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Temperature and pressure induced phase transition in IV-VI compounds

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Résumé. — La structure cristalline de SnS a été étudiée par diffraction neutronique entre 293 K et 1 000 K. Une transition du second ordre de type displacif se produit à 887 K entre la phase α (B16, Pbnm) et la phase β (B33, Cmcn). Près de la transition, le déplacement quadratique moyen des atomes Sn devient anisotrope et anharmonique. Des expériences de diffraction de rayons X sous pression jusqu'à 340 kbar ont été effectuées sur des composés semi-conducteurs IV-VI, PbS, PbSe, PbTe, GeS, GeSe, SnS et SnSe. PbS, PbSe et PbTe présentent une transition de la phase du type NaCl (B1) à une phase orthorhombique (B33 ou B16) à une pression de 22 kbar, 45 kbar et 60 kbar, respectivement. Dans le cas de PbS et PbSe, la phase orthorhombique est de type TII (B33, Cmcn) ; dans le cas de PbTe, il s'agit du type GeS (B16, Pbnm). PbS, PbSe et PbTe subissent une autre transition vers la phase cubique de type CsCl (B2) à des pressions de l'ordre de 215 kbar, 160 kbar et 130 kbar respectivement. Les composés orthorhombiques GeS, GeSe, SnS et SnSe ne présentent pas de transition de phase jusqu'à 340 kbar.

Abstract. — The crystal structure of SnS has been investigated as a function of temperature by elastic neutron scattering from 293 K to 1 000 K. SnS undergoes a second order displacive phase transition from the α -phase (B16, Pbnm) to the high temperature β -phase (B33, Cmcn) at 887 K. The mean square displacement of the Sn atom which is isotropic at room temperature becomes increasingly anisotropic and anharmonic near T_c . Energy dispersive X-ray diffraction experiments have been performed on IV-VI semiconductors PbS, PbSe, PbTe, GeS, GeSe, SnS and SnSe as a function of hydrostatic pressure to 340 kbar. PbS, PbSe and PbTe undergo transition from the NaCl type (B1) phase to the orthorhombic phases (B33 or B16) at about 22, 45 and 60 kbar, respectively. The orthorhombic phases of PbS and PbSe have been found to be of TII type (B33, Cmcn) and that in PbTe has been found to be GeS type (B16, Pbnm). PbS, PbSe and PbTe undergo further phase transitions to the cubic CsCl type (B2) phase at about 215, 160 and 130 kbar, respectively. The orthorhombic IV-VI compounds GeS, GeSe, SnS and SnSe do not undergo any phase transition up to 340 kbar.

1. Introduction.

The nine IV-VI semiconductors MX (M = Ge, Sn, Pb; X = S, Se, Te) are isoelectronic with the group V elements and crystallize at ambient conditions with three different structures which are analogous to those of the group V elements. The lighter compounds GeS, GeSe, SnS and SnSe crystallize with the GeS type (B16) structure which is the binary analogue of the black phosphorus structure [1]. The heavier compounds SnTe, PbS, PbSe and PbTe crystallize with the NaCl (B1) structure [2], a binary analogue of the simple cubic high pressure phase of the black phosphorus [3]. GeTe crystallizes with the rhombohedral structure [4, 5] and is the binary analogue of the grey arsenic

structure (A7). Temperature and pressure induced structural phase transitions in IV-VI semiconductors have already been reported [6-11]. SnS and SnSe undergo second order displacive phase transition from the α -phase (B16, Pbnm) to the high temperature β -phase (B33, Cmcn) at 887 K and 807 K, respectively [7, 8]. The lattice parameters a and c continuously approach the same value and at the critical temperature T_c the axial ratio changes from $a/c > 1$ to $a/c < 1$. The positional parameters, determined from the intensities of a few powder X-ray diffraction lines, were found to change continuously as the critical temperature was approached. However, this X-ray investigation [8] was fraught with great difficulties because of the high vapour pressures and chemical

