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The high temperature structure of β-SnS and β-SnSe and the B16-to-B33 type λ-transition path

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Abstract. The high temperature modifications β-SnS and β-SnSe crystallize in the orthorhombic TlI-type structure [*Cmcm*, No. 63; SnS at 905 K: $a = 4.148(2)$, $b = 11.480(5)$, $c = 4.177(2)$ Å; SnSe at 825 K: $a = 4.410(6)$, $b = 11.705(7)$, $c = 4.318(4)$ Å]. For the λ-type phase transition $\alpha \rightarrow \beta$ from the GeS-type (B16) to the TlI-type (B33) the atomic shifts were determined from about 200° below the critical temperature to T_c (878 K and 807 K). They show a continuous transition from threefold to fivefold bonded atoms. This change in topology and bond character corresponds to the model of a S_N2 chemical reaction. There is an indication of a possible first-order transition near T_c.

Introduction

Recently phase transitions of SnS and SnSe have been reported [1]. The thermal effects associated with these transitions at 878 K and 807 K, respectively, are very small. This is due to the fact that the actual transition is preceded by an induction range extending over several hundred degrees. In this temperature interval, the values of the a-axis and c-axis approach each other while the long b-axis expands continuously. At the so-called transition temperature, the values of a and c are indistinguishable on X-ray Debye powder patterns. The b-axis, however, does not reach the length corresponding to a transition to the NaCl-type structure as observed for GeSe [2]. In connection with the recent refinement of the structures of GeS, GeSe, α-SnS and α-SnSe [3] we have pointed out, that the structural details and also the thermal behavior of these compounds can be seen as if the structures were arranged along a hypothetical reaction path of a phase transition GeS(B16-type) → TlI(B33-type). The present work demonstrates that the high tem-

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perature modifications β-SnS and β-SnSe indeed possess the TlI structure and that these compounds undergo λ-type transitions

Structure of β-SnS and β-SnSe

The preparation of the investigated compounds SnS and SnSe has been discussed earlier [3]. The present investigation of the high temperature structures is based on single crystal film data and Guinier-Simon powder patterns [4]. Single crystal investigations are rather difficult since in the temperature range of interest the vapor pressures of SnS and SnSe are such that the crystals sublime and the quartz capillaries crack. In addition, reactions occur with the cement used for the mounting of the crystals. For the above reasons we have used primarily film data. At these temperatures single crystals remained intact only for a few hours. However, this time was sufficient in order to determine unambiguously such important aspects as the Laue-symmetry and the space group. The single crystal film data reveal unambiguously the change in symmetry from *Pbnm* to *Cmcm* for the transition α-SnS → β-SnS and α-SnSe → β-SnSe. The Laue-symmetry thus remains *mmm*-D_{2h} (not tetragonal [1]).

The axial ratios and the symmetry of β-SnS and β-SnSe suggest strong relations to the structures of TlI, CrB and CaSi [5–9]. These structures differ essentially in the parameters y (M) and y (X) which leads in the case of TlI to a structure with nearly commutable sublattices (CN 5 or 5 + 2), whereas in the structures of CrB and CaSi the changing of y(X) leads to the formation of covalently bonded X–X zig-zag chains. Therefore, the problem is reduced to the determination of only two positional parameters. This clearly can be done well enough with a limited number of powder intensities. The intensities of reflections were obtained from the powder patterns using a Kipp and

Table 1. Crystallographic data of β-SnS and β-SnSe (standard deviations)

	β-SnS	β-SnSe
T(K)	905	825
Space group	*Cmcm* (No. 63)	*Cmcm* (No. 63)
a (Å)	4.148(2)	4.310(6)
b (Å)	11.480(5)	11.705(7)
c (Å)	4.177(2)	4.318(4)
y(Sn)[a]	0.120(3)	0.120(2)
y(S,Se)[a]	0.349(6)	0.356(3)
hkl	20	15
R	0.10	0.06

