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X-ray crystal structure determination of the triclinic misfit layer compound $(\text{SnS})_{1.20}\text{TiS}_2$

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Abstract. $(\text{SnS})_{1.20}\text{TiS}_2$ is a misfit layer compound built of alternately double layers of SnS with distorted rocksalt-type structure and sandwiches of TiS_2 slightly distorted compared with those of 1T-TiS_2 . For comparison with other misfit layer compounds the triclinic subsystems are described in centred unit cells: for the SnS part, $a_1 = 5.683(1) \text{ \AA}$, $b_1 = 5.832(1) \text{ \AA}$, $c_1 = 11.680(5) \text{ \AA}$, $\alpha_1 = 95.85(3)^\circ$, $\beta_1 = 94.78(3)^\circ$, $\gamma_1 = 90.03(2)^\circ$, the space group is $C\bar{1}$ and $Z = 4$; for the TiS_2 part, $a_2 = 3.412(1) \text{ \AA}$, $b_2 = 5.835(1) \text{ \AA}$, $c_2 = 23.289(3) \text{ \AA}$, $\alpha_2 = 95.86(1)^\circ$, $\beta_2 = 90.30(1)^\circ$, $\gamma_2 = 90.01(1)^\circ$, the space group is $F\bar{1}$ and $Z = 4$. In real space, a_1 and a_2 as well as b_1 and b_2 are parallel while the c axes diverge. In reciprocal space both sublattices have the (b^*, c^*) plane in common. Refinements were performed of the SnS part using 1351 independent reflections ($R_F = 0.087$) and of the TiS_2 part using 714 reflections ($R_F = 0.080$). Each Sn atom is coordinated to five S atoms of the SnS double layer with SnS distances of 2.610(3), 2.866(4), 2.873(4), 2.911(4) and 2.976(4) \AA , and at larger distances to S of TiS_2 . The Ti–S distances of the distorted TiS_6 octahedra with symmetry $\bar{1}$ are 2.417(2), 2.429(1) and 2.428(1) \AA . Sn atoms are between rows of sulphur along a of S of TiS_2 . The structural relationship with other misfit layer compounds is discussed.

1. Introduction

The discovery (Wiegiers *et al* 1989) of a large number of misfit layer compounds $(\text{MS})_n\text{TS}_2$ ($\text{M} \equiv \text{Sn, Pb, rare earth metals}$; $\text{T} \equiv \text{Nb, Ta}$) built of alternately double layers of MS and sandwiches of TS_2 with Nb and Ta in trigonal prisms of S prompted us to investigate compounds designated as ‘ MTS_3 ’ ($\text{M} \equiv \text{Pb, rare-earth metals}$; $\text{T} \equiv \text{Ti, V, Cr}$) (Takahashi *et al* 1971, 1973). The misfit layer character of one of the compounds, i.e. ‘ LaCrS_3 ’ was identified by Kato *et al* (1977) using single-crystal x-ray diffraction. The compound was also investigated using electron diffraction (Otera-Diaz *et al* 1985, Williams and Hyde 1988). Recently Kato (1990) published a reinvestigation of ‘ LaCrS_3 ’, based upon the x-ray data of his previous study. ‘ LaCrS_3 ’ with the real composition $(\text{LaS})_{1.20}\text{CrS}_2$ is built of alternate double layers of LaS and sandwiches of CrS_2 with Cr in slightly distorted trigonal anti-prismatic coordination by sulphur; both subsystems are described in the space group $C\bar{1}$. Since ‘ LaCrS_3 ’ and the title compound ‘ SnTiS_3 ’ are structurally related to misfit layer compounds with the transition metal ($\text{T} \equiv \text{Nb, Ta}$) in trigonal prisms of sulphur, the structures of the latter compounds are briefly reviewed.

For all misfit layer compounds there are two subsystems with compositions MS and TS_2 , respectively. Each subsystem is characterized by its own unit cell and space group.

Table 1. Crystal data for $(\text{SnS})_{1.20}\text{TiS}_2$. Standard deviations are given in parentheses.