reactivities of SnS and SnSe in the temperature region of interest. Therefore an accurate determination of the temperature variation of the positional and thermal parameters was not possible. In the present neutron diffraction experiment it has been possible for us to overcome these difficulties by using a larger single crystal ($4 \text{ mm} \times 4 \text{ mm} \times 4 \text{ mm}$) and investigate accurately the variation of the positional and thermal parameters of SnS as a function of temperature from 295 K to about 1 000 K. Pressure induced phase transitions in the cubic SnTe, PbS, PbSe, PbTe have been studied by the volumetric [12, 13], electrical conductivity [14, 15] and X-ray diffraction methods [16-19]. It has been concluded from the high pressure X-ray diffraction experiments that SnTe, PbS, PbSe and PbTe undergo first order phase transition from the cubic NaCl type (B1) phase to the orthorhombic GeS type (B16) phase at about 18, 22, 43 and 40 kbar, respectively. However, the assignment of the GeS type structure to these high pressure orthorhombic phases is not supported with convincing arguments. None of these authors has considered the closely related and more symmetric TII type (B33) for a likely candidate. In the present investigation we have re-examined the structure of the high pressure orthorhombic modifications of PbS, PbSe and PbTe by high pressure X-ray diffraction methods. We have extended the pressure range of the previous high pressure X-ray diffraction investigations (0-100 kbar) to about 340 kbar. We have also performed high pressure X-ray experiments on the hitherto uninvestigated orthorhombic IV-VI compounds GeS, GeSe, SnS and SnSe. Results of these investigations will be presented and discussed in this paper.

2. Experimental procedures.

Large single crystals of SnS and other IV-VI compounds were grown from the gas phase [20]. The crystals were cut to cubes and rectangular parallelepipeds of 3 to 4 mm in linear dimensions. The crystals were cemented on to the tops of quartz rods and were sealed inside quartz tubes under vacuum. The dimension of these quartz rods and tubes were chosen to minimize the open space inside the quartz tube. The crystals were mounted on the diffractometer D9 at the hot neutron source of the high flux reactor of the Institute Laue-Langevin, Grenoble. The high temperature was obtained by blowing hot air on the quartz tube in which the crystal was sealed. The temperature of the sample was determined by comparing the lattice constants with those of the reference [7].

Synthetic single crystals, which were about 2 mm in linear dimensions in the case of PbS, PbSe and PbTe and about 3 cm in the case of GeS, GeSe, SnS and SnSe were cut and ground to fine powders for the high pressure X-ray diffraction investigations. High pressure was generated in a gasketed diamond anvil cell [21]. The pressure generated was measured by the

well-known ruby fluorescence technique [22]. X-ray diffraction patterns were obtained at room temperature in the energy dispersive mode.

3. Temperature induced second order phase transition in SnS.

Figure 1(a) shows the variation of the lattice constants of SnS with temperature. It is seen that the lattice constants a and c approach each other continuously as the critical temperature T_c is approached whereas b increases continuously. At T_c the axial ratio a/c changes from $a/c > 1$ to $a/c < 1$.

Figure 1(b) shows the variation of the positional parameters of Sn and S atoms with temperature. It is seen that these parameters change continuously and approach those of the β -phase. Figure 1(c) shows the variation of the thermal parameters of the Sn and S atoms with temperature. At room temperature the

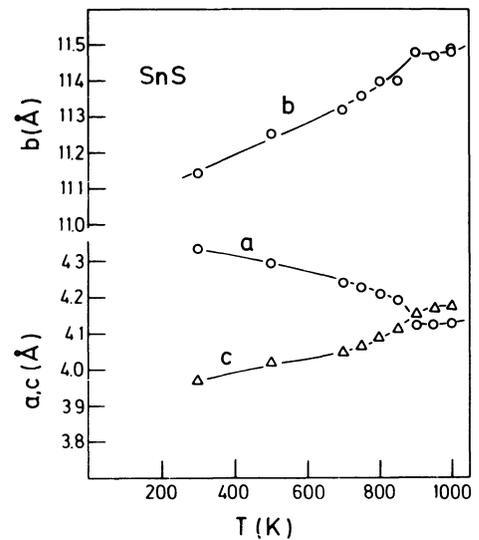


Fig.1(a)