[a] Atoms at position 4 (c) $0, y, \frac{1}{4}$

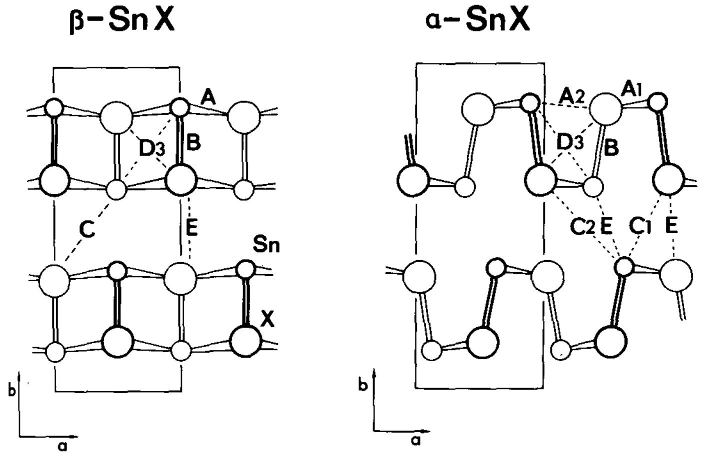

Fig. 1. Projection of the structures of the high temperature modification β (TlI-type) and of the low temperature form α (GeS-type) along [001]. The most important interatomic distances are identified by letters (see Table 2)

Zonen densitometer (DD2) as well as a Syntex AD1 densitometer and were evaluated in a conventional manner. The reflections (0*k*0) which could be affected by textures were checked by single crystal photographs.

For the determination of the atomic positional parameters initially the intensities of overlapping reflections were omitted. Subsequently, these intensities ΣI_0 were apportioned in the ratio of the calculated structure factors F_0^2 and then used in the final refinement. The quantitative evaluation of the powder intensities from the Guinier-Simon films was done by LSQ

Table 2. Interatomic distances (Å); the standard deviations are given in parentheses

A–B	No.	Type[a]	β-SnS (905 K)	β-SnSe (825 K)
M–X	1	B	2.63(8)	2.76(4)
–X	4	A	2.96(1)	3.06(5)
–X	2	C	3.74(6)	3.77(3)
–M	2	D1 = *a*	4.148(2)	4.310(6)
–M	2	D2 = *c*	4.177(2)	4.318(4)
–M	4	D3	4.19(5)	4.31(3)
–M	2	E	3.46(5)	3.54(4)
X–X	2	D1 = *a*	4.148(2)	4.310(6)
–X	2	D2 = *c*	4.177(2)	4.318(4)
–X	4	D3	3.72(8)	3.93(4)
–X	2	E	4.05(12)	4.00(6)

[a] See Figure 1

Table 3. Observed structure factors $|F_o|$ from powder intensities

β-SnS				β-SnSe			
hkl	$\|F_o\|$	*hkl*	$\|F_o\|$	*hkl*	$\|F_o\|$	*hkl*	$\|F_o\|$
200	170	130	69	200	231	151	193
240	151	080	131	240	194	202	181
021	106	131	135	111	190	040	240
061	127	002	170	041	90	080	141
112	76	042	151	002	231	131	150
110	81	040	236	110	47	171	110
150	138	111	137	150	74	042	194
221	80	151	133	021	52		
171	97	202	145				
132	56	152	110				

methods in the usual way. The results are given in Table 1 and Figure 1. The interatomic distances and the structure factors are listed in Table 2 and Table 3, respectively.

Phase transition

In Figure 2 Guinier-Simon photographs [4] of SnS and SnSe as well as a schematic representation of a part of the diffraction pattern of SnS are shown. The following details are clearly evident:

(1) The transition of SnS and SnSe from the α- to the β-modification is a continuous process and becomes increasingly pronounced from about 200° below the critical temperature T_c [1].

(2) All reflections *hkl* with $h + k = 2n + 1$ disappear at T_c. However, their intensities do not change abruptly but reveal measurable changes already about 100° below T_c.

(3) The lattice parameters a and c continuously approach the same value. However, the axial ratio changes from $a/c > 1$ to $a/c < 1$ over a range of about 5° at T_c. It is uncertain whether this last change in unit cell dimensions is continuous or not.

