RESEARCH PAPERS

(3 + 2)-Dimensional Superspace Approach to the Structure of the Stage-2 Misfit Layer Compound $(SbS)_{1.15}(TiS_2)_2$

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Abstract

The inorganic misfit layer compound $(SbS)_{1.15}(TiS_2)_2$ was prepared by high-temperature reaction of the elements. It can be regarded as a stage-2 phase intercalation compound where double layers of SbS are inserted into the van der Waals gaps of TiS_2 with stacking sequence $\cdots[TiS_2][SbS][TiS_2][TiS_2][SbS]-[TiS_2]\cdots$. The structure, determined by single crystal X-ray diffraction on the basis of the (3 + 2)-dimensional superspace group $C\bar{1}$, is described by two interpenetrating, incommensurately modulated subsystems. The first subsystem comprises double sandwiches of TiS_2 with $1T$-TiS_2 structure. The lattice parameters are $a_{11} = 3.404\,(1)$, $a_{12} = 5.908\,(3)$, $a_{13} = 17.068\,(3)\,\text{Å}$, $\alpha_1 = 86.28\,(2)$, $\beta_1 = 96.40\,(2)$ and $\gamma_1 = 90.00\,(2)^\circ$. The second subsystem is built of intrinsically interface modulated double layers of SbS. Unit-cell dimensions of the basic structure are given by $a_{21} = 2.950\,(1)$, $a_{22} = 5.932\,(2)$, $a_{23} = 17.008\,(2)\,\text{Å}$, $\alpha_2 = 85.82\,(1)$, $\beta_2 = 85.30\,(1)$, $\gamma_2 = 84.11\,(1)^\circ$. The interface modulation wavevector of SbS is given by $q = 0.411\,(2)a_{21}^* + 0.822\,(4)a_{22}^*$. The two subsystems have the common $(a_{\nu 2}^*, a_{\nu 3}^*)$ plane. Refinement on 3112 reflections with $I > 2.5\sigma(I)$ converged to $R = 0.088$ $(wR = 0.108)$. The structure consists of both occupational and displacive modulations for the atoms in the SbS subsystem. The SbS subsystem has the same structural features as found in the compound $(SbS)_{1.15}TiS_2$ [Ren, Meetsma, Petricek, van Smaalen & Wiegers (1995), *Acta Cryst.* **B51**, 275–287]. But stacking disorder of SbS is found corresponding to displacements of the layers along the a_{21} axis; the final structure model involves a rigid shift of $0.63\,(2)\,\text{Å}$ of $5.5\,(4)\%$ of SbS to both sides along a_{21}.

1. Introduction

Inorganic misfit layer compounds $(\mathcal{MX})_{1+\delta}(\mathcal{TX}_2)_n$ ($\mathcal{M} = Sn, Pb, Bi, Sb$ and rare earth elements; $\mathcal{T} = Ti$, V, Cr, Nb, Ta; $\mathcal{X} = S$, Se; $0.09 < \delta < 0.23$; and $n = 1$ or 2) can be considered as a special class of intercalation compounds of layered transition metal dichalcogenides where two-atom thick $\mathcal{MX}$ layers with a distorted NaCl-type structure are intercalated into the van der Waals gaps of $\mathcal{TX}_2$ sandwiches (Wiegers & Meerschaut, 1992). Commonly, the layers $\mathcal{MX}$ and $\mathcal{TX}_2$ are stacked alternatingly, forming a stage-1 phase; but also compounds of a stage-2 phase have been found with paired sandwiches of $\mathcal{TX}_2$ of a stacking sequence $\cdots[\mathcal{TX}_2][\mathcal{MX}][\mathcal{TX}_2][\mathcal{TX}_2][\mathcal{MX}][\mathcal{TX}_2]\cdots$ (Meerschaut, Auriel & Rouzel, 1992). There is a structure determination of a stage-3 misfit layer compound $(Gd_\varepsilon Sn_{1-\varepsilon}S)_{1.16}(NbS_2)_3$ (Hoistad, Meerschaut, Bonneau & Rouxel, 1995). Structures of misfit compounds can be described by assigning different unit cells to the $\mathcal{MX}$ and $\mathcal{TX}_2$ layer types. The unit cells have a common (b^*, c^*) plane and the incommensurateness of the complete system is characterized by the irrational number of the length ratio of the two **a** axes, which are parallel to each other. The interaction of the subsystems induces a mutual modulation, where a^* of one subsystem is the modulation wavevector of the other subsystem. A complete description of all structural features is only possible within the superspace approach (van Smaalen, 1992; Janner & Janssen, 1980). But as yet there has not been complete structure determination of stage-2 compounds using the superspace-group description. Recently, we have reported a (3 + 2)-dimensional superspace approach to the structure of an Sb-misfit layer compound $(SbS)_{1.15}TiS_2$ (Ren, Meetsma, Petricek, van Smaalen & Wiegers, 1995), hereafter denoted by (I), in which an interface modulated ordering of Sb and S was found in the SbS subsystem. In this paper we present a structure

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determination of a stage-2 compound $(SbS)_{1.15}(TiS_2)_2$, again on the basis of the $(3+2)$-dimensional superspace.

2. Experimental

The compound $(SbS)_{1.15}(TiS_2)_2$ was synthesized from the elements by high-temperature reaction. Single crystals of thin platelets with a metallic lustre were obtained in the same way as for $(SbS)_{1.15}TiS_2$ (I). A single crystal of a parallelepiped shape of *ca* $0.23 \times 0.09 \times 0.01$ mm^3 was selected for X-ray diffraction experiments. Weissenberg photographs of the crystal showed the diffraction pattern as found for $(SbS)_{1.15}TiS_2$, but with *c* axes of *ca* 17 Å rather than *ca* 11.4 Å, which is in good agreement with a stacking sequence of $\cdots[TiS_2][SbS][TiS_2][TiS_2]-[SbS][TiS_2]\cdots$ along the *c* direction.

Single crystal X-ray diffraction was performed on an Enraf–Nonius CAD-4F diffractometer with monochromatized Mo $K\bar{\alpha}$ radiation $(\lambda = 0.71073\,\text{Å})$. Unit-cell dimensions and their standard deviations were determined independently for each subsystem, from the setting angles in four alternate setting of 22 reflections in the range $26.33 < \theta < 37.94°$ for TiS$_2$ and 22 reflections in the range $9.68 < \theta < 20.99°$ for SbS. For comparison with other misfit layer compounds and facilitating the analysis, non-standard space group settings have been adopted for the average structures, *i.e.* the centring translation $(\frac{1}{2},\frac{1}{2},0)$ for TiS$_2$ and $(0,\frac{1}{2},0)$ for SbS (Table 1). The modulation wavevector **q** with respect to the transformed basic lattice of SbS was determined as $\mathbf{q} = 0.411\,(2)\mathbf{a}_{21}^* + 0.822\,(4)\mathbf{a}_{22}^*$. Within experimental error, the modulation wavevector is equal to that as observed in $(SbS)_{1.15}TiS_2$ (I). The composition of this compound is calculated as $(SbS)_{1.15}(TiS_2)_2$ from the volume ratio $2V_1/V_2$, equal to the length ratio $\mathbf{a}_{11}/\mathbf{a}_{21}$, of the two subsystem unit cells.