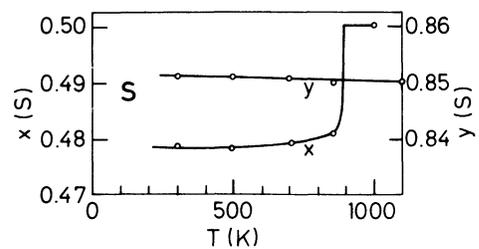
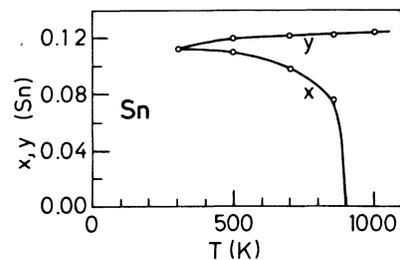


Fig.1(b)

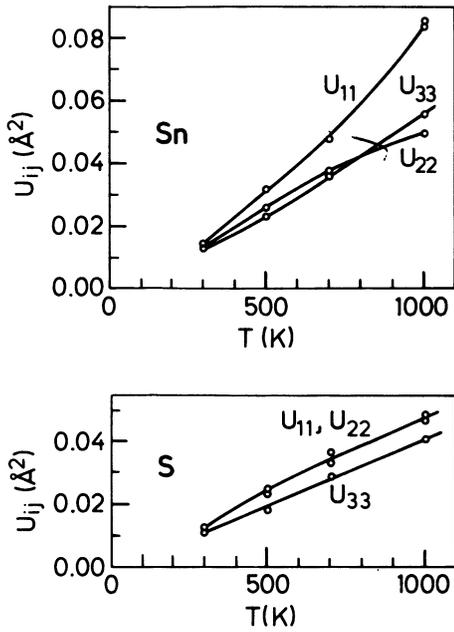


Fig.1(c)

Fig. 1. — Variation of (a) the lattice constants, (b) positional and (c) thermal parameters of the Sn and S atoms of SnS as a function of temperature. The continuous variation of the lattice constants and positional parameters indicate that $\alpha \rightarrow \beta$ transition in SnS is second order in character. At the critical temperature $T_c = 878$ K the axial ratio a/c changes from $a/c > 1$ to $a/c < 1$. The phase transition is accompanied by the movement of the Sn and S atoms almost entirely along [001] direction. Vibrational amplitudes of the Sn and S atoms become very large near T_c . A zone-centre optic A_g phonon is expected to soften as T_c is approached.

components of the thermal ellipsoid U_{11} , U_{22} and U_{33} of the Sn and S atoms are practically the same. However at higher temperature the anisotropy in the thermal parameters becomes pronounced. In the case of Sn atoms the component U_{11} becomes much larger than U_{22} and U_{33} at higher temperatures. In the case of S atoms U_{11} and U_{22} becomes larger than U_{33} . The principal axes of the thermal ellipsoid almost coincide with those of the crystallographic axes ($U_{12} \approx 0$). We have refined the crystal structure of β -SnS and have verified the results of the reference [8]. However, the positional parameters are more accurate in the present investigation and the lacking information of the thermal parameters of β -SnS has been obtained.

4. Pressure induced phase transition in PbS, PbSe and PbTe

Figure 2 shows the variation of the interplanar distances of PbS, PbSe and PbTe as a function of pres-