During the phase transition, the shift of the atoms is solely due to changes of the x-parameters. The determination of the latter is relatively simple through a comparison of intensities I_0 $(h = 0)$ with I_0 $(h \neq 0)$. For the evaluation of the diffraction patterns, the intensities of the reflections *(110)*, *(120)*, *(021)* and *(101)* were measured at six different temperatures. The y-parameters are practically identical in the α- and β-forms. Therefore, only the x-shifts have to be considered which fall in the range $0 \leq x_1 \leq 0.12$ and $0.50 \geq x_2 \geq 0.48$ (x_1 for Sn; x_2 for S, Se). The variation of x_2 is minimal and

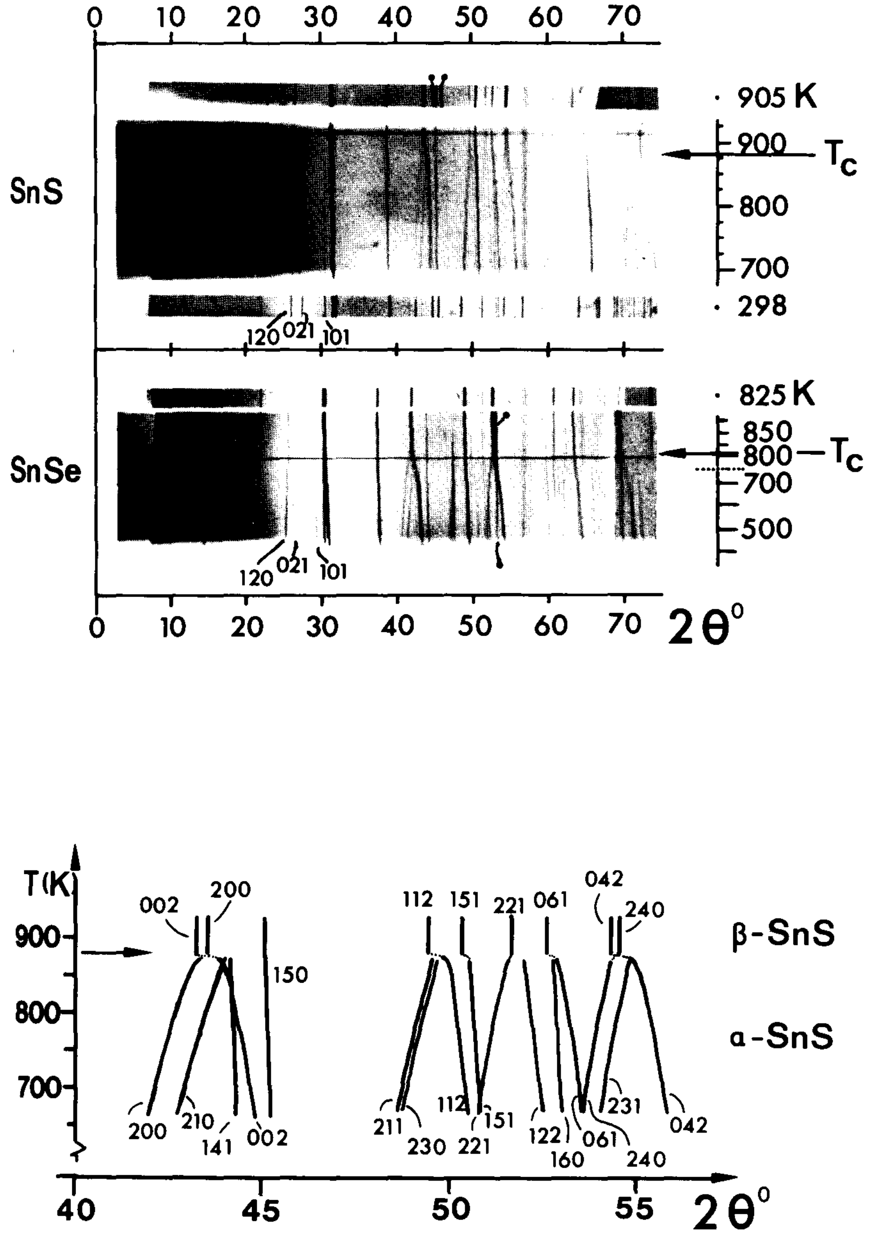

Fig. 2. Guinier-Simon X-ray diffraction powder photographs of SnS and SnSe. The intensities of the reflections (120), (021) and (101) shows clearly the gradual change of the x-parameters from about 200° below T_c. (Some foreign reflections are marked by dots). The bottom part shows schematically the shift of the SnS reflections for a limited range

