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## The Incommensurate Misfit Layer Structure of $(\text{SnS})_{1.17}\text{NbS}_2$ , 'SnNbS<sub>3</sub>'. I. A Study by Means of X-ray Diffraction

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### Abstract

$(\text{SnS})_{1.17}\text{NbS}_2$ ,  $M_r = 334.92$ , is a compound with misfit layer structure consisting of two-atom-thick layers of SnS and three-atom-thick sandwiches of  $\text{NbS}_2$  which alternate along the  $c$  axis. The lattices of SnS and  $\text{NbS}_2$  both have  $C$ -centered orthorhombic unit cells which match along the  $b$  and  $c$  axes but not along the  $a$  axes. The unit cells and space groups are  $a = 5.673$  (1),  $b = 5.750$  (1),  $c = 11.760$  (1) Å, space group  $C2mb$  (no. 39),  $Z = 4$ , for SnS;  $a = 3.321$  (1),  $b = 5.752$  (1),  $c = 11.763$  (1) Å, space group  $Cm2m$  (no. 38),  $Z = 2$ , for  $\text{NbS}_2$ . From the ratio of the lengths of the  $a$  axes of the two parts of the complete structure ( $5.673/3.321 = 1.708$  being irrational) one obtains a composition  $(\text{SnS})_{1.17}\text{NbS}_2$ . The structure determination consisted of three parts: the structures of the SnS and  $\text{NbS}_2$  parts separately and their relative position. Intensities were measured with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at  $T = 293$  K,  $\mu = 102.3$  cm<sup>-1</sup>. For the SnS part  $R_F = 0.088$  for 306 unique reflections; for the  $\text{NbS}_2$  part  $R_F = 0.031$  for 329 unique reflections (for both cases  $0kl$  reflections excluded). The relative position of these two lattices was determined from the common reflections  $0kl$ :  $R_F = 0.072$  for 98 reflections. The SnS part of the structure consists of deformed slices of SnS with a thickness of half the cell edge of (hypothetical) NaCl-type SnS. Each Sn atom is in this way coordinated by five sulfur atoms; four sulfur atoms are in a plane perpendicular to the  $c$  axis with SnS distances 2.74 (1) (1×), 2.913 (1) (2×) and 3.01 (1) Å (1×), whereas the fifth Sn–S bond with length 2.695 (9) Å is approximately along the  $c$  axis. The  $\text{NbS}_2$  part of the structure is that of  $\text{NbS}_2 \cdot 2H$  with Nb in trigonal prisms of sulfur; the Nb–S distances are 2.473 (1) Å. From

refinement of the common  $0kl$  reflections the relative  $y$  and  $z$  positions of the two sublattices were found; along the common  $a$  direction the lattices of SnS and  $\text{NbS}_2$  are incommensurate.

### Introduction

Compounds of assumed composition  $MTX_3$  ( $M = \text{Sn, Pb}$ ;  $T = \text{Ti, V, Nb, Ta}$ ;  $X = \text{S, Se}$ ) have been known for a considerable time (Schmidt, 1970; Sterzel & Horn, 1970; van Maaren, 1972; Donohue, 1975). The crystals obtained by syntheses from the elements have an appearance suggesting a layered structure but owing to very easy plastic deformation it has so far not been possible to determine the structure. X-ray powder diffraction revealed tetragonal or pseudo-tetragonal unit cells with  $a = 4$ ,  $c = 12$  Å. We succeeded in growing single crystals by vapor transport using chlorine as transport agent. In this paper the determination of the misfit layer structure of 'SnNbS<sub>3</sub>' is described; the composition of the compound turned out to be  $(\text{SnS})_{1.17}\text{NbS}_2$ ; it will be designated for brevity as 'SnNbS<sub>3</sub>'.

### Experimental

'SnNbS<sub>3</sub>' could be grown as thin platelets with diameters up to about 5 mm. The black crystals are mechanically very soft and have a brilliant luster. The starting material was SnNbS<sub>3</sub> obtained by syntheses from the elements at 1123 K and the temperature gradient was 1113–1043 K; transport was to the low-temperature side of the quartz tube.

### Structure determination

Single-crystal X-ray diffraction with an Enraf-Nonius CAD-4F diffractometer using monochromatized Mo

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Table 1. *Crystal data and details of the structure determination*

