chemicals Limited, England) was used as a sample. The lattice parameters of this sample at ambient conditions were a = 3.3035(4) Å and c = 5.2474(19) Å, respectively, and showed consistency with previous data Geiselman, 1962). A small piece of the sample was embedded in a hole in an Re metal gasket set in the DAC without the use of a pressure medium. Beveled diamond anvils with center flat sizes of 35, 50 or 75 µm in diameter were used for the pressure generation. Pressures above 100 GPa were determined from the equation of state of Pt (Holmes, 1989). Pressure determination below 100 GPa was achieved by the ruby scale (Mao, 1978). The errors in pressure above 100 GPa were estimated to be within 2 GPa from the standard deviation of the lattice constant of Pt. Diffraction lines from the Pt pressure marker usually covered (masked) the lines from the sample, which made it difficult to analyze the diffraction patterns. Therefore, extra experimental runs without the marker were conducted during this study. In these experiments, the pressure was estimated from the pressure-shift of the Raman band edge of diamond anvils calibrated using the Pt scale (Akahama, 2004). For the measurements above 200 GPa, the x-ray beam was reduced by using a pine-hole collimator of 10  $\mu$ m diameter. The typical exposure time was 20 min. The 20-intensity profiles were obtained by the integration of the recorded two-dimensional diffraction images (Shimomura, 1992).

### **III. Results and Discussion**

The diffraction profiles obtained at 297 K for pressures up to 297 GPa (covering five experimental runs) exhibited four structural phase transitions. A drastic change in the profiles was observed at each transition. Figures 1and 2 show the typical powder diffraction profiles for each phase, which are assigned in order of pressure to Sc-I, II, III, IV and V, respectively. Re-crystallization of the sample was also observed during these transitions, except for the

transition to Sc-IV. The Debye rings that were observed just after the transitions, were recorded as an aggregation of spotty Bragg reflections, though they changed to smooth lines with increasing pressure. The first transition from Sc-I to Sc-II was observed at 23 GPa. This transition pressure agreed with previous studies (Vohra, 1982 and Zhao, 1996). The other three structural-phase transitions, which are newly found in this study, occurred at pressures of 104, 140 and 239 GPa, respectively. In particular, the transition to Sc-V was sharp and was almost complete at 242 GPa. To the best of our knowledge, our observation of this structural transition above 200 GPa is only the second such example in elemental materials, following the transition of phosphorus at 260 GPa (Akahama, 2000). The reproducibility of these transitions was confirmed from the different experimental runs. When the pressure was decreased from 30 GPa, Sc-I was recovered from Sc-II at 10 GPa.



Fig. 1. Typical x-ray diffraction profiles for the high-pressure phases of Sc: Sc-II, III and IV, and the hcp phase at ambient pressure. The asterisks correspond to lines from an Re metal gasket. The diffraction lines of the ambient phase are completely indexed to an hcp lattice.

The profiles of Sc-II, III and IV comprise of a large number of diffraction lines. This suggests that the structures of these phases are not Braves lattices, but are complicated structures with a comparably-large number of atoms in the unit cell (*Z*). Two models have been proposed up to now for the Sc-II structure. The first is a  $\beta$ -Np type tetragonal lattice (Vohra, 1982) and the other is a pseudo-bcc lattice with *Z* = 24 (Zhao, 1996). The present profile of Sc-II at 30 GPa seems to be similar to that of the second of these proposed structures (Zhao, 1996). However, the strongest line at around  $2\theta = 10^{\circ}$  in this profile is found to be a doublet even though it was assigned as a singlet in the previous report (Zhao, 1996).

Furthermore, a few weak diffraction lines that cannot be assigned to these lattices are newly observed in this study. Therefore, the structure of Sc-II could not be fully explained by either of these models. Consequently, the profiles of the high-pressure phases were not different from those of the modifications observed in the other rare-earth elements. However, Sc-V yielded a relatively simple diffraction pattern with a small number of lines. Therefore, we initially tried to determine the structure of Sc-V in order to obtain the atomic volume of this phase. The volume provides a constraint for the analysis of the other high-pressure phases.



