179.5°, respectively. The local energy minima were confirmed by the calculated complete set of harmonic vibrational frequencies.

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The Modulated Structure of the Commensurate Misfit-Layer Compound $(BiSe)_{1.09}TaSe_2$

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Abstract

Single-crystal X-ray diffraction (Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å) was used to determine the structure of the commensurate inorganic misfit-layer compound $(BiSe)_{\alpha_0}TaSe_2$, $\alpha_0 = 12/11 \simeq 1.09$. The structure is described as a (3 + 1)-dimensional intergrowth compound with two subsystems and with symmetry according to the superspace group $P{:}Fm2m(\alpha_0,0,0)\bar{1}\bar{1}1$. The $TaSe_2$ subsystem has $a_{11} = 3.421$ (1), $a_{12} = 5.970$ (1) and $a_{13} = 24.341$ (7) Å, with subsystem space group $Fm2m$ and subsystem superspace group $P{:}Fm2m(\alpha_0,0,0)\bar{1}\bar{1}1$. The BiSe subsystem has lattice parameters $a'_{21} = 3.135$ (1), $a'_{22} = 2.984$ (1)

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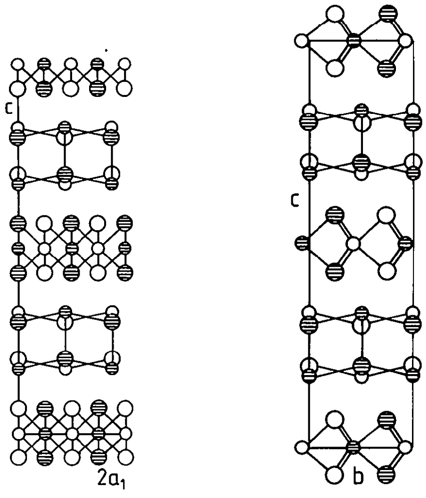
and $a'_{23} = 12.174\,(4)$ Å, with subsystem space group $Pm2m$ and subsystem superspace group $P{:}Pm2m(\alpha_0^{-1},\frac{1}{2},\frac{1}{2})\bar{1}\bar{1}1$. The $(\mathbf{a}^*_{\nu2},\mathbf{a}^*_{\nu3})$ reciprocal-lattice plane is common to the two subsystem lattices, $\nu = 1, 2$. Refinements on 1614 unique reflections converged smoothly to $R = 0.050$. The modulation was divided into a large block-wave occupational modulation describing the Bi/Se ordering and a relatively small displacement modulation. An interpretation is given of the effect of the latter using the bond-valence method. The structural features are compared to the incommensurate misfit-layer compounds, in relation to the inter-subsystem bonding.

Introduction

Inorganic misfit-layer compounds are characterized by the alternate stacking of two different types of layers (Makovicky & Hyde, 1981; Wiegers *et al.*, 1989). The first type is a three-atom-thick layer of composition TX_2 ($X = $ S, Se; $T = $ transition metal) and with a structure as is also found for the individual layers in either NbS_2 or TiS_2 (Nb and Ta are in a trigonal prismatic coordination by X; Ti, V and Cr are in a trigonal antiprismatic coordination). The second type has a structure corresponding to a two-atom-thick (100) slice of a rock-salt-type structure. The composition is MX, with M a metal atom (Fig. 1).

Each of the two sets of layers is ordered according to its own unit cell: $\Lambda_\nu = \{\mathbf{a}_{\nu1},\mathbf{a}_{\nu2},\mathbf{a}_{\nu3}\}$, $\nu = 1, 2$. The interaction between the two layer types makes the $(\mathbf{a}^*_{\nu2},\mathbf{a}^*_{\nu3})$ reciprocal-lattice plane common to the two unit cells. Generally, the periodicities along the colinear $\mathbf{a}_{\nu1}$ axes are mutually incommensurate, thus making two unit cells necessary.