<b>(a) SnS part</b>		$\omega/2\theta$ scan ( $^\circ$ )	$\Delta\omega = 1.00 + 0.35 \tan \theta$
Crystal data		Data set	$h: -6 \rightarrow 6; k: 0 \rightarrow 10; l: -21 \rightarrow 21$
Space group, no.	<i>C2mb</i> , 39	Crystal-to-receiving aperture	
<i>a</i> (Å)	5.673 (1)	distance (mm)	173
<i>b</i> (Å)	5.750 (1)	Horizontal, vertical aperture (mm)	4.0, 4.5
<i>c</i> (Å)	11.760 (1)	Reference reflections r.m.s. dev. (%)	021, 0.55 023, 0.65 008, 0.62
<i>V</i> (Å <sup>3</sup> )	383.6 (1)	Drift correction	0.991–1.000
<i>Z</i>	4	Min. and max. absorption correction	
<i>F</i> (000), electrons	264	factors	1.06–2.48
Approx. crystal dimensions (mm)	0.18 × 0.11 × 0.003	X-ray exposure time (h)	18.4
<b>Data collection</b>		Total data	1464
Diffractometer	Enraf–Nonius CAD-4F	Unique data	429
Radiation (Å)	Mo <i>K</i> α, 0.71073	Observed data [ $I \geq 2.5 \sigma(I)$ ]	427
Monochromator	Graphite	$R1 = [\sum(I - \bar{I})/\sum I]$	0.041
Temperature (K)	298	$R2 = [\sum \sigma/\sum I]$	0.034
$\theta$ range; min. max. ( $^\circ$ )	1.73, 34.99	Number of equivalent reflections	1458
$\omega/2\theta$ scan ( $^\circ$ )	$\Delta\omega = 0.80 + 0.35 \tan \theta$	<b>Refinement</b>	
Data set	$h: -9 \rightarrow 9; k: 0 \rightarrow 9; l: -18 \rightarrow 18$	Number of reflections $h \neq 0$	329
Crystal-to-receiving-aperture		Number of refined parameters	10
distance (mm)	173	Final agreement factors;	
Horizontal, vertical aperture (mm)	4.0, 4.5	$R_F = \sum( F_o  -  F_c )/\sum F_o $	0.031
Reference reflections, r.m.s. dev. (%)	021, 0.53 233, 0.41 008, 0.46	$wR = [\sum w( F_o  -  F_c )^2/\sum w F_o ^2]^{1/2}$	0.036
Drift correction	0.996–1.000	Weighting scheme	1
Min. and max. absorption correction		$S = [\sum w( F_o  -  F_c )^2/(m - n)]^{1/2}$	1.079
factors	1.06–2.08	$m =$ number of observations	
X-ray exposure time (h)	20.3	$n =$ number of variables	
Total data	1828	Residual electron density in final	
Unique data	498	difference Fourier map ( $e \text{ \AA}^{-3}$ )	–1.52, 3.29
Observed data [ $I \geq 2.5 \sigma(I)$ ]	430	Max. (shift/ $\sigma$ ) final cycle	0.224
$R1 = [\sum(I - \bar{I})/\sum I]$	0.055	Average (shift/ $\sigma$ ) final cycle	0.031
$R2 = [\sum \sigma/\sum I]$	0.035	<b>(c) Projection down [100]</b>	
Number of equivalent reflections	1824	Crystal data	
<b>Refinement</b>		Chemical formula	(SnS) <sub>1-17</sub> (NbS <sub>2</sub> )
Number of reflections $h \neq 0$ and $h \neq 5$	306	Mol. wt	334.92
Number of refined parameters	12	Space group, no.	<i>P11m</i> , 6
Final agreement factors;		<i>a</i> (Å)	3.321 (1)
$R_F = \sum( F_o  -  F_c )/\sum F_o $	0.088	<i>b</i> (Å)	2.876 (1)
$wR = [\sum w( F_o  -  F_c )^2/\sum w F_o ^2]^{1/2}$	0.085	<i>c</i> (Å)	11.760 (1)
Weighting scheme	1	<i>V</i> (Å <sup>3</sup> )	112.4 (1)
$S = [\sum w( F_o  -  F_c )^2/(m - n)]^{1/2}$	3.762	<i>Z</i>	1
$m =$ number of observations		<i>D</i> <sub>x</sub> ( $\text{g cm}^{-3}$ )	4.951
$n =$ number of variables		<i>F</i> (000), electrons	150.9
Min. and max. residual densities in final		$\mu$ (Mo <i>K</i> α) ( $\text{cm}^{-1}$ )	102.3
difference Fourier map ( $e \text{ \AA}^{-3}$ )	–3.38, 2.86	Approx. crystal dimensions (mm)	0.18 × 0.11 × 0.003
Max. (shift/ $\sigma$ ) final cycle	0.120	<b>Data collection</b>	
Average (shift/ $\sigma$ ) final cycle	0.059	Diffraction data from the NbS <sub>2</sub> part:	
<b>(b) NbS<sub>2</sub> part</b>		transformation matrix: $\begin{pmatrix} 1.0 & 0.0 & 0.0 \\ 0.0 & 0.5 & 0.0 \\ 0.0 & 0.0 & 1.0 \end{pmatrix}$	
Crystal data		<b>Refinement</b>	
Space group, no.	<i>Cm2m</i> , 38	Number of reflections: $h = 0$	98
<i>a</i> (Å)	3.321 (1)	Number of refined parameters	8
<i>b</i> (Å)	5.752 (1)	Final agreement factors;	
<i>c</i> (Å)	11.763 (1)	$R_F = \sum( F_o  -  F_c )/\sum F_o $	0.072
<i>V</i> (Å <sup>3</sup> )	224.7 (1)	$wR = [\sum w( F_o  -  F_c )^2/\sum w F_o ^2]^{1/2}$	0.075
<i>Z</i>	2	Weighting scheme	1
<i>F</i> (000), electrons	146	$S = [\sum w( F_o  -  F_c )^2/(m - n)]^{1/2}$	1.959
Approx. crystal dimensions (mm)	0.18 × 0.11 × 0.003	$m =$ number of observations	
<b>Data collection</b>		$n =$ number of variables	
Diffractometer	Enraf–Nonius CAD-4F	Min. and max. residual densities in final	
Radiation (Å)	Mo <i>K</i> α, 0.71073	difference Fourier map ( $e \text{ \AA}^{-3}$ )	–1.32, 1.15
Monochromator	Graphite	Max. (shift/ $\sigma$ ) final cycle	$1.6 \times 10^{-4}$
Temperature (K)	298	Average (shift/ $\sigma$ ) final cycle	$4.0 \times 10^{-5}$
$\theta$ range; min. max. ( $^\circ$ )	1.73, 39.99		