Data collection was performed separately for the two subsystems using the θ–2θ scan technique. Intensities were measured at the nodes of the reciprocal lattices based on the two sets of the primitive cell dimensions. All main reflections were measured in one hemisphere up to $\theta = 32.5°$. The first- and third-order satellites of the interface modulation of the SbS part were measured together with its main reflections. The experimental stability was checked by the standard reflections (131), $(11\bar{3})$ and $(0\bar{2}1)$ for TiS$_2$ and $(1\bar{2}0)$, $(10\bar{1})$ and $(0\bar{2}\bar{1})$ for SbS, measured every 2 h of X-ray exposure time. It showed a long-term variation of less than 2%. The intensities were corrected for scale variation, Lorentz and polarization effects, and for absorption $(\mu = 158\,\text{cm}^{-1})$ using a Gaussian integration method (Spek, 1983).

A total of 1262 reflections were measured for the TiS$_2$ subsystem. For the SbS subsystem 4791 reflections were measured, including 2092 first-order and 1412 third-order satellites. The common reflections $(0kl)$ were used to bring the two data sets onto the same scale. 172

Table 1. *Unit-cell dimensions of the TiS$_2$ and SbS subsystems in $(SbS)_{1.15}(TiS_2)_2$*

Subcell	ν	$a_{\nu 1}$ (Å)	$a_{\nu 2}$ (Å)	$a_{\nu 3}$ (Å)	α_ν (°)	β_ν (°)	γ_ν (°)
TiS$_2$	1	3.403 (1)	5.908 (3)	17.068 (2)	86.28 (2)	96.40 (2)	90.00 (2)
SbS	2	2.950 (1)	5.932 (2)	17.008 (2)	85.82 (1)	85.30 (1)	84.11 (1)

common reflections with $I > 2.5\sigma(I)$, present in both sets, resulted in an average scale factor of 0.988 (1) which was used to multiply to the SbS intensities. The two sets of $(0kl)$ were averaged; the internal consistency is $R_I = 0.011$. The result was a single data set for the complete structure with 5880 reflections which were further combined into 5129 unique reflections, using $\bar{1}$ Laue symmetry. The internal consistency is $R_I = (\sum_i |I_i - I_i^{av}|)/(\sum_i I_i) = 0.029$ for the observed reflections with $I > 2.5\sigma(I)$. With this criterion for observability, the number of unique reflections finally reduced to 3112. Refinements on this data set were carried out with the *JANA*93 (Petricek, 1993) computer program system. Plots of the interatomic distances and bond valences as functions of the internal coordinates (t_1, t_2) have been made with the *MISTEK* (van Smaalen, 1991) program.

3. Superspace symmetry

The complete diffraction pattern of $(SbS)_{1.15}(TiS_2)_2$ can be indexed using five integer indices (H, K, L, M_1, M_2) with respect to a set of $(3+2)$ basis vectors: $\mathbf{M}^* = (\mathbf{a}_1^*, \ldots, \mathbf{a}_5^*)$. The first three vectors are chosen as the three reciprocal basis vectors of the TiS$_2$ part (which is chosen as the first subsystem, $\nu = 1$): $\mathbf{a}_i^* = \mathbf{a}_{1i}^*$ for $i = 1, 2, 3$. The fourth and fifth vectors are chosen as $\mathbf{a}_4^* = \mathbf{a}_{21}^*$ ($\mathbf{a}^*$ axis of the SbS part, which is the second subsystem, $\nu = 2$) and $\mathbf{a}_5^* = \mathbf{q}$ describing the interface modulation in the SbS subsystem. The last two vectors can be expressed as a linear combination of the first three by a (2×3) matrix σ

$$\begin{pmatrix} \mathbf{a}_4^* \\ \mathbf{a}_5^* \end{pmatrix} = \sigma \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \end{pmatrix}, \tag{1}$$

where the components of the σ matrix have been determined as

$$\begin{aligned} \sigma &= \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \end{pmatrix} \\ &= \begin{pmatrix} 1.154\,(2) & -0.206\,(2) & -1.118\,(4) \\ 0.474\,(3) & 0.737\,(3) & -0.459\,(5) \end{pmatrix}. \end{aligned} \tag{2}$$

Superspace can be built up in the same way as for the stage-1 compound $(SbS)_{1.15}TiS_2$ (I), by the identification of the five basis vectors of $\mathbf{M}^*$ with the perpendicular projection of five independent translation vectors in $(3+2)$-dimensional space. For subsystem ν, the reciprocal basis vectors Λ_ν^*, together with its modulation

wavevectors $\mathbf{q}_{vi}$ ($i = 1, 2$), can be written as an integral linear combination of the basis vectors in $\mathbf{M}^*$ (van Smaalen, 1992)

$$\begin{pmatrix} \mathbf{a}_{v1}^* \\ \mathbf{a}_{v2}^* \\ \mathbf{a}_{v3} \\ \mathbf{q}_{v1} \\ \mathbf{q}_{v1} \end{pmatrix} = \mathcal{W}^v \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \\ \mathbf{a}_5^* \end{pmatrix}, \tag{3}$$

where the 5×5 matrix $\mathcal{W}^v$ can be written as a juxtaposition of a 3×5 matrix ($\mathcal{Z}^v$) and a 2×5 matrix ($\mathcal{V}^v$), which extract the basis vectors of the basic structures and the modulation wavevectors, respectively

$$\mathcal{W}^v = \begin{pmatrix} \mathcal{Z}^v \\ \mathcal{V}^v \end{pmatrix} = \begin{pmatrix} \mathcal{Z}_3^v & \mathcal{Z}_d^v \\ \mathcal{V}_3^v & \mathcal{V}_d^v \end{pmatrix}. \tag{4}$$

For further application, the 3×5 matrix $\mathcal{Z}^v$ is expressed as a juxtaposition of a 3×3 matrix ($\mathcal{Z}_3^v$) and a 3×2 matrix ($\mathcal{Z}_d^v$), and the 2×5 matrix $\mathcal{V}^v$ as a juxtaposition of a 2×3 matrix ($\mathcal{V}_3^v$) and a 2×2 matrix ($\mathcal{V}_d^v$). The $\mathcal{W}^v$ matrices define a coordinate transformation between superspace based on $\mathbf{M}^*$ and subsystem superspace based on Λ_v^* and $\mathbf{q}_{vi}$ ($i = 1, 2$) for each subsystem. For the present study, the following matrices are used

$$\mathcal{W}^1 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix},$$

$$\mathcal{W}^2 = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}. \tag{5}$$