Fig. 2. The diffraction profiles of the highest pressure phase of Sc: Sc-V (a) at 242 GPa and (b) 297 GPa, together with the diffraction image at 242 GPa. The profiles are completely indexed on the basis of the hexagonal  $P6_{1}22$  or  $P6_{5}22$  lattices. The solid red lines represent the simulated pattern for this lattice with the following the lattice parameters and position; a = 2.355(1) Å and c = 10.446(3) Å, x = 0.461(1) for 6a(x, 0, 0) at 242 GPa, and a = 2.309(1) Å and c = 10.332(4) Å, x = 0.467(3), the lattice parameter of Pt, a (Pt) = 3.450(1) Å at 297 GPa. The solid black lines show the residual intensities. The symbols ▼ in the profile at 242 GPa represent the superlattice reflections for 101, 105, 113 and 205. At 297 GPa, the asterisk represents the line from an Re gasket and the symbols ∇ denote the lines from the Pt pressure marker.

The diffraction profiles of Sc-V at 242 and 297 GPa are shown in Fig. 2. The sharp diffraction lines at 242 GPa reflect the re-crystallization in the transition. All of the diffraction lines at 242 GPa were completely indexed to a hexagonal lattice. The results are summarized in Table I. The lattice parameters were estimated as a = 2.353(1) Å and c = 10.445(3) Å, respectively. In the initial process of indexing, it was found that if we neglect a few weak lines from 101, 105 and 113 and 205 reflections, the pattern can be explained as a trigonal lattice, (S.G.:  $P3_121$  or its enantiomorph  $P3_221$ ), with a = 2.353 Å and c = 5.222 Å (one-half of 10.445 Å) and the relative intensities of the main diffraction lines are also reproduced with the trigonal lattice. Since the (003) reflection was not observed in this profile, the lattice of Sc-V was considered to have a higher symmetry than trigonal.

Table I. Powder diffraction data of Sc-V at 242 GPa. The observed *d*-values and relative intensities are listed as compared with the calculated data on the basis of a hexagonal lattice, S. G.  $P6_{1}22$  (Z = 6) with the lattice parameters, a = 2.355(1) Å and c = 10.446(3) Å, and the position, x = 0.461(1) for the 6a site, (x, 0, 0).

h	k	I	d (obs.)	d (cal.)	2θ (cal)	I (obs.)	l (cal.)
1	0	0	2.0381	2.0381	14.025	14.5	12.0
1	0	1	2.0014	2.0004	14.291	5.4	4.6
1	0	2	1.8988	1.8987	15.061	100.0	82.7
0	0	6	1.7414	1.7410	16.434	18.4	16.0
1	0	4	1.6068	1.6067	17.818	35.0	43.7
1	0	5	1.4565	1.4589	19.640	2.6	1.4
1	0	6	1.3231	1.3237	21.668	7.0	4.1
1	1	0	1.1761	1.1767	24.416	2.5	2.4
1	1	2	1.1477	1.1479	25.037	14.8	13.4
1	1	3	1.1151	1.1148	25.795	3.9	3.2
1	0	8	1.0987	1.0994	26.160	12.6	10.1
1	1	4	1.0726	1.0728	26.822	13.0	10.3
2	0	0	1.0189	1.0190	28.266	13.5	10.3
1	1	6	0.9750	0.9749	29.574	2.8	2.3
1	0	10	0.9293	0.9296	31.051	5.1	5.4
2	0	5	0.9166	0.9159	31.527	1.2	1.2
2	0	6	0.8792	0.8795	32.869	11.5	11.6