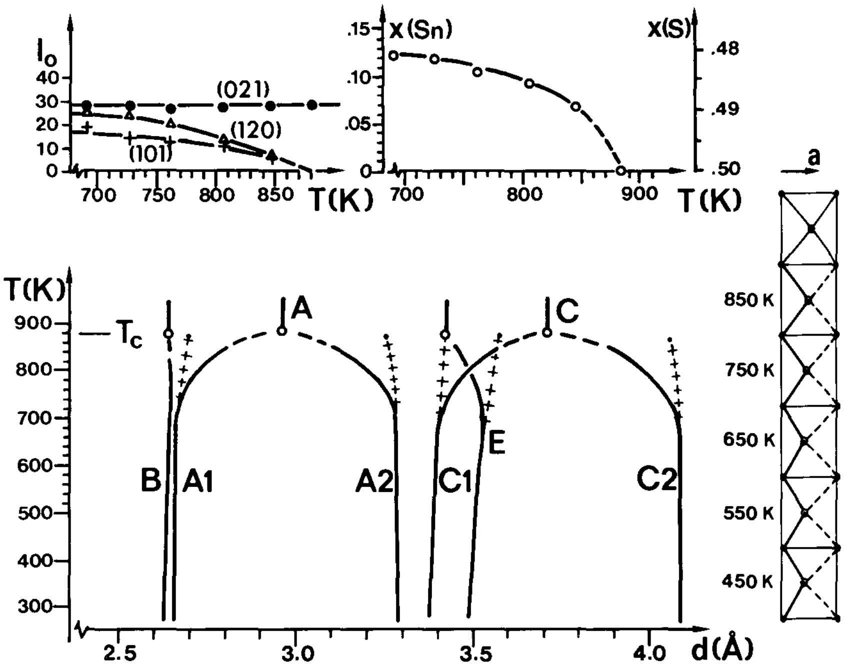

Fig. 3. λ-type transition of SnS. *Upper left:* Change of the intensities of (021), (120) and (101) (compare Fig. 2). *Upper right:* Variation of x(Sn) and x(S) with temperature. *Lower left:* Change of the most important interatomic distances with temperature. The lines indicated by (+) represent the hypothetical changes of distances solely based on lattice parameter changes (constant x-parameters). *Lower right:* Schematic representation of the movement of the two atoms in the plane parallel (010) at $y = 0.120$

negligible as a first approximation. In addition, the atomic scattering factors $f_1 = f(\mathrm{Sn})$ and $f_2 = f(\mathrm{S,Se})$ are nearly unchanged for the four reflections with a ratio of approximately $f_1 : f_2 \simeq 3.1$ in the case of SnS. Thus, the reduced structure factors are given by:

$$F(110) \hat{=} 0.73 \cdot \cos 2\pi x_1 - 0.19, \qquad (1)$$

$$F(120) \hat{=} \sin 2\pi x_1 - 0.04 \simeq \sin 2\pi x_1, \qquad (2)$$

$$F(021) \hat{=} 1 - 0.30 = 0.70, \qquad (3)$$

$$F(101) \hat{=} \sin 2\pi x_1 + 0.04 \simeq \sin 2\pi x_1. \qquad (4)$$

The measured structure factors F_0 were normalized with respect to F(021). The approximations for x_1 obtained with (2) and (4) were averaged including (1). In a second step the variation of x_2 was examined yielding only minimal shifts. The parameters and subsequently calculated most important distances for SnS are represented in Figure 3. The parameters for SnSe are practically identical, however they are less certain because of the similar scattering power of Sn and Se.