(*a*) (*b*)

Fig. 1. Projections along (*a*) the common $\mathbf{a}_{\nu2}$ axes and (*b*) the incommensurate $\mathbf{a}_{\nu1}$ axes of the structure of the incommensurate misfit-layer compound $(LaS)_{1.14}NbS_2$ (van Smaalen, 1991*c*; Wiegers *et al.*, 1990).

A better description of these so-called incommensurate intergrowth compounds is provided by the superspace formalism (Janner & Janssen, 1980; van Smaalen, 1989, 1991*b*, 1992*a*). The complete structure is described in a $(3 + d)$-dimensional space, with the number of dimensions equal to the number of independent reciprocal vectors; here $d = 1$. The symmetry is given by a single $(3 + d)$-dimensional space group, from which the subsystem symmetries can be derived (van Smaalen, 1991*a*).

A single slab MX has a C-centered unit cell, with atoms M and X alternating along $\mathbf{a}$ and along $\mathbf{b}$ ($a \simeq b \simeq 6$ Å, $\gamma = 90°$). An average structure can be defined with $a' \simeq b' \simeq 3$ Å. This cell is primitive, with each atomic site disorderly occupied by equal amounts of M and X. The average structure of a single slab BiX in the bismuth-containing compounds is the same as in the other compounds (Gotoh *et al.*, 1989; Wulff, Meetsma, Haange, de Boer & Wiegers, 1990). However, the real ordered structure is different. Instead of an ordering on a $2a' \times 2b'$ lattice, observed for all other compounds, the unit cell of the BiX layers is $12a' \times 2b' = 6a \times b$. This new unit cell is again C centered. The ordering in $(BiSe)_{1.09}TaSe_2$ is such that four Bi_2 pairs occur in each cell, accompanied by four Se_2 pairs with nonbonding distances (Fig. 2; Zhou, Meetsma, de Boer & Wiegers, 1992). The TX_2 layers in the Bi-containing compounds do have the same structure as in the other compounds.

As we will show in the next section, a second difference between $(BiSe)_{1.09}TaSe_2$ and other misfit-layer compounds is that the former is commensurate, with $12\mathbf{a}'(\mathrm{BiSe}) = 11\mathbf{a}(\mathrm{TaSe_2})$.

In this paper a study is presented of the complete structure of $(BiSe)_{1.09}TaSe_2$. The superspace for-

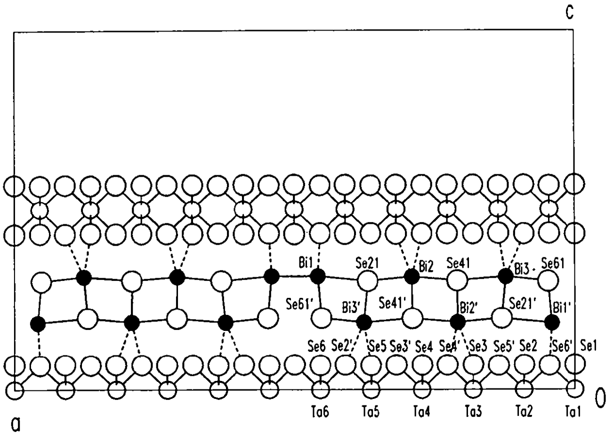


Fig. 2. Projection of the structure along $\mathbf{a}_{\nu2}$, displaying one unit of the supercell but only half a unit cell along $\mathbf{a}_{\nu2}$. Large circles denote Se atoms; small open and filled circles represent Ta and Bi atoms, respectively.

malism is applied to this commensurate misfit-layer compound and the relation with the classical supercell approach is discussed. The commensurate modulations of both subsystems are determined. An analysis is made of the inter-subsystem bonding, which is then compared to the inter-subsystem bonding in several incommensurate misfit-layer compounds.