From the above expressions one can see that each subsystem is modulated with the mutual modulation wavevector given by the periodicity along the **a** axis of the other subsystem, and with a common modulation wavevector **q** which has different components when based on the basis vectors, Λ_v^*, of the two subsystems. For both subsystems, the basic structures have triclinic symmetry. Systematic extinction conditions were found for the (H, K, L, M_1, M_2) reflections as $H + K = $ odd are absent. It implies a C-centring translation

$$(\tfrac{1}{2}, \tfrac{1}{2}, 0, 0, 0). \tag{6}$$

For a centrosymmetric triclinic structure, the following non-standard superspace group setting is used, which is equivalent to the standard class $P_s\bar{1}$

$$G_s = C\bar{1}(\sigma_{11}, \sigma_{12}, \sigma_{13}; \sigma_{21}, \sigma_{22}, \sigma_{23}), \tag{7}$$

with symbol C representing the centring translation as given by (6). With the coordinate transformations defined by the matrices $\mathcal{W}^v$, the elements $(R_s^v | \tau_s^v)$ of the subsystem superspace groups can be derived as (van Smaalen, 1991)

$$\begin{aligned} R_s^v &= \mathcal{W}^v R_s (\mathcal{W}^v)^{\mathrm{inv}} \\ \tau_s^v &= \mathcal{W}^v \tau_s, \end{aligned} \tag{8}$$

where R_s and τ_s represent the rotation and translation operations, respectively, of superspace group G_s. With $\mathcal{W}^1$ the identity, the subsystem superspace group of the first subsystem, G_s^1, is identical with the superspace group G_s. For the second subsystem, the subsystem superspace group is

$$G_s^2 = C'\bar{1}(\sigma_{11}^2, \sigma_{12}^2, \sigma_{13}^2; \sigma_{21}^2, \sigma_{22}^2, \sigma_{23}^2) \tag{9}$$

with a centring translation C' of $(0,1/2,0,1/2,0)$. The σ^2 matrix is given by

$$\begin{aligned} \sigma^2 &= \begin{pmatrix} \sigma_{11}^2 & \sigma_{12}^2 & \sigma_{13}^2 \\ \sigma_{21}^2 & \sigma_{22}^2 & \sigma_{23}^2 \end{pmatrix} \\ &= (\mathcal{V}_3^2 + \mathcal{V}_d^2 \sigma)(\mathcal{Z}_3^2 + \mathcal{Z}_d^2 \sigma)^{\mathrm{inv}} \\ &= \begin{pmatrix} 0.867 & 0.179 & 0.969 \\ 0.411 & 0.822 & 0.000 \end{pmatrix}. \end{aligned} \tag{10}$$

The space groups describing the symmetry of the basic structure of each subsystem can be obtained as the restriction of G_s^v to three-dimensional physical space: $G_1 = C\bar{1}$ for TiS_2 with C representing the normal C-centring translation $(1/2,1/2,0)$ and $G_2 = C\bar{1}$ for SbS with a non-standard C-centring translation $(0,1/2,0)$.

In the superspace description of the composite structure the coordinates of each atom μ can be expressed with respect to the subsystem lattice basis Λ_v to which this atom belongs

$$x_{vi}(\mu) = \bar{x}_{vi}(\mu) + u_{vi}^\mu(\bar{x}_{vs4}, \bar{x}_{vs5}), \tag{11}$$

for $v = 1, 2$ and $i = 1, 2, 3$. u_{vi}^v are the displacive modulation functions for atom μ with periodicities of one, both in $\bar{x}_{vs4}$ and $\bar{x}_{vs5}$, the fourth and fifth subsystem-superspace coordinates. Let (t_1, t_2) be the set of two real numbers characterizing a particular section of superspace, the average structure coordinates $\bar{x}_{vi}$ can be written as (van Smaalen, 1992)

$$\begin{aligned} \bar{x}_{1i}(\mu) &= n_{1i} + x_{1i}^0(\mu), & i = 1, 2, 3; \\ \bar{x}_{21}(\mu) &= n_{21} + x_{21}^0(\mu) - t_1, & \\ \bar{x}_{2i}(\mu) &= n_{2i} + x_{2i}^0(\mu), & i = 2, 3; \end{aligned} \tag{12}$$

where n_{vi} runs over all integers. The coordinates x_{vi}^0 of atom μ with respect to its own subsystem unit cell are to be determined in the structure refinement. The fourth and fifth subsystem-superspace coordinates can be expressed as (van Smaalen, 1992)

$$\begin{pmatrix} \bar{x}_{\nu s4}(\mu) \\ \bar{x}_{\nu s5}(\mu) \end{pmatrix} = \sigma^\nu \begin{pmatrix} \bar{x}_{\nu 1}(\mu) \\ \bar{x}_{\nu 2}(\mu) \\ \bar{x}_{\nu 3}(\mu) \end{pmatrix} + \nu_d^\nu \begin{pmatrix} t_1 \\ t_2 \end{pmatrix}. \quad (13)$$

The complete structure of $(SbS)_{1.15}(TiS_2)_2$ involves both displacive and occupational modulations. The coefficients of the Fourier expansions of the modulation functions are used as independent parameters in the structure refinements: for the displacive modulation

$$u_{\nu i}^\mu(\bar{x}_{\nu s4}, \bar{x}_{\nu s5}) = \sum_{n_1,n_2=0}^{\infty} \{A_{\nu i,n_1 n_2}^\nu \sin[2\pi(n_1 \bar{x}_{\nu s4} + n_2 \bar{x}_{\nu s5})]$$
$$+ B_{\nu i,n_1 n_2}^\mu \cos[2\pi(n_1 \bar{x}_{\nu s4} + n_2 \bar{x}_{\nu s5})]\}, \quad (14)$$

for $i = 1, 2, 3$; and for the occupational modulation

$$P_\nu^\mu(\bar{x}_{\nu s4}, \bar{x}_{\nu s5})$$
$$= P_{\nu 0}^\mu + P_\nu^\mu(\bar{x}_{\nu s4}, \bar{x}_{\nu s5})$$
$$= P_{\nu 0}^\nu + \sum_{n_1,n_2=0}^{\infty} \{P_{\nu,n_1 n_2}^{\mu,s} \sin[2\pi(n_1 \bar{x}_{\nu s4} + n_2 \bar{x}_{\nu s5})]$$
$$+ P_{\nu,n_1 n_2}^{\mu,c} \cos[2\pi(n_1 \bar{x}_{\nu s4} + n_2 \bar{x}_{\nu s5})]\}, \quad (15)$$

for $\nu = 1, 2$ and excluding the term $(n_1, n_2) = (0, 0)$ in both summations.

4. Structure refinements

In the basic structure of $(SbS)_{1.15}(TiS_2)_2$, each atom occupies a general position with respect to its own subsystem unit cell. In the SbS subsystem Sb and S, which are, respectively, denoted by Sb(2,1) and S(2,1) hereafter, are almost at the same position, each with occupancy $1/2$, because main reflections (hkl) of SbS occur only for k even. First, 172 common reflections $(0KL00)$ were used to determine the common projection of the structure along the [100] direction. A good fit resulted in $R = 0.0555$ $\{wR = 0.0749$ with the weight, $w = 1/[\sigma^2(F_{obs}) + (0.02|F_{obs}|)^2]\}$. Subsequently the basic structures of both subsystems were refined independently, using 689 main reflections for TiS_2 and 731 main reflections for SbS, where the common reflections were excluded. It was found that the refined scale factor for the SbS subsystem was much lower than that for TiS_2, although the two data sets are on the same scale. Such a problem has also been found in structure refinements of other stage-2 misfit layer compounds (Evain & van Smaalen, unpublished), and it indicates that there is disorder in the SbS subsystem. The scale factors for the individual refinements on the main reflections of TiS_2 and on the common reflections are the same, indicating that the effect of the disorder has disappeared in the projection along $\mathbf{a}_{21}$, and the disorder in SbS must correspond to an indeterminacy of the x positions of the atoms. A Fourier map obtained from the observed main reflections shows tails around the main peaks in the $\mathbf{a}_{21}$ direction.