Discussion

The results of the present investigation demonstrates that the high temperature modifications of SnS and SnSe have the TlI-type structure (Fig. 1). In this structure the atoms are arranged in double layers and the two crystallographically independent atoms form nearly commutable substructures. The double layers are basically two-dimensional infinite slices of the NaCl structure. The essential difference between the two structures, namely the NaCl- and the TlI-type, is simply an $a/2$ shift which occurs upon stacking of the TlI-blocks along the b-axis. As a result of this shift both atoms have coordination number 7 or coordination number $5 + 2$ with 5 strong bonds within the two-dimensional infinite blocks and 2 additional weak bonds to the neighbouring block. Therefore, the (1,4,2)-polyhedra have the very different bond distances of type A, B and C (Fig. 1 and Table 2). Because of the different y-parameters the Sn atoms slightly stick out of the double layers. This configuration is typical for all members of the TlI-type structure for which the cations have a lone pair electron configuration. For β-SnS and β-SnSe the short bonds of type B are as long as in the predominantly covalent α-modifications [3]. The A-type bonds are longer and correspond very well to the smaller bond order $n = 0.5$. The other bonds of type C are only weaker bonds ($n = 0.2$) [10].

The relations between the structures of GeS, TlI and NaCl have been discussed extensively elsewhere [3, 5]. It should be emphasized again, that the TlI-structure is a natural intermediate between the GeS- and the NaCl-structure. This is particularly important for the phase transformations of IV–VI compounds. In the discussion of this transformation an essential detail must be mentioned. For the TlI-type $a/c < 1$ since only in this way the repulsion of equally charged atoms can be reduced at the common (010) plane of neighbouring blocks. (E-type distances). In the GeS structure, however, $a/c > 1$, because, in this case the covalently bonded nets of condensed six-membered rings are dominant. A further interesting aspect is the relation to the CsCl-type structure (e.g. TlI crystallizes in this type above 448 K). Shearing of the strong B-type bonds through an $a/2$ shift within the double layers directly leads to the CsCl-structure. Then, the b-axis would correspond to $[110]_{CsCl}$ and the a-axis to $[001]_{CsCl}$. It is an interesting speculation to view a CsCl – NaCl transition to proceed via shifts of neighbouring $(110)_{CsCl}$ planes by $c/2_{CsCl}$ creating intermediate TlI configurations.

The significant conclusions concerning the pathway of the above λ-transition (Fig. 3) are as follows. The atomic distances A1, A2 and C1, C2 change gradually and continuously towards equality by changing the atomic positional parameters. A pronounced change begins nearly 200° below the critical temperature T_c where $A1 = A2$ and $C1 = C2$. However, with unchanged positional parameters this equalities cannot be accomplished through lattice parameter changes alone. The change in unit cell dimensions from those typical for the GeS-type ($a/c < 1$) to that for the TlI-type ($a/c > 1$) occurs over a narrow range of about 5°. Thus, the actual transition of a configuration of condensed six-membered rings with threefold covalently bonded atoms to a configuration with degenerate bond state ($1 + 4/2$ bonds) happens in this range. It is not certain whether this last structural switch between $T_c - 5°$ and T_c is continuous or not. However, in view of the magnitude of the change, a discontinuity is not unlikely. Thus, the λ-transition could possibly have some degree of first-order.

The above observations suggest, that the SnS (and SnSe) transformation is characterized by two processes, namely, a shift of atomic positions and a change in unit cell dimensions. Only after the atomic distances A1, A2 and C1, C2 are nearly equal, the switch in lattice parameters can occur and complete the transition. The so-called transition point represents the end temperature of an "induction" period which is dominated by continuous changes in atomic positions. At this temperature T_c (or very close to it) the adjustment in lattice parameters occurs. The apparent reluctance of the unit cell dimensions to change at a rate similar to that of the atomic positions suggests, that the transformation is governed by the change of the latter. In analogy to other homogeneous chemical reactions, this suggest the existence of an energy barrier in the transition mechanism. In this mechanism, the reaction coordinate is the change in atomic positions and the "activated state" of the unit cell is the point where $A1 = A2$ and $C1 = C2$ (or $A1 \simeq A2$, $C1 \simeq C2$). The above interpretation and the topology of the overall transition are consistent with the model of a S_N2 chemical reaction.

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