Experimental

The synthesis, unit-cell dimensions and X-ray intensity data collection have been described by Zhou, Meetsma, de Boer & Wiegers (1992). With neglect of all (commensurate) satellite reflections, the $TaSe_2$ subsystem ($\nu = 1$) is *F*-centered orthorhombic with lattice parameters $a_{11} = 3.421$ (1), $a_{12} = 5.970$ (1) and $a_{13} = 24.341$ (7) Å. The BiSe subsystem ($\nu = 2$) is primitive orthorhombic with lattice parameters $a'_{21} = 3.135$ (1), $a'_{22} = 2.984$ (1) and $a'_{23} = 12.171$ (4) Å.

Satellite reflections can be indexed with respect to the BiSe reciprocal cell with a modulation wavevector equal to the primitive (1,1,1) reciprocal-lattice vector of the first subsystem: $\mathbf{q}^{2'} = (\frac{11}{12},\frac{1}{2},\frac{1}{2})$. For this commensurate wavevector, the maximum order of the satellites is six. Rows of satellite spots $h'_2k'_2l'_2m'_2$ are found parallel with $\mathbf{a}^*_{21}$. Those with half-integer values for k'_2 and l'_2 are of odd order $|m'_2|$, with increasing intensities for increasing order 1, 3, 5 (Fig. 3*b*). Rows of even-order satellites are found for integer values k'_2 and l'_2 (Fig. 3*a*). The second-order satellites have intensities comparable with the first-order satellites. Fourth- and sixth-order satellites are much weaker than the others. In addition to the main reflections and the fifth- and third-order satellites reported by Zhou, Meetsma, de Boer & Wiegers (1992), we have also measured the weaker first- and second-order satellites.

Satellite reflections can also be indexed with respect to the first subsystem reciprocal cell, now with a modulation wavevector equal to the primitive $\mathbf{a}'^*_{21}$ axis of the BiSe reciprocal lattice: $\mathbf{q}^1 = (\frac{12}{11},0,0)$. Rows of satellites $h_1k_1l_1m_1$ are found parallel with $\mathbf{a}^*_{11}$, with all orders 1 through 5 in each row (Fig. 3). These two descriptions provide two equivalent four-integer indexings of the complete diffraction pattern.

With the newly measured intensity data included, a total of 2760 reflections were measured for the $TaSe_2$ subsystem. In Laue symmetry *mmm* these reduced to 700 unique reflections, of which 635 with $I > 3\sigma(I)$ are denoted as observed. The internal consistency R_I was 0.022 for observed reflections. For the BiSe subsystem 8594 reflections were measured, including satellites up to fifth order. Averaging in Laue symmetry *mmm* resulted in 1875 unique reflections, of which there were 1347 observed ($R_I = 0.042$).

The two data sets were brought onto the same scale by use of 416 common reflections to derive a weighted average scale factor. This resulted in 2159 unique reflections, of which there are 1615 observed. This data set was used in the refinements.

The ratio of the *a* axes is $\alpha_0 = a_{11}/a'_{21} = 1.09123$ with a standard deviation of 0.0004. The deviation from the commensurate ratio 12/11 is 0.0003 (4), a much smaller difference than has been found for other misfit compounds. As a further test for the commensurateness the positions were determined of 10 first-order and 13 fifth-order reflections. The average deviations from the commensurate values were 0.0001 (4) and 0.0010 (5), respectively. This gives an estimate for a possible deviation from commensurateness of 0.0002 (1), which is even closer to zero than the value obtained from the ratio of the lattice parameters. It is concluded that $(BiSe)_{1.09}TaSe_2$ is a commensurate misfit compound.