*K*α radiation of a crystal of approximate dimensions 0.18 × 0.11 × 0.003 mm revealed that the reflections can be indexed using two *C*-centered orthorhombic unit cells with cell constants as given in Table 1. These

two lattices have the *b* and *c* axes in common while the lattices do not match along the *a* axes, the ratio of their lengths being  $5.673/3.321 = 1.708$ . Because this ratio is irrational, it is not possible to choose a

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal parameters, with their e.s.d.'s in parentheses

SnS				(SnS) <sub>1-17</sub> NbS <sub>2</sub> (projection down [100])						
	Site	x	y	z	Site	x	y	z	s.o.f.	
Sn(1)	4(c)	0.00000	0.25000	0.1335 (2)	Sn(1)	2(c)	—	0.499 (3)	0.1327 (5)	0.594
S(1)	4(c)	0.476 (2)	0.25000	0.0954 (7)	S(21)	2(c)	—	0.499 (3)	0.0948 (5)	0.594
NbS <sub>2</sub>					Nb(1)	1(b)	—	0.330	0.5000	1.00
Nb(1)	2(a)	0.00000	0.00000	0.00000	S(11)	2(c)	—	0.000	0.6327	1.00
S(2)	4(c)	0.00000	0.3335 (3)	0.1328 (1)						

Anisotropic thermal parameters (Å <sup>2</sup> )						
	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>
Sn(1)	0.040 (1)	0.0362 (9)	0.0245 (7)	0.00000	0.000 (2)	0.00000
S(1)	0.022 (5)	0.040 (4)	0.029 (3)	0.00000	-0.006 (4)	0.00000
Nb(1)	0.0104 (2)	0.0036 (2)	0.0095 (2)	0.00000	0.00000	0.00000
S(2)	0.0124 (5)	0.0054 (5)	0.0104 (5)	0.00000	0.00000	0.00000

$$F(\mathbf{h}) = F_o(\mathbf{h}) \exp \left( -2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j a_i^* a_j^* U_{ij} \right).$$

larger unit cell which describes the complete structure. The *c* axes are perpendicular to the crystal platelet. It was quickly deduced that these lattices belong to different structural units, viz the almost square mesh in the *ab* plane to SnS and the other to NbS<sub>2</sub>; the mesh in the *C*-centered cell with *a* = 3.321, *b* = 5.752 Å agrees almost perfectly with the orthohexagonal cell dimensions (*a* × *a*√3 = 3.324 × 5.757 Å) of NbS<sub>2</sub>-2*H*, space group *P*6<sub>3</sub>/*mmc* (Fisher & Sienko, 1980). The structure determination was therefore split into three different parts, viz the structure determination of the SnS and NbS<sub>2</sub> parts separately, during which the common *0kl* reflections were omitted because their intensities are determined by both lattices together, followed by determination of the relative *y* and *z* position of both structure parts in the complete structure, using the common *0kl* reflections.

