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Refinement of the structures of GeS, GeSe, SnS and SnSe

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Abstract. The orthorhombic structures ($Pbnm\text{-}D_{2h}^{16}$; No. 62) of GeS, GeSe, SnS and SnSe have been refined (X-ray diffractometer data: 319 *hkl*, $R = 0.029$; 370 *hkl*, $R = 0.061$; 386 *hkl*, $R = 0.062$; 506 *hkl*, $R = 0.076$). The bond distances are: Ge–S = 2.438(1), 2.448(2) Å; Ge–Se = 2.574(2), 2.564(3) Å; Sn–S = 2.665(2), 2.627(4) Å; Sn–Se = 2.793(2), 2.744(3) Å. The structures of these compounds reveal systematic variations of bond lengths, bond angles and of non-bonding distances. These properties as well as their temperature dependence compared to those of related compounds allow to treat these structures as different configurations of a hypothetical reaction path of a phase transition GeS type → TlI type → NaCl type.

Introduction

The monochalcogenides GeS, GeSe, GeTe, SnS, SnSe and SnTe are in many respects an interesting group of compounds. They are isoelectronic with the elements of main group V of the periodic table and, thus, form structures which may be considered derivatives of the orthorhombic black phosphorus or of the rhombohedral grey arsenic. This results in the known relationships to the NaCl and also to the TlI structure [1]. The transition of derivatives of the rhombohedral As structure to the NaCl-type (or to the primitive cubic Po structure) occurs in one step,

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whereas for the derivatives of the orthorhombic black phosphorus this transition may occur in two steps via the closely related TlI structure. Accordingly, phase transitions from the rhombohedral to the NaCl-type structure were observed for GeTe [2] and SnTe [3] at about 670 K and 75 K, respectively. However, the orthorhombic compounds GeS, GeSe, SnS and SnSe behave differently. SnS and SnSe transform at 878 K and 807 K, respectively, to the TlI-type structure [4,5] and these compounds melt before the possible transition to the NaCl-type. GeSe transforms at 924 K in one step to the NaCl structure; however, this compound reveals certain anomalies of the thermal expansion in the temperature range of about 670 – 770 K [6]. GeS displays similar anomalies of the thermal expansion in the range 500 – 780 K and melts at 931 K before the possible transition to the NaCl structure [7]. Lastly, because of their physical properties these compounds have recently gained considerable interest [8].

Since presently available structural data are not sufficiently precise (GeS, 1932, [9]; GeSe, 1965, [10]; SnS, 1935, [11]; SnSe, 1956, [12]), we consider an accurate determination of the structure data of the orthorhombic phases necessary. The results of a refinement of GeS [13] published after completion of the present investigation are essentially consistent with those of our measurements.

Procedures and Results

A primary reason for the lack of more recent investigations are probably difficulties in the growth and manipulation of single crystals of required quality. The specimens employed in this work were prepared at Rensselaer Polytechnic Institute and at Max Planck Institute by chemical transport reactions as well as by sublimation [14,15]. In view of the pronounced cleavage properties parallel to the (010) plane, particular care was taken in the manipulation of single crystals to minimize any strain. The mounting of the crystals in glass capillaries was accomplished with kanadabalsam. Despite these precautions, only about 10 % of the mounted crystals were useful for quantitative measurements. The dimensions of the investigated crystals were in the range 0.20 × 0.10 × 0.03 mm.

The refinement of lattice constants and atomic parameters is based on four-circle diffractometer data (Syntex $P\bar{1}$ diffractometer; Mo$K\alpha$; ω-scan; scintillation counter; $2\theta \leq 70°$). The lattice parameters were

Table 1. Crystallographic data of GeS, GeSe, SnS and SnSe. All atoms occupy the position 4(*c*) ± ($x y \frac{1}{4}$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4}$) of space group *Pbnm*. The anisotropic B_{ij} are defined for $T = \exp\left[-\frac{1}{4}\left(B_{11}h^2a^{*2} \pm \ldots + 2B_{12}hka^*b^* + \ldots\right)\right]$. Standard deviations are given in parenthesis