	SnS part	TiS ₂ part
Space group no.	$C\bar{1}$	$F\bar{1}$
<i>a</i> (Å)	5.683(1)	3.412(1)
<i>b</i> (Å)	5.832(1)	5.835(1)
<i>c</i> (Å)	11.680(5)	23.289(3)
α (deg)	95.85(3)	95.86(1)
β (deg)	94.78(3)	90.30(1)
γ (deg)	90.03(3)	90.01(1)
<i>V</i> (Å ³)	383.7(2)	461.2(2)
2	4	4

For the misfit layer compounds with NbS₂ and TaS₂ sandwiches, both MS and TS₂ lattices are *C* or *F* centred orthorhombic, with corresponding axes parallel. The *c* axes, *c*₁ and *c*₂ of MS and TS₂, respectively, are perpendicular to the layers. In a recent paper we argued that, when the sandwich TS₂ (T ≡ Nb, Ta) is replaced by a sandwich with T in octahedral coordination (as expected for T = Ti, V, Cr), monoclinic sublattices result, the monoclinic angle being given by $\sin(\alpha - 90) = b/6c$, using the same setting of axes (Wiegers *et al* 1990a). Misfit layer compounds with monoclinic sublattices are observed for $(\text{PbS})_{1.18}\text{TiS}_2$ and $(\text{PbS})_{1.13}\text{VS}_2$ (Wiegers *et al* 1989, 1990a, van Smaalen 1990, Gotoh *et al* 1990). Triclinic compounds, such as 'LaCrS₃', occur when there is an additional shift along the *a* axes. These shifts, which need not be equal for the two sublattices, are determined by the interaction between subsystems of the same kind. In this paper the structure determination of the triclinic compound $(\text{SnS})_{1.20}\text{TiS}_2$ is described.

2. Experimental details

A powder sample was prepared from the elements; the ratio of the elements was chosen such as to correspond with the expected ratio in view of *a*₁ and *a*₂ from respectively the SnS double layer in $(\text{SnS})_{1.17}\text{NbS}_2$ (Meetsma *et al* 1989) and 1T-TiS₂ (Chianelli *et al* 1975). The mixture of elements was heated at 800 °C in an evacuated quartz tube for 7 d. Crystals suitable for electrical transport measurements and single-crystal x-ray diffraction were obtained by vapour transport using chlorine, for which about 1 wt% $(\text{NH}_4)_2\text{PbCl}_6$ was used. Crystals grow as thin platelets at the cold part of the gradient of 720–650 °C.

3. Structure determination of $(\text{SnS})_{1.20}\text{TiS}_2$

Single-crystal x-ray diffraction was performed on an Enraf-Nonius CAD-4F diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) and a crystal of approximate dimensions of 0.20 mm × 0.27 mm × 0.006 mm. All reflections could be indexed on two mutually incommensurate triclinic unit cells. For comparison with the orthorhombic and monoclinic misfit layer compounds, centred cells (*C* for SnS and *F* for TiS₂) are used, with unit-cell dimensions as given in table 1. In real space the *b* axes are parallel and of equal length while the *a* axes, being parallel, have a length ratio

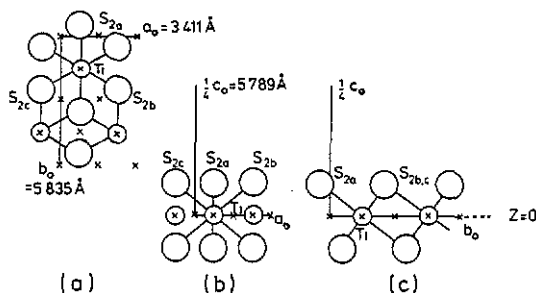


Figure 1. The TiS_2 sandwich in the orthogonal axes a_0 , b_0 , c_0 ($a_0 \parallel a_2$; $c_0 \parallel c_2^*$; $b_0 \parallel c_0 \times a_0$). The small and medium circles are Ti and S atoms, respectively. Only the sandwich at $z = 0$ is shown. The centres of symmetry are indicated by small crosses. (a) Projection along c_0 of the S atoms at $z \approx 0.1$ and the Sn atoms at $z = 0$. (b) Projection along b_0 of the sandwich centred at $z = 0$. (c) Projection along a_0 .