In the first stages of the structure refinements two scale factors are used: one is for the main reflections of TiS_2 and the common reflections, and the other for the main reflections and satellites of the SbS subsystem. In this case the modulated structure of this compound can be described in the same way as used for $(SbS)_{1.15}TiS_2$ (I). Both displacive and occupational modulation parameters are applied to the Sb(2,1) and S(2,1) atoms of SbS. The structure refinement has been performed step by step: in the beginning the first- and third-order Fourier amplitudes of the occupational modulation function (14) for the Sb(2,1) and S(2,1) atoms of SbS were added; then displacive Fourier amplitudes up to the fourth order of the modulation wave $\mathbf{q}_{22}$ for Sb(2,1) and S(2,1) of SbS were employed. Due to the high correlations between sine and cosine amplitudes of the displacement modulation, as also found in $(SbS)_{1.15}TiS_2$, some sine parts of the Fourier amplitudes have been discarded. Further addition of the Fourier amplitudes of higher order did not improve the fit. Because of the two different scale factors for the two subsystems, no mutual modulation was considered in this case. The ordering of Sb(2,1) and S(2,1) at the position (x, y, z) with slightly different coordinates for each is restricted in such a way that the average occupancy of each site is $1/2$ for both Sb(2,1) and S(2,1) and the total occupancy is 1, which indicates

$$P_{\nu,0}^{Sb(2,1)} = P_{\nu,0}^{S(2,1)} = 1/2,$$
$$P_\nu^{Sb(2,1)}(\bar{x}_{\nu s4}, \bar{x}_{\nu s5}) + P_\nu^{S(2,1)}(\bar{x}_{\nu s4}, \bar{x}_{\nu s5}) = 1, \quad (16)$$

for $\nu = 2$. According to (16), suitable restrictions on the Fourier coefficients of Sb(2,1) and S(2,1) for the occupational function (15) can be tersely expressed as

$$\begin{pmatrix} P_{2,0n_2}^{S(2,1),s} \\ P_{2,0n_2}^{S(2,1),c} \end{pmatrix} = - \begin{pmatrix} \psi_{0n_2}^c & \psi_{0n_2}^s \\ -\psi_{0n_2}^s & \psi_{0n_2}^c \end{pmatrix} \begin{pmatrix} P_{2,0n_2}^{Sb(2,1),s} \\ P_{2,0n_2}^{Sb(2,1),c} \end{pmatrix}, \quad (17)$$

where $\psi_{0n_2}^s = \sin(2n_2\pi\Delta\bar{x}_5)$ and $\psi_{0n_2}^c = \cos(2n_2\pi\Delta\bar{x}_5)$ with $\Delta\bar{x}_5 = \mathbf{q} \cdot \{\mathbf{r}^0[S(2,1)] - \mathbf{r}^0[Sb(2,1)]\}$, and $\mathbf{r}^0[S(2,1)]$ and $\mathbf{r}^0[Sb(2,1)]$ being, respectively, the basic positions of S(2,1) and Sb(2,1) with respect to the SbS subsystem unit cell. With the basic structure and modulation parameters as described above and a single anisotropic temperature factor for each independent atom, the refinement converged smoothly to $R = 0.083$ $(wR = 0.103)$. As has been mentioned in (I), the high correlations between sine and cosine parts of the displacive modulation amplitudes are due to the occupational modulation waves which give some intervals in t of (nearly) zero occupancy. The occupational modulation waves are dominated by the sine amplitudes, which indicates that the occupational modulation function of Sb(2,1) has non-zero values only within the interval $[0,1/2]$ of $\bar{x}_{\nu s5}$ in equation (14) or for S(2,1) the non-zero interval is $[1/2,1]$. Thus in the displacive modulation parameters, the sine parts will give non-zero values when averaged over one period in t, while the cosine parts will average

to zero, which lead to high correlations between the basic structure positions and the sine parts of the modulation functions (14). In order to check this a refinement with all sine parts removed was carried out; the refinement gave $R = 0.083$ ($wR = 0.104$), equal to the previous result. Although in the case of a displacive modulation the intensities of the nth-order satellites are affected by Fourier amplitudes of all orders, they are dominated by the Fourier amplitude of the nth-order. Inclusion in the refinement of amplitudes other than the first- and third-order, corresponding to the order of the measured satellites, generally leads to large standard deviations for them [cf. Table 6 in (I)], while the reduction in the R factor was not significant. Therefore, only the cosine parts of the first- and third-order amplitudes for the displacive modulations were involved in the next refinements. The fit with 63 refinable parameters in this case gave slightly higher R factors: $R = 0.086$ ($wR = 0.107$). The partial R factors for this refinement (REF-2S) are listed in column REF-2S in Table 2.

To check whether the large difference of the scale factors for the basic structures can be recovered by the modulated structure, a refinement has also been carried out with only one scale factor for all reflections. Using the same type of structure parameters as mentioned above and suitable restrictions on the occupational modulation functions (equation 17), the final R factor is $R = 0.098$ ($wR = 0.116$), showing a worse fit than the refinements with two scale factors. The partial R factors for the refinement with one scale factor are listed in column REF-1S in Table 2.

Finally, an attempt to solve the stacking disorder has been performed using a shift model, for which a fraction (η) of the SbS layers was assumed to be shifted rigidly along the $\mathbf{a}_{21}$-axis, by a fractional amount $\pm\xi\mathbf{a}_{21}$. Both negative and positive shifts were incorporated in the same structure, thus retaining the overall inversion symmetry. Hereafter, the Sb and S atoms of the shifted SbS to the $-x$ direction are denoted by Sb(2,2) and S(2,2), respectively; while those of the shifted SbS to $+x$ are denoted by Sb(2,3) and S(2,3). Keeping the structure parameters of the shifted SbS slabs the same as those of the unshifted slabs, except the occupancy and x coordinate, refinement on the main reflections converged to $R = 0.065$ ($wR = 0.080$). In order to determine the complete structure, occupational and displacive modulation waves were involved. Assuming that the SbS slabs are just rigidly shifted along $\mathbf{a}_{21}$, which means that at any section of t in superspace the structures of the shifted and unshifted SbS slabs are exactly the same in spite of displacement $+\xi\mathbf{a}_{21}$ or $-\xi\mathbf{a}_{21}$, the restrictions for the occupational and displacive modulation parameters between the same type of atoms in the shifted and unshifted SbS slabs can be derived from [see (14) and (15)]

Table 2. *Reliability factors for the refinements REF-1S (using one scale factor), REF-2S (using two scale factors) and REF-SM (for the shift model) of the modulated structure in (3 + 2)-dimensional superspace*

The R factors are defined as $R = \sum ||F_{\text{obs}}| - |F_{\text{calc}}||/\sum |F_{\text{obs}}|$ and $wR = [\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2/\sum w|F_{\text{obs}}|^2]^{1/2}$, with weights $w = 1/[\sigma^2(F_{\text{obs}}) + (0.02|F_{\text{obs}}|)^2]$. Partial R factors are defined with a subset of the reflections. Satellites of order M_2 are defined as $HKLM_1M_2$ reflections.