Compound	GeS		GeSe		SnS		SnSe	
a (Å)	4.299(2)		4.388(4)		4.334(1)		4.445(1)	
b (Å)	10.481(4)		10.825(9)		11.200(2)		11.501(2)	
c (Å)	3.646(2)		3.833(4)		3.987(1)		4.153(1)	
hkl	319		370		386		506	
R	0.029		0.061		0.062		0.076	
Atom	Ge	S	Ge	Se	Sn	S	Sn	Se
x	0.1277(1)	0.5023(4)	0.1115(3)	0.5020(2)	0.1198(2)	0.4793(8)	0.1035(3)	0.4819(4)
y	0.1221(1)	0.8495(1)	0.1211(1)	0.8534(1)	0.1194(1)	0.8508(3)	0.1185(1)	0.8548(2)
B (Å^2)	1.11(2)	1.02(3)	0.68(3)	0.53(3)	1.37(3)	1.05(5)	1.98(3)	1.65(3)
B_{11} (Å^2)	1.08(3)	0.98(4)	0.76(4)	0.57(4)	1.46(4)	1.15(9)	2.25(5)	1.84(5)
B_{22} (Å^2)	0.88(3)	0.75(4)	0.91(5)	0.79(5)	1.27(4)	0.98(9)	2.00(5)	1.70(6)
B_{33} (Å^2)	1.34(2)	1.27(4)	0.29(5)	0.18(4)	1.39(4)	1.16(9)	1.67(4)	1.40(6)
B_{12} (Å^2)	−0.23(2)	−0.09(4)	−0.28(4)	0.00(3)	−0.21(2)	0.03(8)	−0.20(3)	0.01(4)

Table 2. Interatomic distances (Å) and bond angles (°). Standard deviations are given in parenthesis

A(1) – *A*(2)	No.	Type[a]	GeS	GeSe	SnS	SnSe
M – X	2	*A*1 in	2.438(1)	2.574(2)	2.665(2)	2.793(2)
– X	1	*B* in	2.448(2)	2.564(3)	2.627(4)	2.744(3)
– X	2	*A*2 in	3.278(2)	3.316(3)	3.290(3)	3.343(2)
– X	1	*C*1 ex	3.280(2)	3.367(3)	3.388(4)	3.468(3)
– X	1	*C*2 ex	3.923(2)	3.943(3)	4.093(4)	4.103(3)
– M	2	*D*1 in	3.646(2)	3.833(4)	3.987(1)	4.153(1)
– M	2	*D*2 in	4.299(2)	4.388(4)	4.334(1)	4.445(1)
– M	4	*D*3 in	3.890(2)	4.034(3)	4.151(2)	4.290(2)
– M	2	*E* ex	3.329(2)	3.392(3)	3.494(2)	3.548(2)
X – X	2	*D*1 in	3.646(2)	3.833(4)	3.987(1)	4.153(1)
– X	2	*D*2 in	4.299(2)	4.388(4)	4.334(1)	4.445(1)
– X	4	*D*3 in	3.506(2)	3.674(2)	3.711(4)	3.881(3)
– X	2	*E* ex	3.644(2)	3.708(3)	3.896(6)	3.936(4)
Angle						
X – M – X	2		91.72(4)	91.31(4)	89.03(8)	88.99(5)
X – M – X	1	in (010)	96.81(7)	96.24(9)	96.82(12)	96.04(7)
M – X – M	2		105.54(4)	103.49(4)	103.30(9)	101.55(6)
M – X – M	1	in (010)	96.81(7)	96.24(9)	96.82(12)	96.04(7)

[a] in = intra double layer, ex = inter double layers

determined from a set of 15 reflections each which included symmetry-equivalent and Friedel reflections. The observed data (Table 1) agree within 2σ with lattice constants determined from powder diffraction patterns [4,6,7]. The intensities were corrected experimentally for absorption by ψ-scan. The refinement of positional and thermal parameters was done by least-squares methods using the XTL program system (Syntex) and a Nova 1200 computer. We used reflections with $I \geq 2\sigma(I)$ which were weighted with σ^{-2}. Lattice parameters, atomic positions, thermal parameters and the most important interatomic distances and bond angles are summarized in Table 1 and Table 2.

It should be noted that we selected the space group setting *Pbnm* as was originally chosen by Zachariasen [9] for the B16-type. We omit the structure factor tables which are available upon request from one of us (H.G.v.S.).