### 'SnS' part

Unit-cell dimensions and their standard deviations were determined from the setting angles of 16 reflections in the range 13.97 < θ < 19.62° in four alternate settings (de Boer & Duisenberg, 1984). All reflections were measured in one hemisphere up to θ = 35°. The three reference reflections measured every 2 h showed a long-term variation of less than 1% during the 20.3 h of X-ray exposure time. A 360° ψ scan for reflection 040 showed an intensity variation up to 20% about the mean value. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian integration method (Spek, 1983) (grid: 10 × 10 × 10; corrections in the range 1.06 to 2.08). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the three reference reflections: σ<sup>2</sup>(*I*) = σ<sub>cs</sub><sup>2</sup>(*I*) + (*PI*)<sup>2</sup> where *P* (=0.0047) is the instability

constant (McCandlish, Stout & Andrews, 1975). Averaging equivalent reflections resulted in 430 unique reflection data with *I* ≥ 2.5 σ(*I*). The *C*-centered orthorhombic unit cell was checked for the presence of higher lattice symmetry (Le Page, 1982). The space groups possible from the systematic extinctions (*hkl*: *h* + *k* = 2*n* + 1; *hk0*: *h*, *k* = 2*n* + 1) are *C*2*mb*, *C*m2*a*, *C*mma and *C*mmb. The structure was solved by Patterson methods (*SHELXS*86; Sheldrick, 1986). In space groups *C*mma and *C*mmb the Sn and S atoms are on the special positions 4(*g*): 0, 1/4, *z*, *z* ≈ 0.13 for Sn and *z* ≈ -0.10 for S, with site symmetry *mm*. In space groups *C*2*mb* and *C*m2*a* the atoms are on site 4(*c*); *x*, 1/4, *z* for *C*2*mb* and 1/4, *y*, *z* for *C*m2*a*. As a choice of the origin *x* and *y* of Sn can be chosen respectively equal to zero. From the Patterson synthesis it follows that *x* or *y* of S is close to 1/2. Therefore the deviation from centrosymmetry is very small and the true space group will be difficult to find. Refinements were performed in space groups *C*mma, *C*2*mb*, and *C*m2*a*. The lowest *R* factor was found for *C*2*mb* with coordinates given in Table 2. It was observed during the refinement that *F*<sub>o</sub> of a number of reflections with *h* = 5 was systematically larger than *F*<sub>c</sub>; this is possibly due to the nearby reflections 3*kl* of the strong reflecting NbS<sub>2</sub> lattice. Reflections with *h* = 5 (as well as those with *h* = 0) of the SnS lattice were therefore omitted. Refinement on *F* in space group *C*2*mb* with Sn and S at sites 4(*c*), by full-matrix least squares with 306 unique reflections with *I* ≥ 2.5 σ(*I*), converged at *R*<sub>F</sub> = 0.088, *wR* = 0.085, *S* = 3.762; the weighting scheme was *w* = 1; cell data, details of data collection and refinement are given in Table 1, coordinates are given in Table 2. The polarity of the structure was tested by refinement with *if*<sup>n</sup> and -*if*<sup>n</sup> values, respectively, giving also only marginally different *R* values, probably due to twinning in this respect. A final difference Fourier map showed a peak of 10.5 e Å<sup>-3</sup> located at 0.8 Å from the Sn site.

**'NbS<sub>2</sub>' part**

Unit-cell dimensions and their standard deviations were determined from the setting angles of 20 reflections in the range  $24.98 < \theta < 25.97^\circ$  in four alternate settings (de Boer & Duisenberg, 1984). All reflections were measured in one hemisphere up to  $\theta = 40^\circ$ . The three reference reflections measured every 2 h showed a long-term variation of less than 1% during the 18.4 h of X-ray exposure time. The net intensities of the data were corrected for the scale variation, Lorentz and polarization effects and for absorption (Spek, 1983) (corrections in the range 1.06 to 2.485). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the three reference reflections. The C-centered orthorhombic unit cell was checked for the presence of higher lattice symmetry (Le Page, 1982). Space group *Cm2m* was determined from the systematic extinctions (*hkl*:  $h + k = 2n + 1$ ) and discriminated from *C222*, *C2mm* and *Cmm2* during the structure determination process. The structure was solved by Patterson methods (*SHELXS86*; Sheldrick, 1986). Refinements by full-matrix least squares performed in space group *Cm2m* with Nb at 000 and 1/2, 1/2, 0 and sulfur at 4(*d*) using 329 unique reflections converged at  $R_F = 0.031$ ,  $wR = 0.036$ ,  $S = 1.079$ , unit weights were applied. A final difference Fourier map did not show significant residual features. Cell data, data collection and refinement details are given in Table 1.

**'The complete structure'**

From the size of the unit cells in the *ab* plane and the number of formula units SnS and NbS<sub>2</sub> per cell one finds that the composition of the compound is (SnS)<sub>1.17</sub>NbS<sub>2</sub> ( $1.17 = 2/1.708$ ; the factor 2 arises because the number of SnS units per cell is twice the number of NbS<sub>2</sub> units per cell). The composition of the compound is therefore determined by the relative size of the unit meshes in the *ab* plane of the two structural units.