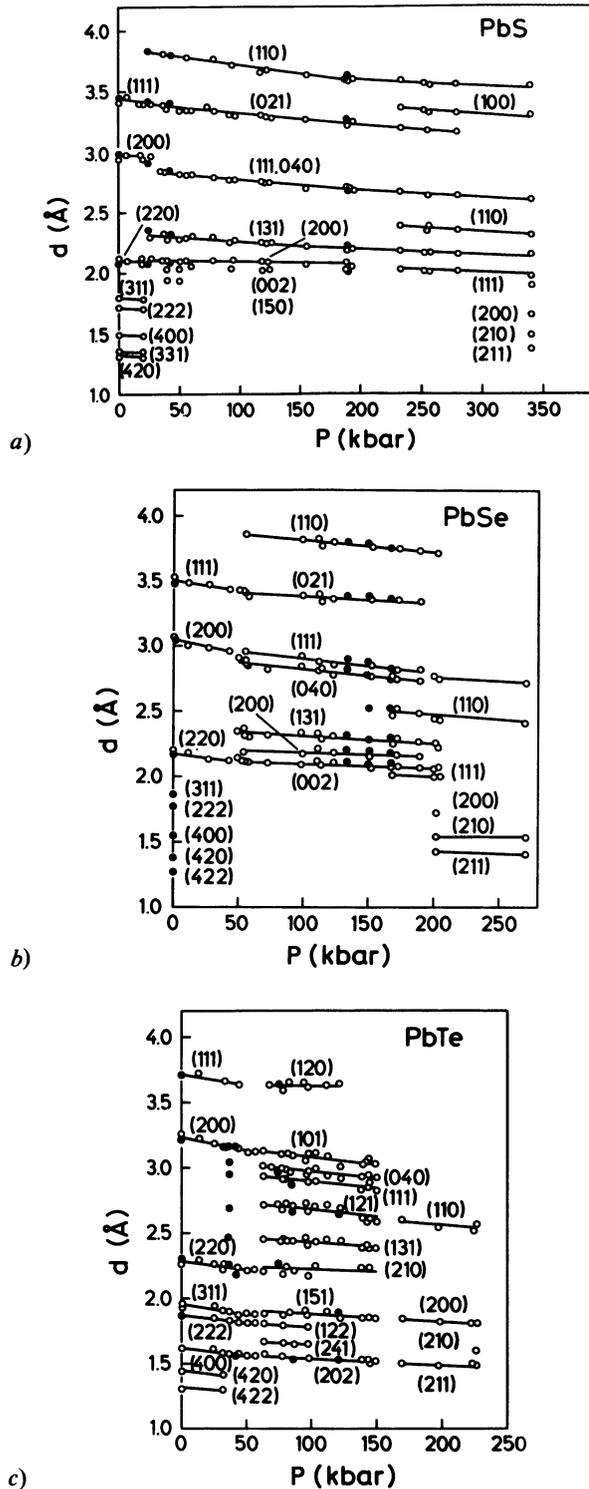


Fig. 2. — Variation of the interplanar distances d of PbS, PbSe and PbTe as a function of pressure. For all of these compounds d - P curves have two discontinuities. The discontinuities at the lower pressures have been interpreted as the first order structural phase transition from the NaCl type (B1) to the orthorhombic (B16 or B33) phase whereas the discontinuities at the higher pressures have been interpreted as the first order phase transition from the orthorhombic (B16 or B33) to the CsCl type (B2) phase. Because of the presence of the wide two phase regions the critical pressure for these phase transitions can only be roughly estimated.

sure. In all these curves we observe two prominent discontinuities. The discontinuities which occur at about 22, 45 and 60 kbar for PbS, PbSe and PbTe, respectively, correspond to the first order phase transition from the cubic NaCl type (B1) phase to the orthorhombic phase. The discontinuities at higher pressures have been interpreted as the first order structural phase transition from the orthorhombic to the CsCl type (B2) phase. Wide two phase regions exist for these phase transitions and critical pressures can only be very roughly estimated. These critical pressures for the transition from the orthorhombic to the CsCl type phases have been estimated to be 215, 160 and 130 kbar for PbS, PbSe and PbTe, respectively. The orthorhombic to the CsCl type transitions in PbS, PbSe and PbTe have been observed by us for the first time to our knowledge [23]. However, this phase transition in PbTe has been also reported by Fuji *et al.* [24]. Figure 3 shows the variation of the

interplanar distances with pressure for the orthorhombic IV-VI compounds GeS and GeSe. No discontinuities have been observed for these compounds and also for SnS and SnSe to about 340 kbar. The orthorhombic IV-VI compounds retain their crystal structure up to about 340 kbar. Figure 4 shows the variation of the volume as a function of pressure for PbS, PbSe, PbTe and GeS. The bulk modulus B_0 and its pressure derivative B'_0 at $P = 0$ obtained by fitting Birch equation to the volume — pressure data are given in table I. The orthorhombic GeS, GeSe and SnSe and the high pressure orthorhombic modifications of PbS, PbSe and PbTe have comparable bulk modulus. The NaCl type phases of PbS, PbSe and PbTe have lower bulk moduli compared to the orthorhombic modifications whereas the CsCl type phases have higher bulk moduli. The pressure derivative of the bulk modulus B'_0 at $P = 0$ is almost the same for all phases of the IV-VI compounds with the average value of about 5.