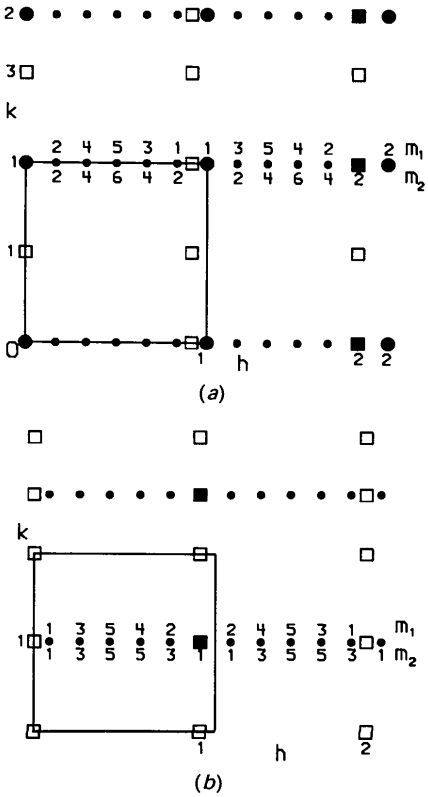


Fig. 3. Schematic representation of the diffraction pattern. Filled and open symbols represent present and absent Bragg reflections, respectively. Squares and large circles correspond to the main reflections of $TaSe_2$ and BiSe, respectively. Small circles are satellites; their order is indicated as a $TaSe_2$ satellite by m_1 and as a BiSe satellite by m_2. The primitive reciprocal unit cell of the basic structure of the second subsystem is outlined. (*a*) A section of the reciprocal lattice at l = even. (*b*) Section at l = odd of the c = 24 Å unit cells. For the BiSe subsystem only satellites are found.

Supercell and superspace symmetry

To facilitate the analysis, the BiSe subsystem is described on the unit cell $a \times b \times c = a' \times 2b' \times 2c'$. This introduces the centering translations $(0,\frac{1}{2},0)$ and $(0,0,\frac{1}{2})$. With respect to the reciprocal lattice of the new unit cell, the modulation wavevector for the second subsystem is $\mathbf{q}^2 = (\frac{11}{12},0,0)$.

An integer indexing of the complete diffraction pattern is obtained with four reciprocal vectors, $M^* = \{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3, \mathbf{a}_4\}$, chosen as: $\mathbf{a}_1^* = \mathbf{a}_{11}^*$, $\mathbf{a}_2^* = \mathbf{a}_{12}^*$, $\mathbf{a}_3^* = \mathbf{a}_{13}^*$, and $\mathbf{a}_4^* = \mathbf{a}_{21}^*$. Superspace is obtained in the usual way, by identification of the four basis vectors of M^* with the perpendicular projection of four independent translation vectors in a (3 + 1)-dimensional space (Janner & Janssen, 1980). The fourth element of M^* can be expressed in terms of the first three. This defines the incommensurability (here reduced to a commensurate value), expressed by the sigma matrix,

$$\sigma = (\alpha_0,0,0). \qquad (1)$$

The relation between the set M^* and the subsystem reciprocal lattices and the subsystem modulation wavevectors is given by the matrices W^ν according to (van Smaalen, 1991*a*)

$$\mathbf{a}_{\nu i}^* = \sum_{k=1}^{4} W_{ik}^{\nu} \mathbf{a}_k^*, \qquad i = 1, 2, 3, \qquad (2a)$$

$$\mathbf{q}^{\nu} = \sum_{k=1}^{4} W_{4k}^{\nu} \mathbf{a}_k^*, \qquad (2b)$$

with

$$W^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad W^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \qquad (3)$$

The W^ν matrices can be interpreted as defining a coordinate transformation in superspace. In particular, for the reflection indices it follows that

$$(H, K, L, M) = (h_\nu, k_\nu, l_\nu, m_\nu)W^\nu, \qquad (4)$$

where *HKLM* are the indices with respect to M^* and $h_\nu k_\nu l_\nu m_\nu$ are the reflection indices with respect to Λ_ν^* and q^ν ($\nu = 1, 2$). Because W^1 is chosen to be the unit matrix, the $h_1k_1l_1m_1$ and *HKLM* indices are identical.