The *y* and *z* coordinates of all atoms in the complete structure were found from the Patterson function calculated using the common reflections of both lattices, *viz* the *0kl* reflections. The symmetry element in the structure projected along [100] is a mirror plane perpendicular to the *c* axis. Since the *0kl* reflections are only present for  $k = 2n$ , a smaller unit cell can be chosen for the refinement, *viz* the unit cell with  $b' = (1/2)b$ ,  $c' = c$ ; this unit cell contains one NbS<sub>2</sub> and  $2 \times (1/1.708) = 1.17$  SnS units. The two-dimensional space group is *Pm* [no. 3 of the 17 two-dimensional space groups (*International Tables for Crystallography*, 1983)]. Niobium of the NbS<sub>2</sub> sandwich was placed at the mirror plane at  $z' = 1/2$ ; from the refinement of the NbS<sub>2</sub> lattice one finds for the  $z'$

coordinates of the two sulfurs of the NbS<sub>2</sub> unit  $z' = 1/2 \pm 0.1327$ . The  $y'$  coordinate of sulfur was fixed at  $y' = 0$ ; using the *y* coordinates of the atoms in the NbS<sub>2</sub> lattice, one finds  $y'$  of niobium equal to 0.3330. From the Patterson projection the  $y'$  coordinates of Sn and S of the SnS unit were found, the  $z'$  coordinates being equal to the *z* coordinates of the atoms in the sublattice of SnS. For the refinement we choose the monoclinic space group *P11m*, Nb(1) being at 1(*b*), S(11), Sn(1) and S(21) at sites 2(*c*). The full-matrix least-squares refinement (on *F*) using 98 reflections with  $I \geq 2.5 \sigma(I)$  and isotropic thermal parameters was carried out with the S(21) atom in the riding mode on the Sn(1) atom. The coordinates of Nb(1) and S(11) of NbS<sub>2</sub> were kept fixed. Parameters in the refinement were the *y* and *z* coordinates of Sn(1), the site occupancy factor of Sn(1) [s.o.f. of S(21) kept equal to the s.o.f. of Sn(1)] and the isotropic thermal parameters of all atoms. It may be noted that it is useless to relate the *x* coordinates in the complete structure because of the incommensurate character of the structure along the *a* axes. The composition of the compound obtained from the occupancy of the Sn(1) and S(21) sites is (SnS)<sub>1.17</sub>NbS<sub>2</sub>, in very good agreement with the composition calculated from the ratio of the lengths of the *a* axes of the two structural units.

Crystal data and experimental details of this part of the structure determination are compiled in Table 1. Final fractional atomic coordinates and anisotropic thermal parameters and s.o.f.'s are given in Table 2.\*

In all our calculations scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion factors are those given by Cromer & Liberman (1970). All calculations are carried out on the CDC-Cyber 170/760 computer of the University of Groningen with the program packages *XTAL* (Hall & Stewart, 1987) and *EUCLID* (Spek, 1982; calculation of geometric data).

**Discussion of the structure**

(SnS)<sub>1.17</sub>NbS<sub>2</sub>, 'SnNbS<sub>3</sub>', has, according to our structure determination, an incommensurate misfit layer structure with alternately two-atom-thick layers of SnS (centered on  $z = 0$ , Fig. 1) and three-atom-thick sandwiches of NbS<sub>2</sub> centered on  $z = 1/2$  (Fig. 2). Each Sn atom is coordinated to five sulfur atoms of the SnS layers; four S atoms are in a plane perpendicular to the *c* axis with Sn-S distances of 2.74 (1) (1×), 2.913 (1) (2×), and 3.01 (1) Å (1×). The Sn-S bond

\* Lists of structure factors, anisotropic thermal parameters and bond lengths have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51411 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of length 2.695 (9) Å makes an angle of 87.1° with this plane. In this way two-atom-thick layers of SnS are formed, looking like layers made of NaCl-type SnS by cutting slices with a thickness one half of the cubic cell edge. It must be noted that the crystal structure of  $\alpha$ -SnS (the low-temperature form) is a much more deformed version of the NaCl-type structure, with each Sn having three pyramidal S neighbors, one at 2.627 Å and two at 2.665 Å; three other sulfur atoms are at rather larger distances [3.290 (2 $\times$ ), 3.388 Å (1 $\times$ )] (Wiedemeier & von Schnering, 1978). The  $\beta$ -SnS structure (von Schnering & Wiedemeier, 1981) (the high-temperature form) with TII structure contains double layers of SnS with four equal Sn-S bonds of 2.96 Å with bond order 0.5

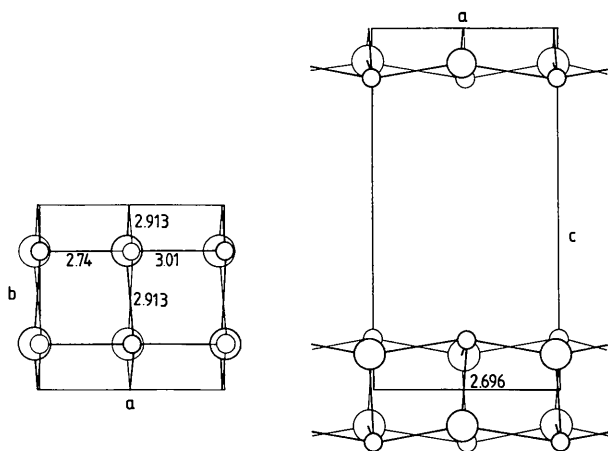


Fig. 1. The SnS part of the structure projected along [001] (left) and [010] (right). Large and small circles are sulfur and tin respectively.