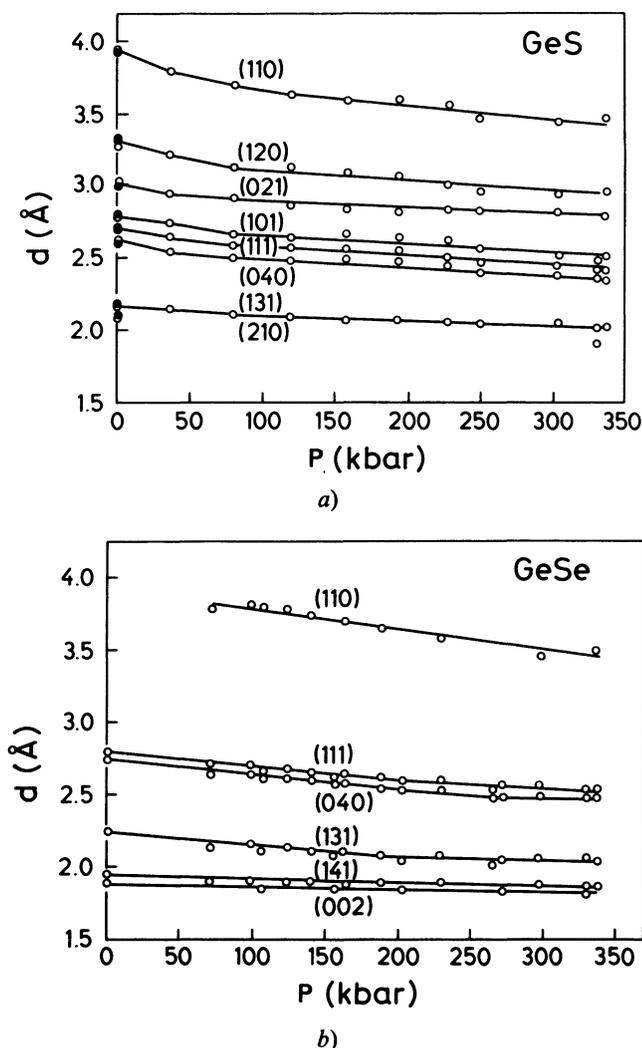


Fig. 3. — Variation of the interplanar distances d of the orthorhombic IV-VI compounds GeS and GeSe as a function of pressure. Absence of discontinuity indicates that GeS and GeSe retain their orthorhombic (B16) structure up to about 340 kbar. Similar results have been obtained for SnS and SnSe.

Table I. — Bulk modulus B_0 and its pressure derivative B'_0 at $P = 0$ for IV-VI compounds.

Compound	B_0 (kbar)	B'_0	Compound	B_0 (kbar)	B'_0
GeS	583(4)	5.0	PbS (NaCl)	—	—
GeSe	475(4)	5.1	PbSe (NaCl)	288	4.1
SnSe	503(5)	6.3	PbTe (NaCl)	389(1)	5.4
PbS (orth.)	622(8)	4.2	PbS (CsCl)	1890(6)	4.8
PbSe (orth.)	730(9)	4.5	PbSe (CsCl)	1969	5.0
PbTe (orth.)	368(2)	4.5	PbTe (CsCl)	381(6)	5.4

We have compared the observed and calculated intensities of the diffraction peaks of the high pressure orthorhombic modifications of PbS, PbSe and PbTe. The calculated peak positions and intensities have been obtained from two different structure models — the GeS type (B16) and the TII type (B33). The projections of these two types of structures along [001] direction have been shown in figure 5. A careful comparison of the peak positions and intensities suggest that the high pressure orthorhombic modifications of PbS and PbSe have the TII type (B33) structure and not the GeS type (B16) as the previous authors [16-18] have suggested. The orthorhombic PbTe has, however, the GeS type structure. In the case of orthorhombic PbS and PbSe we could not identify any reflection with $h + k = 2n + 1$ characteristic of the GeS type structure. GeS and TII type structures are closely related. TII type (B33, Cmc m) is more symmetrical and possesses C face centring whereas the GeS type (B16, Pbn m) has a primitive lattice. It is to be noted that SnS and SnSe undergo a second order displacive phase transition from the GeS type α -phase to the TII type β -phase [8, 10]. However, the conventional energy dispersive high pressure X-ray diffraction technique has low resolution and the intensities can be obtained only approximately. We therefore plan to