Reflection subset	Number of reflections	R/wR		
		REF-1S	REF-2S	REF-SM
All	3112	0.098.0.116	0.086/0.107	0.088/0.108
Main	1592	0.085/0.099	0.068/0.085	0.072/0.088
TiS$_2$	689	0.075/0.094	0.058/0.078	0.066/0.085
SbS	731	0.098/0.107	0.082/0.090	0.082/0.093
Common	172	0.083/0.098	0.066/0.094	0.068/0.087
$M_2 = 1$	1238	0.111/0.136	0.108/0.132	0.104/0.130
$M_2 = 3$	282	0.294/0.331	0.294/0.329	0.300/0.338

$$u_{vi}^{\mu'}(\bar{x}_{vs4}, \bar{x}_{vs5}) = u_{vi}^{\mu}(\bar{x}_{vs4}, \bar{x}_{vs5}),$$
$$P_v^{\mu'}(\bar{x}_{vs4}, \bar{x}_{vs5}) = P_v^{\mu}(\bar{x}_{vs4}, \bar{x}_{vs5}) \tag{18}$$

to be for the displacive modulation

$$\begin{pmatrix} A_{vi,n_1n_2}^{u'} \\ B_{vi,n_1n_2}^{u'} \end{pmatrix} = \begin{pmatrix} \phi_{v,n_1n_2}^c & \phi_{v,n_1n_2}^s \\ -\phi_{v,n_1n_2}^s & \phi_{v,n_1n_2}^c \end{pmatrix} \begin{pmatrix} A_{vi,n_1n_2}^{\mu} \\ B_{vi,n_1n_2}^{\mu} \end{pmatrix}, \tag{19}$$

for $i = 1, 2, 3$; and to be for the occupational modulation

$$\begin{pmatrix} P_{v,n_1n_2}^{\mu',s} \\ P_{v,n_1n_2}^{\mu',c} \end{pmatrix} = \begin{pmatrix} \phi_{v,n_1n_2}^c & \phi_{v,n_1n_2}^s \\ -\phi_{v,n_1n_2}^s & \phi_{v,n_1n_2}^c \end{pmatrix} \begin{pmatrix} P_{v,n_1n_2}^{\mu,s} \\ P_{v,n_1n_2}^{\mu,c} \end{pmatrix}, \tag{20}$$

for $v = 2$, where μ' and μ represent the same type of atom in the shifted and the unshifted SbS slabs, respectively; and $\phi_{v,n_1n_2}^s = \sin[2\pi(n_1\mathbf{q}_{v1} \cdot \Delta\mathbf{r} + n_2\mathbf{q}_{v2} \cdot \Delta\mathbf{r})]$ and $\phi_{v,n_1n_2}^c = \cos[2\pi(n_1\mathbf{q}_{v1} \cdot \Delta\mathbf{r} + n_2\mathbf{q}_{v2} \cdot \Delta\mathbf{r})]$ with $\Delta\mathbf{r} = [\mathbf{r}^0(\mu') - \mathbf{r}^0(\mu)] = +\xi\mathbf{a}_{21}$ and $-\xi\mathbf{a}_{21}$, corresponding to the shifted SbS slabs to $+x$ and $-x$ directions, respectively. In this case, only one scale factor was used for all reflections and the independent parameters for the unshifted SbS slab are the same as in the REF-2S refinement, except that here one occupancy factor was also added as an independent parameter. For the shifted SbS slabs, only the x coordinate was refinable and other parameters are either equal to the unshifted slab or given by (19). Using one more parameter than the refinement with two scale factors, the refinement converged to $R = 0.088$ ($wR = 0.108$), almost the same as those of the REF-2S refinement. The partial R factors are listed in column REF-SM of Table 2. The large R factors for the third-order satellites can be understood because the intensities of the 282 reflections are relatively weak and the established R factor for this data set is $R = \sum \sigma(F_o)/\sum F_o = 0.130$ (where F_o's

Table 3. *Atomic coordinates in the unit cell given in Table 1 and the site occupancy factor (s.o.f.) as obtained by the REF-SM refinement in (3 + 2)-dimensional super-space of the modulated structure*

Coordinates refer to the subsystem lattice bases. Values without standard deviations are obtained from restrictions in the refinement.

Atom	ν	$x_{\nu 1}^{0}$	$x_{\nu 2}^{0}$	$x_{\nu 3}^{0}$	S.o.f.
Ti(1,1)	1	0.3436(4)	0.2185(2)	0.16749(8)	1
S(1,1)	1	0.8902(5)	0.0361(3)	0.2524(1)	1
S(1,2)	1	0.7965(5)	0.4013(3)	0.0841(1)	1
Sb(2,1)	2	−0.0324(4)	0.2322(2)	0.58053(5)	0.809(9)
Sb(2,2)	2	−0.247(4)	0.2322	0.58054	0.055
Sb(2,3)	2	0.183	0.2322	0.58054	0.055
S(2,1)	2	−0.0204(14)	0.2433(7)	0.5640(3)	0.890
S(2,2)	2	−0.236	0.2433	0.5638	0.055
S(2,3)	2	0.195	0.2433	0.5638	0.055

are observed structure factors).* Further adding of mutual modulation parameters to both subsystems did not lead to any improvement of fit. The basic coordinates, temperature parameters and modulation parameters as obtained from this refinement, REF-SM, are summarized in Tables 3–6.

5. Discussion

The orthogonal projection of the average structure of $(SbS)_{1.15}(TiS_2)_2$ along the **a** axes is depicted in Fig. 1. In fact, in the average structure the occupancy of Sb and S of the SbS subsystem is 1/2, because main reflections of SbS occur only for k even. The difference from the previous compound $(SbS)_{1.15}TiS_2$ is that the double layers SbS are separated by two sandwiches of TiS_2, where the van der Waals gaps between TiS_2 sandwiches are unoccupied. The paired TiS_2 sandwiches have a distorted $1T$–TiS_2 structure. The Ti atoms are coordi-

* A list of structure factors has been deposited with the IUCr (Reference: JS0020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England
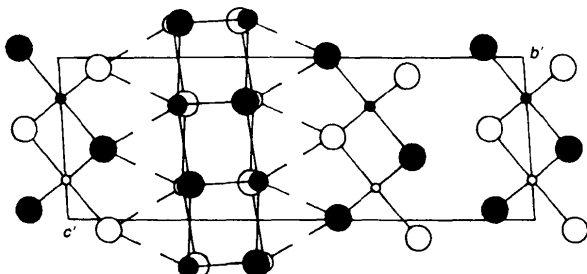

Fig. 1. Orthogonal projection of the structure of $(SbS)_{1.15}(TiS_2)_2$ along the common [100] direction. $b' = a_{\nu 2}\sin\gamma_\nu$ and $c' = a_{\nu 3}\sin\beta_\nu$ for $\nu = 1, 2$. Large open and filled circles denote S atoms, small open and filled circles denote Ti atoms and middle ones denote Sb atoms.