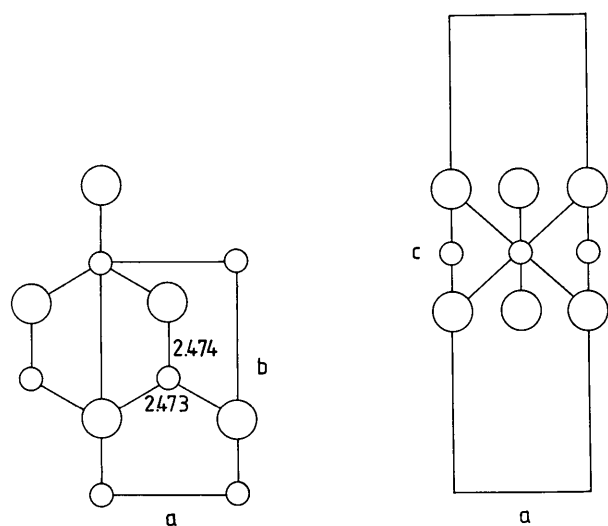


Fig. 2. The NbS<sub>2</sub> part of the structure projected along [001] (left) and [010] (right). Large and small circles are sulfur and niobium respectively. The NbS<sub>2</sub> sandwich is centered on  $z = 1/2$ .

approximately in the  $ab$  plane and a fifth Sn-S bond along the  $c$  axis of 2.63 Å with bond order 1. The SnS slices in (SnS)<sub>1.17</sub>NbS<sub>2</sub> are intermediate between those of  $\alpha$ - and  $\beta$ -SnS. Niobium atoms of the NbS<sub>2</sub> part of the structure are in trigonal-prismatic coordination by sulfur with Nb-S 2.474 (2) Å; this distance is close to those found in the intercalates Cu<sub>0.5</sub>NbS<sub>2</sub> (2.482 Å) (Paulus, Meetsma, de Boer & Wiegiers, 1989) and Ag<sub>0.6</sub>NbS<sub>2</sub> (2.480 Å) (van der Lee, Bouwmeester & Wiegiers, 1989). The Nb-S distance in NbS<sub>2</sub>-2H is not known accurately because no accurate structure determination has been performed so far.

It is seen that 'long' and 'short' Sn-S bonds alternate along the  $a$  axis. It may be remarked that in space group  $Cm2a$ , 'long' and 'short' bonds alternate along the  $b$  axis, while in  $Cmma$  the Sn-S bonds do not alternate in length. In a recent study of the application of superspace-group symmetry on composite crystals, van Smaalen (1989) deduced that the space group of the SnS part must be  $Cm2a$  in order to fit with the space group  $Cm2m$  of the NbS<sub>2</sub> lattice. The observation that in  $C2mb$  a slightly lower  $R_F$  was obtained was explained by the effect of the modulation. Not including the modulation is probably also the cause of the rather high  $R_F$  of the SnS part.

An interesting feature of the structure is the relative position of the SnS and the NbS<sub>2</sub> parts (Figs 3 and 4). It is seen that Sn lies exactly between rows of sulfur of NbS<sub>2</sub> running parallel to the  $a$  axis, at  $y = 0$  and  $y = 1/2$  (Table 2). In this way the coordination of Sn (at  $y = 1/4$  and  $y = 3/4$ ) by S of NbS<sub>2</sub> varies between two and three. Some Sn atoms fit in the hole formed by three S of NbS<sub>2</sub>, while other Sn atoms show a coordination of one relatively short Sn-S

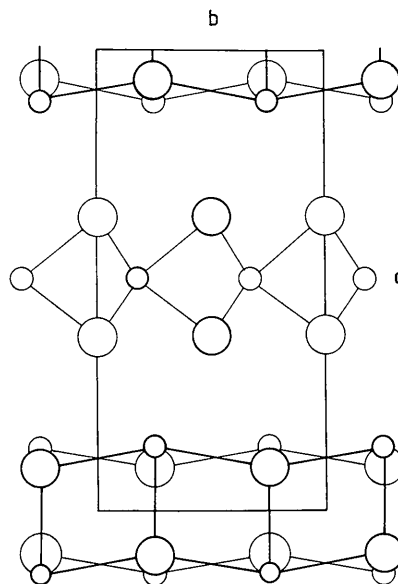


Fig. 3. The complete structure projected along the misfit axes [100].

distance and two relatively long Sn–S distances. The observed coordination variation is a consequence of the incommensurate character of the structure. A second interesting feature is the distortion of the lattices of  $\text{NbS}_2$  and  $\text{SnS}$  compared with an ideal hexagonal and tetragonal lattice, respectively. It is seen that for  $\text{NbS}_2$  no distortion occurs: for an ideal hexagonal mesh the ratio  $b/a = \sqrt{3} = 1.732$ , to compare with 1.732 experimentally. For  $\text{SnS}$ , the deviation from a quadratic mesh in the  $ab$  plane,  $b/a = 1.014$ , corresponds to an elongation along the  $b$  axis.