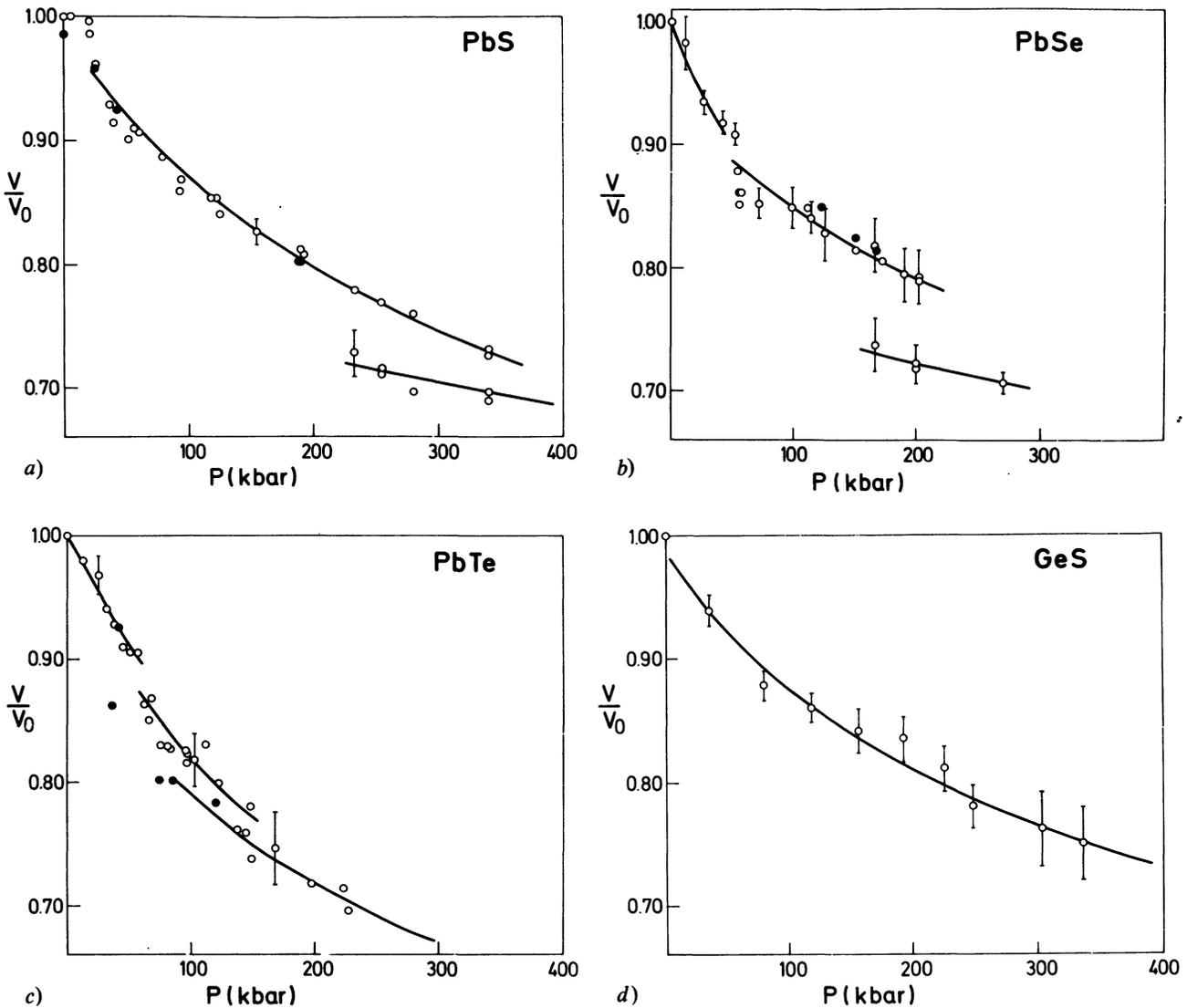


Fig. 4. — Variation of the reduced volume V/V_0 of PbS, PbSe, PbTe and GeS as a function of pressure. In the case of cubic PbS, PbSe and PbTe two discontinuities corresponding to $B1 \rightarrow B16/B33$ and $B16/B33 \rightarrow B2$ phase transitions have been observed. In the case of orthorhombic IV-VI compounds GeS, GeSe, SnS and SnSe no discontinuities have been observed.