These indices showed systematic absences that are consistent with the space group  $P6_{1}22$  or its enantiomorph  $P6_{5}22$ . The relative intensities were well explained as a  $P6_{1}22$  structure with six Sc atoms in the 6a Wyckoff positions (x, 0, 0), (0, x, 1/3), (-x, -x, 2/3), (-x, 0, 1/2), (0, -x, 5/6) and (x, x, 1/6) with 0.46, while the weak lines of 101, 105, 113 and 205 disappear when x = 0.5. The simulated diffraction profile is shown by the solid line in this figure. Based on Rietveld refinements of the profile using the computer program RIETAN

(Izumi, 2000), the positional parameter *x* was estimated to be 0.461(2) with an *R* factor of  $R_{wp} = 25\%$ . The deviation in *x* from 0.5 results in a 6-screw helical chain structure (as mentioned below). We are not aware of the existence of the  $P6_122$  or  $P6_522$  structures in monatomic systems, though a trigonal lattice of  $P3_121$  (or  $P3_221$ ) with triad-screws is well known in the trigonal phases of Se and Te (Donahue, 1982 and Hippel, 1948). In the profile at 297 GPa, the observation of a weak peak for the 105 reflection means  $x \neq 0.5$ , i.e., the chain structure remains, even at this pressure. However, superposition with the diffraction lines of the Pt pressure marker and/or a line-broadening due to the shear stress effect make it difficult to estimate a precise value of the parameter *x* from the profiles at higher pressure.



Fig. 3. Structural models of the highest pressure phase (Sc-V) at 242 GPa on the basis of the  $P6_122$  lattice. (a) is viewed along the *c* axis and (b) along the [110] direction. The Sc atoms occupied the 6a site, (0.461, 0, 0). It can be seen that the structure consists of infinite  $6_1$  chains parallel to the *c* axis.

The unique new chain structure of Sc-V is illustrated with the P6<sub>1</sub>22 lattice in Fig. 3. Six Sc atoms are included in the unit cell (Z = 6). The Sc atoms of Sc-V at 242 GPa have two nearest neighbor atoms, with an intra-chain distance of 2.051 Å. The chain is formed along the *c* axis, with a bond angle of  $149.36^{\circ}$ . The nearest-neighbor distance between chains is 2.155 Å, which is 5 % longer than in the intra-chain distance. Each atom has a pseudo-coordination number of four. In the cases of trigonal-Se and Te under ambient conditions, these distances are longer by 44% and 20%, respectively. These phases of Se and Te are evidently molecular solids and are therefore different from Sc-V. The characteristic feature of this lattice is the layered structure of the hexagonal planes perpendicular to the c axis, that is, ABCDEF. Since x = 0.5, the stacking is a simplified form of ABCABC for the trigonal lattice.  $P6_{1}22$  is a supergroup of  $P3_{2}21$ . In addition, if we select x = 1/3 and c/a =2.4495 in the trigonal lattice, then the fcc lattice can be derived from the trigonal lattice. A distorted fcc phase has been proposed as the ultimate high-pressure phase of La and Y (Vohra, 1984 and Hamaya, 1993). This structure, which was identified as a trigonal space group *R-3m* with eight atoms in a rhombohedral unit cell (Hamaya, 1993), is considerably different from the present trigonal lattice.

The pressure dependence of the lattice parameters is shown in Fig. 4. With increasing pressure from 240 to 297 GPa, the value of *a* contracts by 2% while that of *c* contracts by 1%, so *a* is therefore more compressible than *c*. The Sc-V structure therefore shows anisotropy under compression. Consequently, the c/a ratio increases from 4.44 to 4.48 but these values are too small when compared with the value of 4.89 for an ideal close-packed lattice.



Fig. 4. The pressure dependence of the lattice parameters a and c, and the ratio c/a for Sc-V up to 297 GPa. The a direction is more compressible than the c direction, and the ratio c/a increases with pressure.