$a_1/a_2 = 5.683/3.412 = 1.6656$ (standard deviation, 0.0006) close to $5/3 = 1.667$. It is not possible to describe the whole structure in a supercell with $a = 3a_1 \approx 5a_2$, because the c axes diverge. The structures of the SnS and TiS_2 parts were determined separately. The $0kl$ reflections were omitted from these refinements because their intensities are determined by both lattices (there is a common (b^*, c^*) reciprocal lattice plane). The $0kl$ reflections are used to determine the relative origin of the two sublattices.

Unit-cell dimensions and their standard deviations were for each subsystem determined from the setting angles of a number of reflections in the range $25.95^\circ < \theta < 27.89^\circ$ in four alternative settings (de Boer and Duisenberg 1984). All reflections were measured in one hemisphere up to $\theta = 35^\circ$. The two reference reflections, 0, 4, 0 and 0, 0, 10, are common to the two subsystems which has the advantage that the intensities of the two subsystems can be put on the same scale. The intensities were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian integration method (grid, $10 \times 10 \times 6$) (Spek 1983). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance of the two reference reflections: $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (PI)^2$, where P is the instability constant (McCandlish *et al* 1975).

For the SnS subsystem refinements were performed in space group $C\bar{1}$ (no. 2 in the *International Tables for Crystallography* (1983)) with four units SnS in the unit cell. All atoms are at general positions. The midplane of the SnS double layer was taken at $z = \frac{1}{2}$; starting coordinates were deduced from the geometry of the SnS double layer in $(\text{SnS})_{1.17}\text{NbS}_2$ (Meetsma *et al* 1989). Refinements on F by full-matrix least squares using 1351 reflections with $I \geq 2.5\sigma(I)$, converged at $R_F = 0.087$, $wR = 0.095$, $S = 4.253$, using units weights.

For the TiS_2 part the centric space group $F\bar{1}$ was adopted with Ti at centres of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$; $(\frac{3}{2}, \frac{3}{2}, 0)$; $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$. There are four formula units TiS_2 in the unit cell. It may be noted that there two sets of four symmetry centres in the F centred unit cell. Those given above and one starting with $(0, 0, 0)$ (figure 1). For the TiS_2 subsystem, putting the Ti atoms at the centres of either set leads to equivalent descriptions of the same structure. The complete structure will be different when using one or the other set to define the Ti positions. The refinement using the $0kl$ reflections showed the choice for the Ti positions given above to be correct. The starting coordinates of S(2) were from a model with Ti in trigonal anti-prismatic coordination. Refinements,

performed by full matrix refinement using 714 reflections ($0kl$ excluded), converged at $R_F = 0.080$, $wR = 0.096$, $S = 4.310$; unit weights were applied.

From the size of the unit cells in the (a , b) plane and the number of SnS and TiS_2 formula units per cell, one finds that the composition of the compound is $(\text{SnS})_{1.20}\text{TiS}_2$ (i.e. $1.20 = 2(3.412/5.683)$). Because of the common (b^* , c^*) reciprocal plane, the two sublattices have a common projection along $[100]$. In this projection, c_1 and c_2 project along the same line with length $c_1 \sin(\beta_1)$ for the SnS lattice and length $c_2 \sin(\beta_2) = 2c_1 \sin(\beta_1)$ for the TiS_2 lattice. The unit mesh in the projection is given by $b'' = \frac{1}{2}b_1 = \frac{1}{2}b_2$ and $c'' = c_1 \sin(\beta_1) = (c_2/2) \sin(\beta_2)$. This is also obvious considering the extinctions of the $0kl$ reflections, i.e. $0kl$ of SnS only present for $k = 2n$ and $0kl$ of TiS_2 only present for $k = 2n$ and $l = 2n$. The two-dimensional space group is $p2$ (no. 3 of the 17 two-dimensional space groups (*International Tables for Crystallography* 1983)). For the refinement using XTAL the three-dimensional space group which describes the symmetry of this projection is $P\bar{1}$. The coordinates of the SnS and TiS_2 refinements were transformed to this smaller unit cell. Parameters in the full matrix refinement were the coordinates, the site occupancy factor of Sn and S(1) (kept equal) and the isotropic thermal parameters of all atoms. The refinement converged to $R_F = 0.083$, $wR = 0.078$ for 124 $0kl$ reflections, indicating that Ti at $(\frac{1}{4}, \frac{1}{4}, 0)$, etc, for the TiS_2 refinement was the correct choice. The z coordinates are, within standard deviation, equal to those of the subsystem refinements (which are more accurate), taking into account the different unit cells. The composition of the compound obtained from the occupancy of the Sn and S(1) sites (0.592(1)) is in good agreement with the occupancy, 0.600, calculated from the lengths of the a axes of the substructures; the same occupancy is calculated from the ratio of the scale factors for the SnS and TiS_2 refinements (see the supplementary material†).