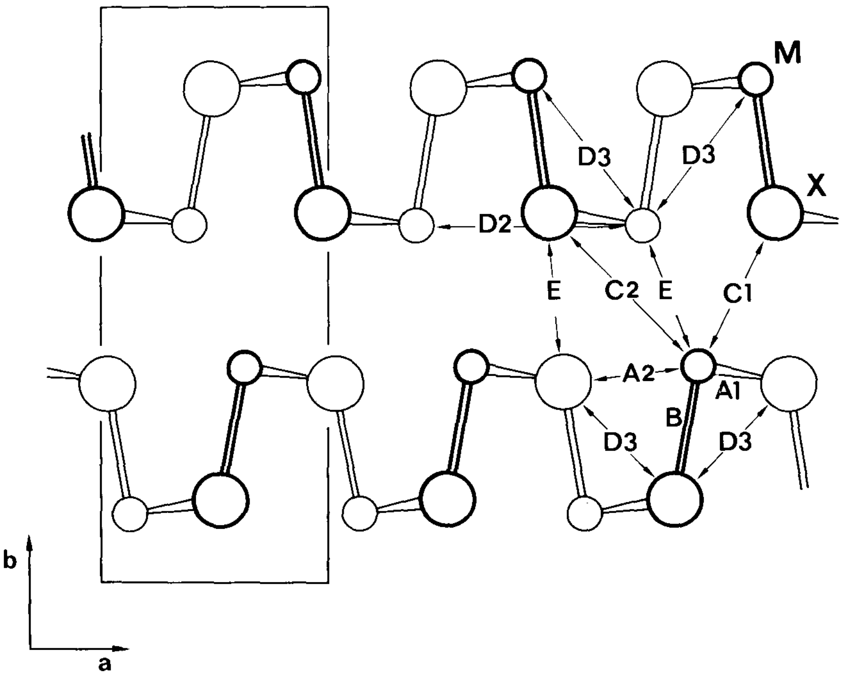

Fig. 1. Projection of the SnS structure down [001]. Sn (M = small circles) and S (X = large circles) in different heights are represented by light ($z = \frac{1}{4}$) and heavy ($z = \frac{3}{4}$ lines. The different types of important interatomic distances are given as listed in Table 2

Discussion

The present redetermination of the structure of GeS, GeSe, SnS and SnSe yielded accurate distances and bond angles which are of interest for detailed discussions. The deviations from the bond distances of earlier investigations are in the range ± (0.01 – 0.03) Å. This shows again how well the positional parameters have been determined in earlier studies on the basis of film data [10 – 12]. The recently published work by Bissert and Hesse [13] revealed surprising deviations for some data up to 3σ. Our standard deviations of the positional parameters are, however, considerably smaller since a larger number of reflections (*hkl*) is available in the present work.

Since the structure of these IV – VI phases has been treated frequently, a detailed description is not necessary. The projection of the structure along the shortest axis [001] is shown in Figure 1. The different types of interatomic distances listed in Table 2 are also given in Figure 1.

Some relationships to other structures are important. The GeS structure type (B16) is related to the TlI and NaCl structure as well as to the zincblende structure. Analogous relations exist for the structures of black phosphorus, of polonium and of diamond. The IV–VI compounds may be viewed as pseudo group-V-elements, whose structures display three covalent bonds. A system of condensed six-membered rings in chair comformation is the common feature of the two dominant structures, namely of that of the orthorhombic black phosphorus and of the rhombohedral grey arsenic. They differ essentially only in the conformation of the ring connection which in the case of As is exclusively equatorial (eq_6), in the case of P, however, partially axial ($eq_4\ ax_2$). This yields relatively flat 2-dimensional six-membered rings (As and GeTe) in one case and strongly puckered double layers (black phosphorus and GeS) in the other. Both structure types can be cut out of the diamond structure, namely parallel (111) and parallel (110), respectively. Since the breaking of the fourth bond is equivalent to the formation of lone electron pairs, the remaining 6-ring nets have to shift with respect to each other. In the case of the As nets, this shift moves the atoms in a 'natural way' into positions very close to those of the *Po* structure (NaCl structure). A shift by a quarter of the diagonal [110] brings the puckered (110) nets from the diamond structure into the positions of the orthorhombic phosphorus structure. In other words, the GeS structure is different from a diamond like structure by a $c/2$ shift (*Pbnm* setting with $c<a<b$). On the other hand, the GeS structure can be transformed by a shift of $a/2$ to a NaCl like arrangement. Therefore, the GeS structure is similarly related to the diamond and NaCl type structure. The above mentioned $a/2$ shift differentiates also the TlI structure and the NaCl structure. Thus, the GeS and TlI structures are very closely related. The packing of the double layers of these two structures is hardly different. Only within the double layers there is a change from a (3 + 2) coordination to a 5 coordination which is caused by a movement of one atom into the center of the a,c-plane.