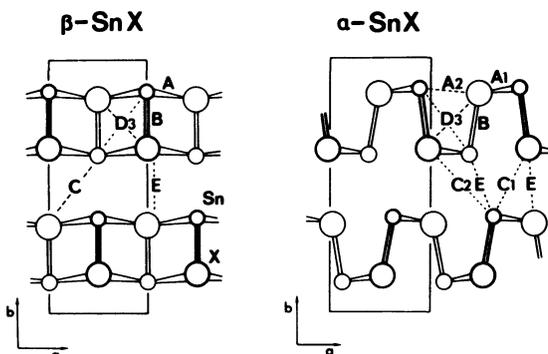


Fig. 5. — Projection of the structures of the high temperature β (TII type, B33) and the low temperature modification α (GeS type, B16) of SnS and SnSe along [001] direction. The interatomic distances shown in this figure have been explained in the reference [8]. The change in these interatomic distances at the phase transition has also been explained in the same reference.

re-examine the structure of the high pressure modifications of PbS, PbSe and PbTe with synchrotron radiation.

5. Structural stabilities of IV-VI compounds.

Temperature induced structural phase transitions in IV-VI compounds have been discussed by several authors [1, 4-9, 25, 26]. Wiedemeier and von Schnering [1] and von Schnering and Wiedemeier [8] have concluded that with increasing temperature the general trend in structural stability for the IV-VI orthorhombic compounds is $B16 \rightarrow B33 \rightarrow B1$ whereas the rhombohedral GeTe transforms to the NaCl (B1) type in one step [4, 5]. Among the orthorhombic IV-VI compounds SnS and SnSe undergo second order phase transition from GeS type (B16) phase to the TII type (B33) phase at 887 and 807 K respectively [6, 8]. GeSe

transforms at 924 K in one step to the NaCl type phase whereas GeS melts at 931 K before the possible transition to the NaCl structure [6, 9]. The mechanism of the second order phase transition in SnS and SnSe is of special interest. As is illustrated in figures 1 and 5 this phase transition is caused by the continuous movement of the Sn and S atoms mainly along [100] direction. The thermal parameters U_{11} of the Sn atoms increase anomalously and this indicates anomalous increase in the vibrational amplitudes along [100] direction. Softening of a zone-centre optical A_g mode (intralayer) is expected as the critical temperature T_c is approached.

The observed trend of the structural stability with pressure (GeTe type \rightarrow B1 \rightarrow B16 or B33 \rightarrow B2) in IV-VI compounds is approximately consistent with that with temperature (B16 \rightarrow B33 \rightarrow B1) assuming that increase in pressure is approximately equivalent to decrease in temperature. One can even understand this behaviour on the basis of the St. John Bloch plot [26, 27] for the IV-VI compounds and group V elements, using the bond orbital coordinates of Chelikowsky and Philips [38]. These bond orbital coordinates r'_σ and r''_π , defined in the reference [26], represent ionicity and covalency, respectively. We notice that the B1 \rightarrow B16 or B33 phase transition involves increase in covalency whereas GeTe \rightarrow B1 phase transition involves increase in ionicity.

Pressure induced B1 \rightarrow B2 transition is well known

and is present in many compounds including NaCl itself [29]. However, in the present investigation we have established that B1 \rightarrow B2 transition may take place indirectly through an intermediate B16 or B33 phase. This trend is not restricted to the IV-VI compounds and has also been observed recently in NaBr and NaI [30]. Whereas NaF and NaCl transform directly to the CsCl type phase at about 300 and 270 kbar, respectively, NaBr and NaI transform to the GeS type phase at 290 and 260 kbar, respectively [30]. At higher pressures NaBr and NaI might transform ultimately to the CsCl type phase. We therefore conclude that the general trend of pressure induced structural phase transition is B1 \rightarrow B16 or B33 \rightarrow B2. This is also expected if one looks closely at the geometry of these structures — TII type structure can be shown to be a logical intermediate between B1 and B2 phases [1].