nated by six S atoms in a trigonal antiprismatic arrangement. The Ti—S distances of the TiS_2 subsystem are listed in Table 7 and the average distance (2.427 Å) is
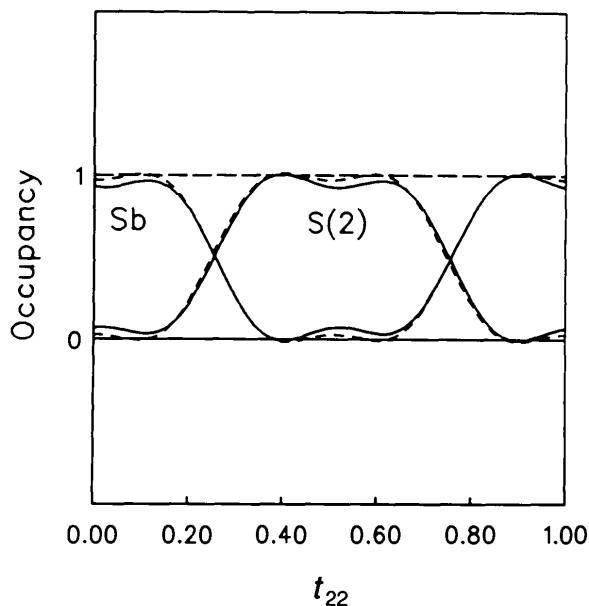

Fig. 2. Occupational modulation waves as functions of t_{22} for the atoms in the SbS subsystem. The solid and broken lines are for $(SbS)_{1.15}(TiS_2)_2$ and $(SbS)_{1.15}TiS_2$, respectively.
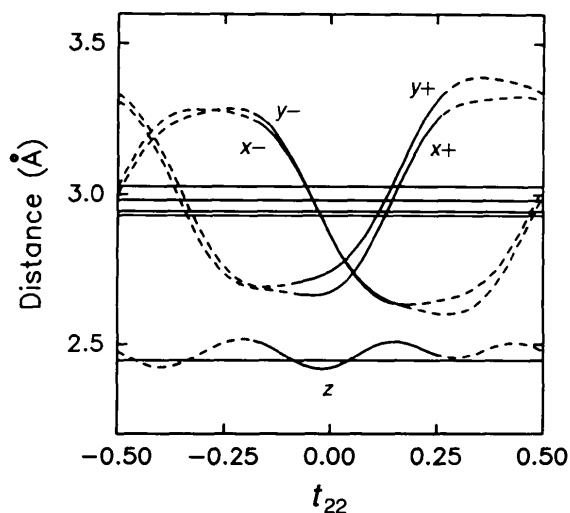

Fig. 3. Coordination of Sb(2,1) by S(2,1) of the same subsystem SbS as a function of t_{22} at $t_{21} = 0.0$. The distances for the basic structure are the horizontal lines (refer to Table 7) and the wavy curves show the distances for the modulated structure. The curves correspond to the distance between $(E|,0,0,0,0,0)Sb$ and the five following symmetry equivalents of S(2,1): $S(2,1)^{x+} = (\bar{1}|0,0,1,1,0)S(2,1)$, $S(2,1)^{x-} = (\bar{1}|0,0,1,-1,0)S(2,1)$, $S(2,1)^{y+} = (\bar{1}|0,0.5,0,1,0,0)$-$S(2,1)$, $S(2,1)^{y-} = (\bar{1}|0,-0.5,1,0,0)S(2,1)$, $S(2,1)^z = (\bar{1}|0,0.5, 1,0,0)S(2,1)$. The curve marked z is the distance Sb(2,1)—S(2,1)^z; $x+$ is Sb(2,1)—S(2,1)$^{x+}$; $x-$ is Sb(2,1)—S(2,1)$^{x-}$; $y+$ is Sb(2,1)—S(2,1)$^{y+}$ and $y-$ is Sb(2,1)—S(2,1)$^{y-}$.

Table 4. *Final values for the temperature factors* (Å^2) *as obtained from the REF-SM refinement in* $(3+2)$-*dimensional superspace of the modulated structure*

Atom	ν	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ti(1,1)	1	0.0087(5)	0.0083(5)	0.0113(5)	0.0012(4)	0.0017(4)	−0.0006(4)
S(1,1)	1	0.0075(7)	0.0068(6)	0.0065(7)	0.0014(5)	0.0009(5)	0.0001(5)
S(1,2)	1	0.0066(7)	0.0065(6)	0.0070(7)	0.0024(5)	0.0008(5)	0.0004(5)
Sb(2,1)	2	0.0327(17)	0.0222(4)	0.0087(3)	0.0026(3)	−0.0005(3)	0.0001(2)
S(2,1)	2	0.0165(31)	0.0226(25)	0.0172(15)	0.0007(18)	0.0009(16)	0.0030(16)

The temperature factor appearing in the expression of the structure factor is defined by $T = \exp[-(\beta_{11}h_\nu^2 + \beta_{22}k_\nu^2 + \beta_{33}l_\nu^2 + \beta_{12}h_\nu k_\nu + \beta_{13}h_\nu l_\nu + \beta_{23}k_\nu l_\nu)]$ and $\beta_{ij} = 2\pi^2 U_{ij}\mathbf{a}_{\nu i}^*\mathbf{a}_{\nu j}^*$.

Table 5. *Final values for the amplitudes of the occupational modulation functions for the atoms Sb(2,1) and S(2,1) as obtained from the REF-SM refinement in* $(3+2)$-*dimensional superspace of the modulated structure [equation (15)]*

The amplitude is calculated as $[(P_{2,n_1n_2}^{\mu,s})^2 + (P_{2,n_1n_2}^{\mu,c})^2]^{1/2}$.

Atom(μ)	n_1	n_2	$P_{2,n_1n_2}^{\mu,s}$	$P_{2,n_1n_2}^{\mu,c}$	Amplitude
Sb(2,1)	0	0		0.5	0.5
	0	1	0.544(4)	0.104(3)	0.554(5)
	0	3	0.117(5)	0.048(6)	0.126(7)
S(2,1)	0	0		0.5	0.5
	0	1	−0.551(4)	−0.056(3)	0.554(5)
	0	3	−0.125(5)	−0.015(6)	0.127(6)

Table 6. *Displacive modulation parameters,* $B_{\nu i,n_1n_2}^{\mu}a_{\nu i}$ (Å) *for i = 1, 2, 3 and* $\nu = 2$, *for the atoms Sb(2,1) and S(2,1) as obtained from the REF-SM refinement in* $(3+2)$-*dimensional superspace of the modulated structure [equation (14)]*

Atom(μ)	n_1	n_2	$B_{\nu1,n_1n_2}^{\mu}a_{21}$	$B_{\nu2,n_1n_2}^{\mu}a_{22}$	$B_{\nu3,n_1n_2}^{\mu}a_{23}$
Sb(2,1)	0	1	−0.007(2)	0.044(2)	−0.003(1)
	0	3	−0.010(4)	0.008(3)	0.011(3)
S(2,1)	0	1	0.335(8)	0.305(8)	−0.010(8)
	0	3	−0.038(13)	−0.031(12)	−0.029(14)

equal to that observed in $1T$–TiS_2 (Chianelli, Scanlon & Thompson, 1975) and close to that (2.431 Å) in $(SbS)_{1.15}TiS_2$ (I).