One expects, besides the observed diffraction pattern, reflections due to the mutual modulation of one sublattice by the other. These reflections have been observed by electron diffraction (Kuyper, van Tendeloo, van Landuyt, Amelinckx, Wiegers & Meetsma, 1988). Such a mutual modulation implies that the refined structures of  $\text{SnS}$  and  $\text{NbS}_2$  are average structures, the modulation becoming apparent as an enhanced temperature motion of the atoms. The observed high temperature factors of the atoms of the  $\text{SnS}$  part, compared with those of the  $\text{NbS}_2$  part, may indicate that the  $\text{SnS}$  lattice is more susceptible to modulation by  $\text{NbS}_2$  than  $\text{NbS}_2$  by  $\text{SnS}$ ; this is supported by the observation that the  $\text{SnS}$  lattice is distorted but the  $\text{NbS}_2$  lattice is not. In electron diffraction the strongest satellites are due to the modulation of  $\text{SnS}$  by  $\text{NbS}_2$ . The electrical transport and magnetic properties of  $(\text{SnS})_{1.17}\text{NbS}_2$  (Wiegers, Meetsma, Haange & de Boer, 1988) strongly resemble those of  $\text{NbS}_2 \cdot 2H$  and intercalates of  $\text{NbS}_2 \cdot 2H$  with electron-donating species (e.g.  $\text{Cu}$ ,  $\text{Ag}$ ; donor molecules like  $\text{NH}_3$ ); it indicates that the stability of  $(\text{SnS})_{1.17}\text{NbS}_2$  is due to the same type of interaction, viz donation of electrons, or overlap with lone-pair electrons as occurs in the intercalates.

It is interesting to note that in the powder pattern of ' $\text{SnNbS}_3$ ' only the  $\text{SnS}$  part of the structure is observed; the  $a$  axis of the tetragonal unit cell reported by van Maaren (1972),  $a = 4.05$ ,  $c = 11.77$  Å, is half of the diagonal in the  $ab$  plane of the  $C$ -centered cell of the  $\text{SnS}$  part of the structure (Table 1); owing to the small deviation from  $90^\circ$  of the angle between  $a$  and  $b$ , the primitive cell is monoclinic with  $a = 4.039$ ,  $b = 4.039$  Å,  $\gamma = 90.78^\circ$ . The only structure

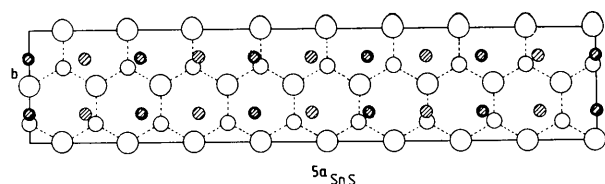


Fig. 4. The complete structure {five units with  $a$  ( $\text{SnS}$ ) projected along  $[001]$ } showing the incommensurate character. Tin atoms above and below  $\text{NbS}_2$  sandwiches are indicated by thick and thin hatched circles, respectively; small and large open circles are niobium and sulfur respectively. Sulfur atoms of the  $\text{SnS}$  part are omitted for the sake of clarity.

determination of a misfit layer compound containing a transition-metal dichalcogenide as structural unit reported so far in the literature is  $(\text{LaS})_{1.20}\text{CrS}_2$ , ' $\text{LaCrS}_3$ ', with two-atom-thick layers of  $\text{LaS}$  and sandwiches of  $\text{CrS}_2$  with  $\text{Cd}(\text{OH})_2$ -type structure, the sublattices being monoclinic (Kato, Kawada & Takahashi, 1977; Otero-Diaz, Fitzgerald, Williams & Hyde, 1985). The ratio of the lengths of the axes along the misfit direction is equal to  $5/3$  and the complete structure can be described in a larger unit cell; moreover, the periodicity along the  $c$  axis of the  $\text{CrS}_2$  part is six times that of the  $\text{LaS}$  lattice.

We have found a structure similar to that of ' $\text{SnNbS}_3$ ' for ' $\text{PbNbS}_3$ ' also with  $C$ -centered orthorhombic lattices of  $\text{PbS}$  and  $\text{NbS}_2$ ; the length of the  $c$  axis of the  $\text{NbS}_2$  lattice here being twice that of the  $\text{PbS}$  lattice. In ' $\text{PbTaS}_3$ ' we found  $F$ -centered orthorhombic lattices of  $\text{PbS}$  and  $\text{TaS}_2$ . Along the  $c$  axes of length  $24.0$  Å four structural units of  $\text{PbS}$  and  $\text{TaS}_2$  alternate; units of the same type  $\frac{1}{2}c$  apart are displaced with respect to each other over  $\frac{1}{2}b$ . Structure determinations and physical properties will be published in due course.