Crystal data and experimental details of the structure determination are compiled in tables 1–4. Final fractional atomic coordinates, sofs and temperature factors are given in table 5. It may be noted that in this way the structure is completely described by the tables for the SnS and TiS_2 parts.

In all our calculations, scattering factors were taken from Cromer and Mann (1968). Anomalous dispersion factors are those given by Cromer and Libermann (1970). All calculations are carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL (Hall and Stewart 1989) and EUCLID (calculation of geometric data) (Spek 1982).

4. Discussion of the structure

$(\text{SnS})_{1.20}\text{TiS}_2$ is built of alternately double layers of SnS (approximately a $\{001\}$ slice of SnS with the (hypothetical) rocksalt structure) and sandwiches of TiS_2 with Ti in distorted octahedral coordination by S as shown in the projection along $[100]$ of both subsystems (figure 2(a)). The symmetry of this projection is that of the two-dimensional space group $p2$, with unit mesh b'' and c'' . The figure shows the cell doubled in both directions in order to show the effect of the centring conditions. Since the SnS lattice is C centred, while the TiS_2 is F centred, the structure type is designated as CF . In this way the relationship with the orthorhombic compound $(\text{LaS})_{1.14}\text{NbS}_2$, also of CF type becomes clear (figure 2(b)). $(\text{LaS})_{1.20}\text{CrS}_2$ which has the CC -type structure may be considered as the analogue of $(\text{SnS})_{1.17}\text{NbS}_2$ with the orthorhombic CC -type structure.

† The supplementary material (lists of F_o , F_c and $\sigma(F)$) can be obtained from the authors.

Table 2. Data collection for $(\text{SnS})_{1.20}\text{TiS}_2$.

	SnS part	TiS ₂ part
Diffractometer		Enraf-Nonius CAD-4F
Radiation		Mo K α
Wavelength (\AA)		0.71073
Monochromator		Graphite
Temperature (K)		295
Range: minimum, maximum (deg)	1.76, 35.0	1.76, 35.0
ω - 2θ scan (deg)	$\Delta\omega = 1.30 + 0.35 \tan \theta$	$\Delta\omega = 1.00 + 0.35 \tan \theta$
Data set	$h, -9 \rightarrow 9; k, 0 \rightarrow 9;$ $l, -18 \rightarrow 18$	$h, -5 \rightarrow 5; k, -9 \rightarrow 0$ $l, -36 \rightarrow 36$
Crystal-to-receiving-aperture distance (mm)		173
Horizontal aperture vertical aperture (mm)		4.0, 4.5
Reference reflections, RMS deviation (%)	0, 4, 0; 2.20	0, 4, 0; 0.59 0, 0, 10; 0.73
Instability constant P	0.0011	0.0082
Drift correction	1.000-1.000	1.000-1.018
Minimum to maximum absorption correction factor	1.05-2.60	1.051-2.55
X-ray exposure time (h)	60.1	20.5
Total data	1831	1105
Unique data	1117	410

Table 3. Details of the refinement of the SnS and TiS₂ parts.

	SnS	TiS ₂
Number of reflections: $h \neq 0$	1351	714
Number of refined parameters	19	16
Final agreement factors		
$R_F = \Sigma(F_o - F_c) / \Sigma F_o $	0.087	0.080
$wR = \{\Sigma[w(F_o - F_c)^2] / \Sigma w F_o ^2\}^{1/2}$	0.095	0.096
Weighting scheme	1	1
$S = [\Sigma w(F_o - F_c)^2 / (m - n)]^{1/2}$ where m is the number of observations and n the number of variables	4.253	4.310
Minimum residual density, maximum residual density in final difference Fourier map (electrons/ \AA^3)	-4.6, 7.9	-2.8, 2.7
Maximum (shift/ σ) final cycle	0.25×10^{-2}	0.27×10^{-2}
Average (shift/ σ) final cycle	0.68×10^{-3}	0.10×10^{-3}