The stacking disorder of the SbS subsystem indicates that the coupling between successive SbS double layers is weakened by the paired TiS_2 sandwiches. The structure refinement using the shift model shows that 11.0(9)% of the SbS layers are in shifted positions along a_{21}, half of which displace over $+\xi a_{21}$ and the other half over $-\xi a_{21}$ with $\xi = 0.215(4)$. Each SbS layer has a similar structure to SbS in $(SbS)_{1.15}TiS_2$. The ordering of Sb/S atoms on the rock-salt structure can be described by an occupational wave (Table 5), which is not a simple block wave. The occupational modulation waves of Sb(2,1) and S(2,1) are plotted in Fig. 2, together with those for $(SbS)_{1.15}TiS_2$. In the normal region of SbS, the Sb(2,1) atoms are coordinated by five S(2,1) atoms of the same subsystem. The variation of the five Sb(2,1)—S(2,1) distances of SbS are plotted in Fig. 3, where the solid lines of the undulatory curves represent the Sb(2,1)—S(2,1) distances for the occupancy of both Sb(2,1) and S(2,1) larger than 0.6. The out-of-plane distortion of the average SbS structure can be described by the dimensionless parameter ϵ_o (Ren, Baas, Meestma, de Boer & Wiegers, 1996)

$$\epsilon_o = 2\frac{\Delta^+ - \Delta^-}{\Delta^+ + \Delta^-}, \qquad (21)$$

where Δ^+ and Δ^- are, respectively, the average perpendicular distances of Sb(2,1) and S(2,1) to the midplane of the SbS double layers. In this stage-2

compound $\epsilon_o = 0.232(5)$, close to 0.221(7) of $(SbS)_{1.15}TiS_2$. Using a supercell approximation $(22a_{21} \times 11a_{22} \times a_{23})$ to the interface modulation structure of the SbS subsystem, the same as for $(SbS)_{1.15}TiS_2$ (I), one layer of the ab planes of the SbS structure is illustrated in Fig. 4, where an occupancy larger than 0.6 is considered as one, otherwise as zero.
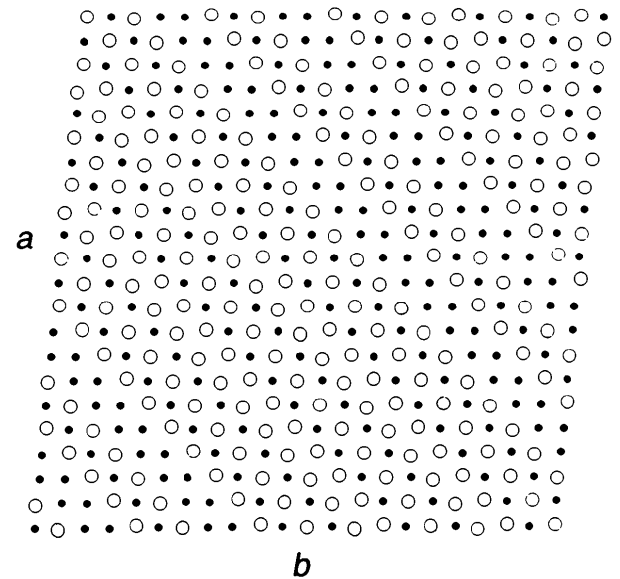

a

b

Fig. 4. One layer of the ab planes of the interface modulated structure of the SbS subsystem looking along the normal direction of the layer. Large open circles denote S atoms and small filled ones denote Sb atoms. Note that in the antiphase boundaries only Sb—Sb and S—S clusters exist instead of the continuous chains as shown here for clarity.

Table 7. *Selected interatomic distances (Å)*

The basic structure positions of the atoms are: $Sb(2,1) = (x_{21}^0, x_{22}^0, x_{23}^0)$, $Sb(2,1)^{x+} = (x_{21}^0 + 1, x_{22}^0, x_{23}^0)$, $Sb(2,1)^{x-} = (x_{21}^0 - 1, x_{22}^0, x_{23}^0)$, $Sb(2,1)^{y+} = (x_{21}^0, x_{22}^0 + \frac{1}{2}, x_{23}^0)$, $Sb(2,1)^{y-} = (x_{21}^0, x_{22}^0 - \frac{1}{2}, x_{23}^0)$; $S(2,1) = (x_{21}^0, x_{22}^0, x_{23}^0)$, $S(2,1)^{x+} = (x_{21}^0 + 1, x_{22}^0, x_{23}^0)$, $S(2,1)^{x-} = (x_{21}^0 - 1, x_{22}^0, x_{23}^0)$, $S(2,1)^{y+} = (x_{21}^0, x_{22}^0 + \frac{1}{2}, x_{23}^0)$, $S(2,1)^{y-} = (x_{21}^0, x_{22}^0 - \frac{1}{2}, x_{23}^0)$, $S(2,1)^z = (-x_{21}^0, \frac{1}{2} - x_{22}^0, 1 - x_{23}^0)$; $Ti(1,1) = (x_{11}^0, x_{12}^0, x_{13}^0)$; $S(1,1) = (x_{11}^0, x_{12}^0, x_{13}^0)$, $S(1,1)^i = (-1 + x_{11}^0, x_{12}^0, x_{13}^0)$, $S(1,1)^2 = (-\frac{1}{2} + x_{11}^0, \frac{1}{2} + x_{12}^0, x_{13}^0)$, $S(1,1)^i = (n - x_{11}^0, -x_{12}^0, 1 - x_{13}^0)$, $S(1,1)^{ii} = (n + \frac{1}{2} - x_{11}^0, \frac{1}{2} - x_{12}^0, 1 - x_{13}^0)$, $S(1,2) = (x_{11}^0, x_{12}^0, x_{13}^0)$, $S(1,2)^1 = (-1 + x_{11}^0, x_{12}^0, x_{13}^0)$, $S(1,2)^2 = (-\frac{1}{2} + x_{11}^0, -\frac{1}{2} + x_{12}^0, x_{13}^0)$, where n runs over all integers and the basic coordinates x_{vi}^0, corresponding to each atom, refer to Table 3.

| | | Modulated structure | |
Atom pair	Basic structure	Normal region	Antiphase boundaries
Sb(2,1)—Sb(2,1)$^{x\pm}$	2.950	–	2.964–2.969
Sb(2,1)—Sb(2,1)$^{y\pm}$	2.966	–	2.874–2.882
S(2,1)—S(2,1)$^{x\pm}$	2.950	–	3.636–3.642
S(2,1)—S(2,1)$^{y\pm}$	2.966	–	3.618–3.621
Sb(2,1)—S(2,1)$^{x+}$	2.983	2.668–3.145	2.665–3.243
Sb(2,1)—S(2,1)$^{x-}$	2.944	2.653–3.172	2.636–3.248
Sb(2,1)—S(2,1)$^{y+}$	3.028	2.732–3.297	2.707–3.328
Sb(2,1)—S(2,1)$^{y-}$	2.931	2.661–3.188	2.627–3.271
Sb(2,1)—S(2,1)^z	2.445	2.417–2.510	2.417–2.513
Sb(2,1)—S(1,1)^i	3.154	3.134–	3.134–
Sb(2,1)—S(1,1)^{ii}	3.225	3.201–	3.201–
Ti(1,1)—S(1,1)	2.432	2.432	
Ti(1,1)—S(1,1)^1	2.436	2.436	
Ti(1,1)—S(1,1)^2	2.436	2.436	
Ti(1,1)—S(1,2)	2.420	2.420	
Ti(1,1)—S(1,2)^1	2.422	2.422	