The analogy in the unit cells from powder diffraction of a number of compounds ' $\text{PbMX}_3$ ' and ' $\text{SnMX}_3$ ' ( $M = \text{Ti}, \text{V}, \text{Nb}, \text{Ta}$ ) (Schmidt, 1970; Sterzel & Horn, 1970; van Maaren, 1972; Donohue, 1975) reveals that the structures are strongly related to, or even isostructural with, ' $\text{SnNbS}_3$ '. Similarly one may expect from the unit-cell dimensions that the compounds ' $\text{LnMX}_3$ ' ( $\text{Ln}$  the rare earth metals,  $M = \text{Ti}, \text{V}, \text{Nb}, \text{Ta}$ ;  $X = \text{S}, \text{Se}$ ), first described by Donohue (1975), are of a related structure type, with probably a monoclinic mesh in the  $ab$  plane. The compounds ' $\text{LnMS}_3$ ' ( $M = \text{V}, \text{Cr}$ ) reported by Murugesan, Ramesh, Gopalakrishnan & Rao (1981) are probably structurally related to ' $\text{LaCrS}_3$ '. A recent review of misfit layer structures including ' $\text{LaCrS}_3$ ' has been given by Makovicky & Hyde (1981).

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## The Incommensurate Misfit Layer Structure of $(\text{SnS})_{1.17}\text{NbS}_2$ , 'SnNbS<sub>3</sub>'. II. A Study by Means of Electron Microscopy

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### Abstract

Electron diffraction and high-resolution imaging are used to study the remarkable incommensurable misfit layer compound  $(\text{SnS})_{1.17}\text{NbS}_2$ , 'SnNbS<sub>3</sub>'. Electron diffraction patterns along the zone axis perpendicular to the layer planes are analysed in detail based on the mixed-layer assumption proposed in paper I [Meetsma, Wiegiers, Haange & de Boer (1989). *Acta Cryst.* **A45**, 285-291]. The relative intensities of the  $hk0$  reflections due to the two types of constituent layers are strongly influenced by the foil thickness. Stacking variants along the  $c$  axis are frequently observed and strongly complicate the diffraction patterns. Under particular conditions of thickness and defocus, high-resolution images are shown to reflect the varying degree of coincidence of the atom columns in the misfit layers and thus they directly reveal the incommensurate misfit.

### 1. Introduction

In paper I (Meetsma, Wiegiers, Haange & de Boer, 1989) the structure determination by means of X-ray diffraction from single crystals of the compound  $(\text{SnS})_{1.17}\text{NbS}_2$ , 'SnNbS<sub>3</sub>', a member of the series

$\text{MTX}_3$  ( $M = \text{Sn, Pb}$ ;  $T = \text{Ti, V, Nb, Ta}$ ;  $X = \text{S, Se}$ ), was reported. The compound was found to consist of a periodic alternation of SnS layers and NbS<sub>2</sub> layers along a common  $c$  axis (Fig. 3 of paper I). The SnS layers have a slightly deformed NaCl-type structure, whereas the NbS<sub>2</sub> layers have the hexagonal (trigonal prismatic) NbS<sub>2</sub>-2H structure. Both structures can be described with reference to  $C$ -centred orthorhombic unit cells with lattice parameters:  $a = 5.673$ ,  $b = 5.750$ ,  $c = 11.760$  Å for SnS and  $a' = 3.321$ ,  $b' = 5.752$ ,  $c' = 11.763$  Å for NbS<sub>2</sub>. The orientation relationship is:  $(001)_{\text{SnS}} \parallel (001)_{\text{NbS}_2}$ ;  $[010]_{\text{SnS}} \parallel [010]_{\text{NbS}_2}$ . The unit meshes in the plane of the layers fit along the  $b$  direction; however, along the  $a$  direction there is an obvious misfit. The ratio  $a/a'$  is approximately 12/7, but in actual fact it may be incommensurate.

Thus far the only electron microscopy study, and in fact also the only structure determination, of a misfit layer compound containing a transition-metal dichalcogenide was reported for  $(\text{LaS})_{1.20}\text{CrS}_2$ , 'LaCrS<sub>3</sub>' (Kato, Kawada & Takahashi, 1977; Otero-Diaz, Fitzgerald, Williams & Hyde, 1985). In the present investigation of SnNbS<sub>3</sub>, electron diffraction patterns are reported which are very similar to those for LaCrS<sub>3</sub> (Otero-Diaz *et al.*, 1985); furthermore, and in contrast with the former study, high-resolution images could be obtained which clearly reveal the incommensurate misfit in the plane of the layers.

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