The estimated atomic volume ( $V_A$ ) of Sc-V is illustrated as a function of pressure in Fig.5. The value of  $V_A$  is 8.36 Å3 at 242 GPa and decreases to 7.96 Å3 at 297 GPa. The value at 297 GPa corresponds to 0.32 of 24.79 Å3 under ambient conditions. Comparing this with our previous results for titanium, Sc is considerably compressive and the compression curve of Sc-V is coincident with that of titanium in the multi-megabar pressure range (Akahama, 2001). The value of  $V_A$  for Sc-I that was determined in this study is also plotted in this figure. The data were fitted by the Birch-Murnaghan equation of state (Birch, 1947) and the bulk modulus  $B_0$  is estimated to be 60.2(3.7) GPa with a fixed value of  $B_0$ ' = 4.0. The estimated value is in good agreement with the previous data (Zhao, 1996).



Fig. 5. The change with pressure of the atomic volume  $V_A$  for Sc, together with previous data for Sc-I compared with those of the similar 3*d* transition metal, Ti. The present data are shown by solid circles for Sc-I and open circles for Sc-V. The solid line represents the result of a least-squares fit of the Birch-Murnaghan equation of state to the data for Sc-I,  $B_0 = 60.2(3.7)$ GPa with a fixed value of  $B_0' = 4.0$ . The dashed lines show the previous results for Ti (Akahama, 2001). It is found that the value of  $V_A$  for Sc-V seems to be coincident with that of Ti at extremely high pressures, up to 300 GPa.

It was found in this study that an anisotropic chain structure occurs in Sc under high pressure. The nearest neighbor intra-chain distance between Sc atoms is 2.05 Å at 242 GPa, and is lower at higher pressures. Considering the radius of the 3*d* electron state of the Sc atom ( $r_d = 1.24$  Å) as quoted by Harrison (1980), the atomic distance means that the 3*d* orbitals of an Sc atom overlap with those of the neighbor atoms in the chain. This suggests that the  $3d_{zz}$ -orbital localized near the inner core is hybridized with the 4*s*-orbital, and directional covalent bonding between the hybridized orbitals results in an anisotropic structure for Sc-V. The fact that a zigzag chain structure also occurs (Akahama, 2001) in high-pressure phases ( $\gamma$  and  $\delta$ -Ti) of the same 3*d* metal of Ti (as mentioned earlier) would support this idea.

#### **IV. Conclusion**

The powder x-ray diffraction studies of Sc presented in this work reveal that four structural phase transitions occur up to 297 GPa. The highest pressure-phase, Sc-V, which is observed above 240 GPa, has a hexagonal structure and is stable up to 297 GPa. Rietveld refinements of the diffraction profiles of Sc-V in the space groups  $P6_122$  or  $P6_522$  (Z = 6) provided an atomic positional parameter for a 6-screw helical chain structure. The structure was different from any of the structures observed for the other rare-earth metals or the

transition metals. The occurrence of the anisotropic structure suggested the importance of interactions of the 3d orbitals between nearest-neighbor atoms for the stability of the crystal structures under extremely high pressures. The atomic volumes that were obtained should provide important information to determine the unsolved structures of the high-pressure phases of Sc.

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## References

AKAHAMA Y., KAWAMURA H., CARLSON S., LE BIHAM T. and HÄUSERMANN D., 2000. Structural stability and equation of state of simple-hexagonal phosphorus to 280 GPa: Phase transition at 262 GPa, Phys. Rev. B, 61(5), 3139-3142.

AKAHAMA Y., KAWAMURA H. and LE BIHAN T., 2001. New  $\delta$  (distorted-bcc) titanium to 220 GPa, Phys. Rev. Lett., 87(27), 275503 1-4.

AKAHAMA Y. and KAWAMURA H., 2004. High-pressure Raman spectroscopy of diamond anvils to 250 GPa: Method for pressure determination in the multimegabar pressure range, J. Appl. Phys. 96(7), 3748-3751.