The transition GeS→TlI equilibrates the distances $A1$ and $A2$ ($A1 = A2 \simeq B$). The intralayer distances of type $D1$, $D2$ and $D3$ change because of the reversal of the axial ratio a/c, however, the weighted mean value remains $\bar{D} \simeq (A,B) \cdot \sqrt{2}$. This behavior of the distances A,B,D satisfies also the transition GeS→NaCl and, there-

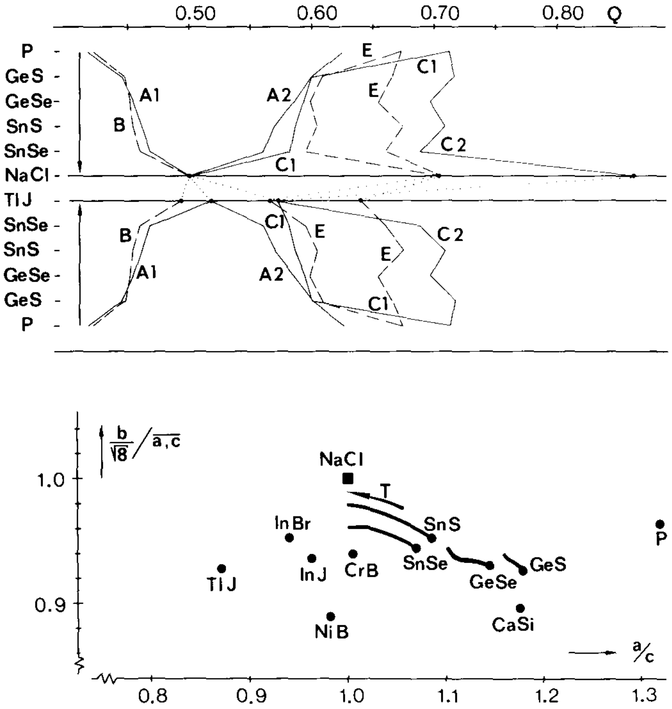

Fig. 2. *Top:* Change of the reduced distances Q for related structures. Types and values of distances are listed in Table 2. The distances have been reduced dividing by the cube root of the cell volume. *Bottom:* Plot of the important axial ratios for some IV – VI and related compounds. For SnS, SnSe, GeS and GeSe the change of axial ratios from room temperature (●) up to the phase transition [4,6] and the melting point [7], respectively, are indicated by heavy lines

fore, they cannot be criteria for the primary structure relation and for structural transitions. The interlayer distances of type C and E differ considerably from types A,B and D with respect to structural relations. Because of the necessary relative $a/2$ shift of the double layers in the transition to NaCl, the type C distances split into two completely different lengths A and $A\sqrt{3}$. However, in the transition to TlI, the C distances remain essentially the same type. Similar arguments can be presented for the interlayer distances of type E. In the upper part of Figure 2 we have plotted the reduced interatomic distances (reduced with respect to the cuberoot of the cell volume) of some structures. The different kind of changes of the distances of types

A and *B* on the one hand and of types *C* and *E* on the other are obvious.

In addition, the upper part of Figure 2 clearly shows that the structures of *P*(black), GeS, GeSe, SnS and SnSe may be considered in this order a reaction path for the phase transitions P→TlI→NaCl or, with some restriction, for the transition *P*→NaCl. This is supported by a graphical representation of the axial ratios (Fig. 2, lower part) of these and related compounds. In particular, the unit cells of SnS and SnSe change continuously between room temperature and 878 K and 807 K, respectively (broad lines), at which temperatures the transition to the TlI structure with $a/c \simeq 1.00$ occurs without a further marked change of the unit cell [4,5]. This behavior supports the concept of a reaction path in a most instructive way. The reason why the axial ratios during the transition SnS→TlI do not directly approach the TlI values but proceed via an upper value for the ratio $(b/\sqrt{8}):(\overline{a,c})$ is not yet fully understood. This effect could be the reason for the observation that GeSe and GeS, whose structures obviously differ more from the TlI-type than those of the Sn compounds, after an intermediate period change abruptly to the NaCl type, respectively melt before the transformation [6, 7].

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