Using these centred lattices (table 1) one observes that $b_1 = b_2$, $\gamma_1 = \gamma_2 = 90^\circ$ and $\alpha_1 = \alpha_2$, $2c_1 = c_2$, but $a_1 \neq a_2$ and $\beta_1 \neq \beta_2$. In reciprocal space the sublattices have a common (b^* , c^*) plane. By analysing the latter condition in real space, writing $c_1 = c_\perp + \lambda_1 a_1 + \rho_1 b_1$ in which c_\perp is perpendicular to the (a , b) plane and using $\gamma_1 = \gamma_2$ (but not necessarily 90°) it follows that a_1 and a_2 and that b_1 and b_2 are parallel, that the interplanar distances d_{001} are equal, and that the components of c_i along the b axes are equal ($\rho_1 = \rho_2$). It also follows that there will be a slight difference between α_1 and α_2 ,

Table 4. Details of the refinement of the projection along [100] ($b^* = 2.916(1) \text{ \AA}$, $c^* = 11.64(3) \text{ \AA}$; space group, $P\bar{1}$).

Number of reflections, $h = 0$	124
Number of refined parameters	12
Final agreement factors	
$R_F = \Sigma(F_o - F_c) / \Sigma F_o $	0.083
$wR = \{\Sigma[w(F_o - F_c)^2] / \Sigma w F_o ^2\}^{1/2}$	0.078
Weighting scheme	1
$S = [\Sigma w(F_o - F_c)^2 / (m - n)]^{1/2}$ where m is the number of observations and n the number of variables	1.773
Residual electron density in final difference Fourier map (electrons/ \AA^3)	-1.14, 1.29
Maximum (shift/ σ) final cycle	0.94×10^{-1}
Average (shift/ σ) final cycle	0.17×10^{-1}

given by $\cos(\alpha_i) = \rho_i b_i / c_i$. The calculated difference between α_1 and α_2 of 0.01° is less than the estimated standard deviation. The angles β_i , which are not equal, are determined by $\lambda_i a_i$, i.e. $\cos(\beta_i) = \lambda_i a_i / c_i$. Because of the incommensurate character of the complete structure along the a axes, the energy due to nearest-neighbour interaction of layers will not change when λ_i is changed. The constants λ_i are therefore determined by the interaction between layers of the same kind and therefore one does not expect a relation between λ_1 and λ_2 . For $\lambda_1 = \lambda_2 = 0$, $\beta_1 = \beta_2 = 90^\circ$, the two sublattices are monoclinic and corresponding axes are parallel. Monoclinic lattices with $\beta_i = \gamma_i = 90^\circ$ are observed for 'PbTiS₃' and 'PbVS₃' (Wiegiers *et al* 1989, 1990a, van Smaalen *et al* 1990, Gotoh *et al* 1990).

That the subsystems of all misfit layer compounds (including those with T \equiv Nb and Ta) have a common (b^* , c^*) reciprocal plane seems to be a necessary condition for their existence. A common c^* is a consequence that layers cannot intersect. A common (b^* , c^*) plane means that the a axes of the subsystems must be parallel, which in turn means that [001] is the direction along which the bonding interaction of alternate layers takes place. A common (b^* , c^*) plane occurs also for a system of ab axes with the a axes parallel and b axes such that $b_1 \sin(\gamma_1) = b_2 \sin(\gamma_2)$, which means that a rectangular shape of the (a , b) planes and $b_1 = b_2$ as observed for all compounds is not essential in having a common (b^* , c^*) plane.

In the projection of the substructures along [100], c_1 and c_2 project with length $c_1 \sin(\beta_1) = c_2 \sin(\beta_2)$ along the same line, the angle between b and the projected c_1 and c_2 being almost equal: $\alpha_1 = \alpha_2$ (figure 2(a)).

The structure of the SnS double layer is shown more clearly in figure 3. Each Sn atom is coordinated by five S atoms within the same double layer and at larger distances by two or three S atoms of the TiS₂ subsystem (indicated by broken and full lines, respectively, in figure 2(a)). It is seen that, compared with an {001} slice of SnS with rocksalt structure (hypothetical, since SnS adopts a different structure), the SnS double layer is corrugated with Sn atoms on the outside. The Sn bond to the apex S atom of the SnS double layer, in projection almost perpendicular to the b axis, is much shorter (2.610(3) \AA), than the other four Sn-S distances which are 2.866(4), 2.873(4), 2.911(4) and 2.976(4) \AA (table 6). The same phenomenon is observed for the SnS double layer in (SnS)_{1.17}NbS₂ (Meetsma *et al* 1989).