BIRCH F., 1947. Finite elastic strain of cubic crystal, Phys. Rev., 71(11), 809-827.

DONAHUE J., 1982. *The Structure of the Elements* Wiley New: York, p.370.

DUTHIE J. C. and PETTIFOR D. G., 1977. Correlation between *d*-band occupancy and crystal structure in the rare earths, Phys. Rev. Lett., 38(10), 564-567.

GEISELMAN J., 1962. J. Less-Common Metals, 4, 362.

HAMAYA N., SAKAMOTO Y., FUJIHISA H., FUJII Y., TAKEMURA K., KIKEGAWA T. and SHIMOMURA O., 1993. Crystal structure of the distorted FCC high-pressure phase of praseodymium, J. Phys.: Condens. Matter, 5(31), L369-L374.

HARRISON W. A., 1980. *Electronic Structure and the Properties of Solid: The Physics of the Chemical Bond*, W. H. Freeman and Company: San Francisco.

HIPPEL A. V., 1948. Structure and conductivity in the VIb group of the Periodic System, J. Chem. Phys. 16(4), 372-380.

HOLMES N. C., MORIARTY J. A., GATHERS G. R. and NELLIS W. J., 1989. The equation of state of platinum to 660 GPa (6.6 Mbar), J. Appl. Phys., 66(7), 2962-2967.

IZUMI F. and IKEDA T., 2000. A Rietveld-analysis program RIETAN-98 and its applications to zeolites, Mater. Sci. Forum, 321-324, 198-204.

JAYARAMAN A., 1978. in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr. and L. Eyring North-Holland: Amsterdam, Vol. 1, Chap. 9.

MAO H. K., BELL P. M. SHANER J. W. and STEIBERG D. J., 1978. Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of the ruby *R*<sub>1</sub> fluorescence pressure gauge from 0.06 to 1 Mbar, J. Appl. Phys. 49(6), 3276-3283.

PORSCH F. and HOLZAPFEL W. B., 1993. Novel reentrant high pressure phase transition in lanthanum, Phys. Rev. Lett., 70(26), 4087-4089.

SHIMOMURA O., TAKEMURA K., FUJIHISA H., FUJII Y., OHISHI Y., KIKEGAWA T., AMEMIYA Y. and MATSUSHITA T., 1992. Application of an imaging plate to high-pressure x-ray study with a diamond anvil cell, Rev. Sci. Instrum., 63(1), 967-973.

SKIRVER H. L., 1985. Crystal structure from one-electron theory, Phys. Rev. B, 31(4), 1909-1923, and references therein.

VOHRA Y. K., OLIJNIK H., GROSSHANS W. and HOLZAPFEL W. B., 1981. Structural phase transitions in yttrium under pressure, Phys. Rev. Lett., 47(15), 1065-1066.

VOHRA Y. K., VIJAYAKUMAR V., GODAL B. K., and SIKKA S. K., 1984. Structure of the distorted fcc high-pressure phase of the trivalent rare-earth metals, Phys. Rev. B, 30(10), 6205-6207.

VOHRA Y. K., GROSSHANS W. and HOLZAPFEL W. B., 1982. High-pressure phase transition in scandium, Phys. Rev. B, 25(9), 6019-6021.

VOHRA Y. K. and SPENCER P. T., 2001. Novel  $\gamma$ -phase of titanium metal at megabar pressures, Phys. Rev. Lett., 86(14), 3068-3071.

WITTIG J., PROBST C., SCHMIDT F. A. and GSCHNEIDNER Jr. K. A., 1979. Superconductivity in a new high-pressure phase of scandium, Phys. Rev. Lett., 42(7), 469-472.

ZHAO Y. C., PORSCH F. and HOLZAPFEL W. B., 1996. Evidence for the occurrence of a prototype structure in Sc under pressure, Phys. Rev. B, 54(14), 9715-9720.