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References

- [1] WIEDEMEIER, H., VON SCHNERING, H. G., *Z. Krist.* **148** (1978) 295.
- [2] WYCKOFF, R. W. G., *Crystal Structure* (John Wiley) vol. 1, 1963, p. 89.
- [3] KIKEGAWA, T., IWASAKI, H., *Acta Crystallogr.* **B 39** (1983) 158.
- [4] SCHUBERT, K., FRICKE, H., *Z. Naturforsch.* **6a** (1951) 781.
- [5] SCHUBERT, K., FRICKE, H., *Z. Metallkunde* **44** (1953) 457.
- [6] WIEDEMEIER, H., SIEMERS, P. A., *Z. anorg. allg. Chem.* **411** (1975) 90.
- [7] WIEDEMEIER, H., CSILLAG, F. J., *Z. Krist.* **149** (1979) 17.
- [8] VON SCHNERING, H. G., WIEDEMEIER, H., *Z. Krist.* **156** (1981) 143.
- [9] WIEDEMEIER, H., SIEMERS, P. A., *Z. anorg. allg. Chem.* **431** (1977) 299.
- [10] CHATTOPADHYAY, T., VON SCHNERING, H. G., PANNETIER, J., Annex to the Annual Report, Institute Laue-Langevin, Grenoble (1982) 131.
- [11] PISTORIUS, C. W. F. T., *Progress in Solid State Chemistry* (Pergamon) **11** (1976) 1.
- [12] BRIDGEMAN, P. W., *Proc. Am. Acad. Arts Sci.* **74** (1940) 21.
- [13] BRIDGEMAN, P. W., *Proc. Am. Acad. Arts Sci.* **76** (1948) 55.
- [14] SAMARA, G. A., DRICKAMER, H. G., *J. Chem. Phys.* **37** (1962) 1159.
- [15] SEMERCHAN, A. A., KUZIN, N. N., DROZDOVA, L. N., VERESHCHAGIN, L. F., *Sov. Phys. Dokl.* **8** (1964) 982.
- [16] MARIANO, A. N., CHOPRA, K. L., *Appl. Phys. Lett.* **10** (1967) 282.
- [17] KABALKINA, S. S., SEREBRYANAYA, N. R., VERESHCHAGIN, L. F., *Sov. Phys. Solid State* **10** (1968) 574.
- [18] WAKABAYASHI, I., KOBAYASHI, H., NAGASAKI, H., MINOMURA, S., *J. Phys. Soc. Jpn* **25** (1968) 227.
- [19] KABALKINA, S. S., VERESHCHAGIN, L. F., SEREBRYANAYA, N. R., *Sov. Phys. JETP* **24** (1967) 917.
- [20] SCHÖNHERR, E., STETTER, W., *J. Cryst. Growth* **30** (1975) 96.
- [21] HOLZAPFEL, W. B., *High Pressure Chemistry* (Reidel, ed. H. Kelm) 1978, p. 177.
- [22] BARRETT, J. C., BLOCK, S., PIERMARINI, G. J., *Rev. Sci. Instrum.* **44** (1973) 1.
- [23] CHATTOPADHYAY, T., WERNER, A., VON SCHNERING, H. G., Proc. IX AIRAPT, Internat. High Pressure Conference, Albany (1983).
- [24] FUJII, Y., KITAMURA, K., ONODERA, A., YAMADA, Y., to be published in *Solid State Commun.*
- [25] LUCOVSKY, G., MARTIN, R. M., BRUSTEIN, E., Proc. Conf. on Phys. of IV-VI Compounds and Alloys (University of Pennsylvania, Philadelphia, U.S.A., ed. Rabin, S., Gordon and Breach) 1974, p. 93.
- [26] LITTLEWOOD, P. B., *J. Phys. C* **13** (1980) 4855.

- [27] ST. JOHN, J., BLOCH, A. N., *Phys. Rev. Lett.* **33** (1974) 1095.
- [28] CHELIKOWSKY, J. R., PHILIPS, J. C., *Phys. Rev. B* **17** (1978) 2453.
- [29] BASSET, W. A., TAKAHASHI, T., MAO, H. K., WEAVER, J. S., *J. Appl. Phys.* **39** (1968) 319.
- [30] YAGI, T., SUZUKI, T., AKIMOTO, S., *J. Phys. Chem. Solids* **44** (1983) 135.
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