The Sn atoms fall in between rows of sulphur in TiS₂ along a , making the total number of coordinating S atoms 5 + 2 or 5 + 3, depending on the actual position along the misfit

Table 5. Atomic positions and temperature factors of $(\text{SnS})_{1.20}\text{TiS}_2$. Values of the fractional coordinates of the SnS and TiS_2 parts are with respect to the unit cell defined in table 1. Estimated standard deviations are given in parentheses. $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. The thermal vibration amplitudes (\AA^2) are $F(\mathbf{h}) = F_0(\mathbf{h}) \exp(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j a_i^* a_j^* U_{ij})$.

	x	y	z	U_{eq} (\AA^2)	U_{11} (\AA^2)	U_{22} (\AA^2)	U_{33} (\AA^2)	U_{23} (\AA^2)	
Sn(1)	-0.0225(1)	-0.28060(2)	0.37000(7)	0.0228(2)	0.0210(2)	0.0160(2)	0.0084(1)	0.0016(5)	
S(1)	0.0160(6)	-0.2320(6)	0.5954(3)	0.0289(8)	0.0171(6)	0.0108(8)	0.0079(5)	0.004(1)	
Ti(1)	$\frac{1}{2}$	$\frac{1}{2}$	0.0	0.0122(4)	0.0141(6)	0.0014(6)	0.0005(5)	0.0000(0)	
S(2)	0.2480(4)	0.5587(2)	0.06175(6)	0.0083(3)	0.016(1)	0.004(1)	0.002(1)	0.001(1)	
	x''	y''	z''	sof	U_{iso} (\AA^2)				
Common part (coordinates a unit cell with $b'' = 2.883(1) \text{\AA}$, $c'' = 11.41(1) \text{\AA}$)									
Sn(1)	-	-0.561(1)	0.3704(3)	0.592(1)	0.026(1)				
S(1)	-	-0.466(5)	0.592(1)	0.592(1)	0.029(4)				
Ti(1)	-	$\frac{1}{2}$	0	1.0	0.011(1)				
S(2)	-	0.119(2)	-0.1236(4)	1.0	0.009(1)				

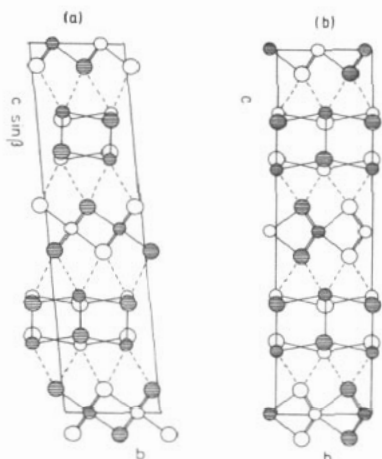


Figure 2. (a) The structure of the common projection (along [100]) of $(\text{SnS})_{1.20}\text{TiS}_2$. (b) The corresponding projection of $(\text{LaS})_{1.14}\text{NbS}_2$. The centring (C for SnS (LaS) and F for TiS_2 (NbS_2)) is demonstrated using open and shaded circles for atoms of the same type, $\frac{1}{2}a$ apart. For $(\text{SnS})_{1.20}\text{TiS}_2$ the c axes of the subsystems project onto the same vector.

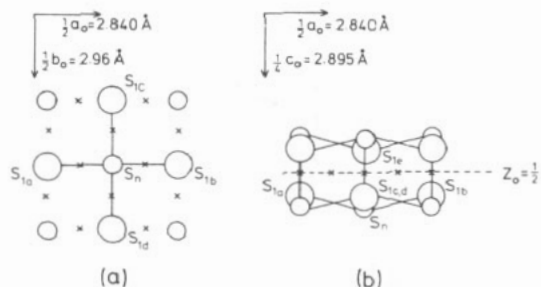


Figure 3. The structure of the SnS double layer of $(\text{SnS})_{1.20}\text{TiS}_2$ in orthogonal axes a_0 , b_0 , c_0 ($a_0 \parallel a_1$; $c_0 \parallel c_1^*$; $b_0 \parallel c_0 \times a_0$). The small and medium circles are Sn and S atoms, respectively. The centres of symmetry are indicated by small crosses. (a) Projection along c_0 ; only the lower half of the double layer is shown. (b) Projection along b_0 .