In the antiphase boundaries of SbS, the bonding Sb—Sb and non-bonding S—S contacts zigzag along the $[1\bar{1}0]$ direction. Using the atomic coordinates (Table 3) together with the displacive (Table 5) and occupational modulation parameters (Table 6), one finds that 22% of Sb is involved in the metallic Sb—Sb bonding, being consistent with the result of X-ray photoemission spectroscopy performed on a single crystal of $(SbS)_{1.15}(TiS_2)_2$ which showed 24% of Sb in a metallic-like state (Ren, Haas & Wiegers, 1995). The shortest Sb—Sb and S—S distances are 2.964 and 3.618 Å, respectively, larger than those (2.84 and 3.43 Å, respectively) observed in $(SbS)_{1.15}TiS_2$. The shortest Sb(2,1)—S(2,1) distance of 2.417 Å is found for the Sb(2,1)—Sb(2,1) pair along the c direction in SbS, equal to that of $(SbS)_{1.15}TiS_2$. The different values obtained in this refinement (Table 7), compared with those in $(SbS)_{1.15}TiS_2$, may be due to the different approaches to the displacive modulations. The shortest distance from a Sb(2,1) atom to a S(1,1) atom of the TiS_2 subsystem is several tenths of an angstrom longer than the intra-subsystem distances of Sb(2,1)—S(2,1) within SbS. The variation of these inter-subsystem distances of Sb(2,1)—S(1,1) is plotted against the phase parameter t_{21} at $t_{22} = 0.0$ in Fig. 5. As for the valence of the Sb(2,1) atom, assuming that the site occupancy factor for the Sb(2,1) atoms is one, and using the same valence bond method as described in (I), the average valence of Sb(2,1) is 3.11, including a contribution of 0.25 from the inter-subsystem Sb(2,1)—S(1,1) bonding. These values are close to those of $(SbS)_{1.15}TiS_2$. The parameters $R_{ij}^0(Sb—Sb) = 2.80$, $R_{ij}^0(Sb—S) = 2.45$ and $b = 0.37$ Å have been used in the calculation (Brese & O'Keeffe, 1991). The variation of the Sb(2,1) valence is illustrated
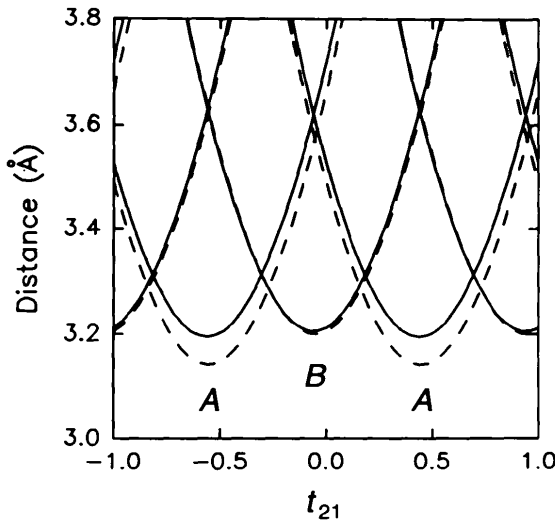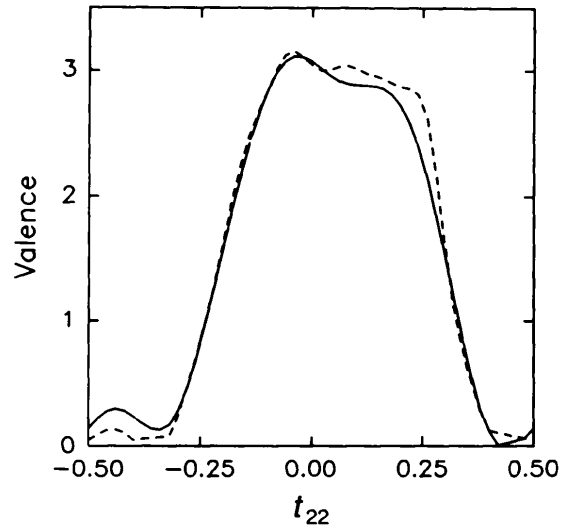

Fig. 5. Coordination of Sb(2,1) of SbS by S(1,1) of TiS_2 as a function of the subsystem superspace coordinate t_{21} at $t_{22} = 0.0$. Distances are given for the basic structure (broken curves) and for the modulated structure (solid lines). The curves are from Sb(2,1) at $(x_{21}^0, x_{22}^0, x_{23}^0)$ to S(1,1) at $(n_{11} - x_{11}^0, -x_{12}^0, 1 - x_{13}^0)$ for the lines marked A and to S(1,1) at $(n_{11} + \frac{1}{2} - x_{11}^0, \frac{1}{2} - x_{12}^0, 1 - x_{13}^0)$ for the curves marked B (n_{11} is an integer and x_{vi} refers to Table 3). The curves with the same mark correspond to different values for n_{11}, but translationally equivalent S(1,1) atoms.

Fig. 6. Variation of the bond valence of Sb(2,1) as a function of t_{22} at $t_{21} = 0.0$. The parameters $R_{ij}^0(Sb—Sb) = 2.80$ Å, $R_{ij}^0(Sb—S) = 2.45$ Å and $b = 0.37$ Å have been used in the calculation.

in Fig. 6, where the occupancy of Sb(2,1) (see Fig. 2) is multiplied to the total valence as has been done in (I).

6. Concluding remarks

The $(3 + 2)$-dimensional superspace description has been applied to the new misfit layer compound $(SbS)_{1.15}(TiS_2)_2$. This is the first example of the super-space approach to the crystal structure of a stage-2 misfit layer compound. The paired TiS_2 sandwiches have a slightly distorted $1T$–TiS_2 structure. The lower scale factor for the reflections (excluding the common ones) of the SbS subsystem and the observed Fourier map showed stacking disorder of the SbS subsystem along the **a** axis, which indicates that the paired sandwiches of TiS_2 in this stage-2 phase weaken the coupling between two successive slabs of SbS. Using the shift-model we are able to understand the nature of the disorder: two fractions of the SbS layers, each with 5.4 (4)% in occupancy, shift along the $\mathbf{a}_{2_1}$ axes with an equal displacement of $\xi a_{2_1} = 0.64\,(2)\,\text{Å}$ in both $+x$ and $-x$ directions. However, each slab of SbS retains the interface modulated structure, the same as found in the previous compound $(SbS)_{1.15}TiS_2$. The average valence of Sb is calculated as 3.11. The incommensurate ordering of the Sb/S atom in the SbS double layers is apparently independent of the staging order.

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