Table 6. Interatomic distances and angles in $(\text{SnS})_{1.20}\text{TiS}_2$. The numbering of atoms refers to figures 1 and 3.

	Interatomic distance (Å)	Angle (deg)	Angle (deg)
Sn-S(1a)	2.866(4)	S(1a)-Sn-S(1b)	163.9(1)
Sn-S(1b)	2.873(4)	S(1c)-Sn-S(1d)	164.4(1)
Sn-S(1c)	2.911(4)	S(1a)-Sn-S(1e)	89.6(1)
Sn-S(1d)	2.976(4)	S(1b)-Sn-S(1e)	82.0(1)
Sn-S(1e)	2.6109(3)	S(1c)-Sn-S(1e)	82.4(1)
		S(1d)-Sn-S(1e)	81.9(1)
Ti-S(2a)	2.417(2)	S(2a)-Ti-S(2b)	88.46(4)
Ti-S(2b)	2.428(1)	S(2a)-Ti-S(2c)	88.45(4)
Ti-S(2c)	2.429(1)	S(2b)-Ti-S(2c)	89.26(5)

a direction. In the case of an undistorted TiS_2 sandwich the rows of S above and below Ti are displaced over $(\frac{1}{2})b$; when rows of S of the Sn double layer have no displacement along b , then $\rho_i = \frac{1}{2}$, and the angles α_i , given by $\cos(\alpha_i) = \rho_i b_i / c_i$ are 94.77° (SnS) and 94.79° (TiS_2). The difference with the observed values is caused by the distortion of SnS and TiS_2 .

The TiS_2 sandwich is slightly distorted compared with 1T- TiS_2 . The Ti-S distances and angles S-Ti-S in table 6 show that the symmetry of a TiS_6 polyhedron is $2/m$ (note

that the space group of 1T-TiS₂ in an orthohexagonal cell is $C2/m$). The Ti-S distances (table 6), with an average of 2.425 Å, are close to those observed in 1T-TiS₂, 2.4279 Å (Chianelli *et al* 1975).

5. Superspace group symmetry

Analogous to the discussion for the orthorhombic misfit layer compounds (Wiegiers *et al* 1990b, van Smaalen 1989) the superspace group defines a relation between the subsystem space groups. Here it shows that both subsystems must be centrosymmetric (as found in this study) or both subsystems are acentric. Furthermore, the superspace group gives information about the centring of the individual unit cells. The combination CF as found for $(\text{SnS})_{1.20}\text{TiS}_2$ is possible; however, a loss of centring in one subsystem (e.g. $C \rightarrow P$) implies the loss of a related centring in the other subsystem. The (3 + 1)-dimensional superspace group which characterizes the complete structure of $(\text{SnS})_{1.20}\text{TiS}_2$ is $P:\bar{1}:\bar{1}(\alpha\beta\gamma)$, the centring representing

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} & 0 \end{pmatrix}.$$

The reciprocal lattice vectors of the two subsystems SnS ($\nu = 1$) and TiS₂ ($\nu = 2$), $a_{\nu j}^*$ ($\nu = 1, 2; j = 1, 2, 3$), are as follows associated with the four reciprocal lattice vectors a_i^* ($i = 1, 2, 3, 4$) in (3 + 1)-dimensional superspace:

$$\begin{bmatrix} a_{\nu 1}^* \\ a_{\nu 2}^* \\ a_{\nu 3}^* \end{bmatrix} = Z^{\nu} \begin{bmatrix} a_1^* \\ a_2^* \\ a_3^* \\ a_4^* \end{bmatrix}$$

with

$$Z^1 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{bmatrix} \quad Z^2 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}.$$

Not yet discussed is the mutual modulation of the two sublattices which gives rise to satellite reflections with indices $hklm$ ($h, m \neq 0$) using the four reciprocal lattice vectors given above. Satellites due to this modulation are visible by electron diffraction (Wiegiers *et al* 1989) but they are too weak to be observed on Weissenberg photographs taken with Cu K α radiation. In the average structure as obtained by our structure determinations (see, e.g., the discussion given for $(\text{LaS})_{1.14}\text{NbS}_2$ and $(\text{PbS})_{1.14}\text{NbS}_2$ by Wiegiers *et al* (1990b)), the modulation is visible in the temperature factors of the atoms. The rather

high *R*-factors of our structure determination may arise because the mutual modulation is not taken into account.

6. Phase relationships

The compounds 'SnTiS₃' and 'SnTi₂S₅' were reported by Guemas *et al* (1988). The unit-cell dimensions deduced from Weissenberg photographs of poorly crystallized 'SnTiS₃' (orthorhombic with unit-cell dimensions $a = 23.3 \text{ \AA}$, $b = 5.79 \text{ \AA}$ and $c = 23.3 \text{ \AA}$) indicate that their compound 'SnTiS₃' is essentially the triclinic compound of our study. The compound 'SnTi₂S₅' with $c = 35.13 \text{ \AA}$ is presumably a stacking of one SnS double layer followed by two TiS₂ sandwiches. In the mixed-valence compound Sn₂S₃ with Sn(II) and Sn(IV), part of Sn(IV) can be replaced by Ti(IV), forming a compound Sn_{1.2}Ti_{0.8}S₃ (Gressier *et al* 1987).

References

- Chianelli R R, Scanlon J C and Thompson A H 1975 *Mater. Res. Bull.* **10** 1379
Cromer D T and Mann J B 1968 *Acta Crystallogr. A* **24** 321
Cromer D T and Libermann D 1970 *J. Chem. Phys.* **53** 1891
de Boer J L and Duisenberg A 1984 *Acta Crystallogr. A* **40** C410
Gotoh Y, Goto M, Kawaguchi K, Oosawa Y and Onoda M 1990 *Mater. Res. Bull.* **25** 307
Gressier P, Meerschaut A and Rouxel J 1987 *Mater. Res. Bull.* **22** 1573
Guemas L, Rabu P and Meerschaut A 1988 *Mater. Res. Bull.* **23** 1061
Hall S R and Stewart J M (ed) 1989 *XTAL 2.2 User's Manual* (Perth: University of Western Australia) (Baltimore, MD: University of Maryland)
International Tables for Crystallography 1983 vol A, ed T Hahn (Dordrecht: Reidel)
Kato K, Kawada T and Takahashi T 1977 *Acta Crystallogr. B* **33** 3437
Kato K 1990 *Acta Crystallogr. B* **46** 39
McCandlish L E, Stout G H and Andrews L C 1975 *Acta Crystallogr. A* **31** 245
Meetsma A, Wiegiers G A, Haange R J and Boer J L de 1989 *Acta Crystallogr. A* **45** 285
Otera-Diaz J D, FitzGerald J D, Williams T B and Hyde B G 1985 *Acta Crystallogr. B* **41** 405
Spek A L 1982 *Computational Crystallography* ed D Sayre (Oxford: Clarendon) p 528
Spek A L 1983 *Proc. 8th Eur. Crystallographic Meet. (Liège, 1983)*
Takahashi T, Oka T, Yamada O and Ametani K 1971 *Mater. Res. Bull.* **6** 173
Takahashi T, Osaka S and Yamada O 1973 *J. Phys. Chem. Solids* **34** 1131
van Smaalen S 1989 *J. Phys.: Condens. Matter* **1** 1789
van Smaalen S, Meetsma A, Haange R J, de Boer J L and Wiegiers G A 1990 *Acta Crystallogr.* at press
Wiegiers G A, Meetsma A, van Smaalen S, Haange R J, Wulff P J, Zeinstra Th J, de Boer J L, Kuypers S, van Tendeloo G, van Landuyt J, Amelinckx S, Meerschaut A, Rabu P and Rouxel J 1989 *Solid State Commun.* **70** 409
Wiegiers G A, Meetsma A, van Smaalen S, Haange R J and de Boer J L 1990a *Solid State Commun.* **75** 689
Wiegiers G A, van Smaalen S, Meetsma A, Haange R J, de Boer J L, Meerschaut A, Rabu P and Rouxel J 1990b *Acta Crystallogr. B* **46** 324
Williams T B and Hyde B G 1988 *Acta Crystallogr. B* **44** 467