Because of the commensurability, the structure can also be described with respect to the common supercell: $\mathbf{a}_c = 11\mathbf{a}_{11} = 12\mathbf{a}_{21}$, $\mathbf{b}_c = \mathbf{a}_{12} = \mathbf{a}_{22}$ and $\mathbf{c}_c = \mathbf{a}_{13} = \mathbf{a}_{23}$. The supercell diffraction indices $h_ck_cl_c$ can be derived from the four-integer indexings as $h_c = 11H + 12M = 11h_1 + 12m_1 = 12h_2 + 11m_2$, $k_c = K = k_1 = k_2$ and $l_c = L = l_1 = l_2$.

With (4) the subsystem indexings of the reflections were transformed to the superspace indexing. Conditions for systematic absences were found as $H + K = 2n + 1$, $H + L = 2n + 1$ and $K + L = 2n + 1$ for the *HKLM* reflections. This corresponds to the set of centering translations

$$(\tfrac{1}{2},\tfrac{1}{2},0,0),\ (\tfrac{1}{2},0,\tfrac{1}{2},0),\ (0,\tfrac{1}{2},\tfrac{1}{2},0). \qquad (5)$$

Table 1. *Elements of the superspace group G_s, together with the corresponding elements of both subsystem superspace groups G_s^ν, $\nu = 1, 2$*

The listed elements may be combined with any of the lattice translations or with the centering translations. n_i, $i = 1,\ldots,4$, assumes all integer values. The real parameters τ_i define the relative position of the symmetry elements and the origin. They have been chosen as zero.

$G_s = G_s^1$	G_s^2
$(E1\vert n_1,n_2,n_3,n_4)$	$(E1\vert n_4,n_2,n_3,n_1)$
$(E1\vert \frac{1}{2},\frac{1}{2},0,0)$	$(E1\vert 0,\frac{1}{2},0,\frac{1}{2})$
$(E1\vert \frac{1}{2},0,\frac{1}{2},0)$	$(E1\vert 0,0,\frac{1}{2},\frac{1}{2})$
$(E1\vert 0,\frac{1}{2},\frac{1}{2},0)$	$(E1\vert 0,\frac{1}{2},\frac{1}{2},0)$
$(m_x\bar{1}\vert \tau_1,0,0,\tau_4)$	$(m_x\bar{1}\vert \tau_4,0,0,\tau_1)$
$(2_y\bar{1}\vert \tau_1,0,\tau_3,\tau_4)$	$(2_y\bar{1}\vert \tau_4,0,\tau_3,\tau_1)$
$(m_z1\vert 0,0,\tau_3,0)$	$(m_z1\vert 0,0,\tau_3,0)$

The (3 + 1)-dimensional Bravais class follows as $P{:}Fmmm(\alpha_0,0,0)\bar{1}11$, with F representing the centering translations (5). Other extinction conditions could not be found. With the basic structures of the individual layers taken into account, the superspace group is determined as $P{:}Fm2m(\alpha_0,0,0)\bar{1}\bar{1}1$. The subsystem superspace groups can be derived with use of (3) (van Smaalen, 1991*a*), $G_s^1 = G_s$ and $G_s^2 = P{:}F'm2m(\alpha_0^{-1},0,0)\bar{1}\bar{1}1$, with F' representing three translations obtained from (5) by an interchange of the first and fourth components (see Table 1). The standard setting for the second subsystem is obtained by use of the primed axes. Then the superspace group symbol for G_s^2 becomes $P{:}Pm2m(\alpha_0^{-1},\frac{1}{2},\frac{1}{2})\bar{1}\bar{1}1$. The subsystem space groups are $G_1 = Fm2m$ and $G_2 = Pm2m$.

The supercell symmetry can be derived from the superspace group. Denote an element of the superspace group by $(R_s|\boldsymbol{\tau}_s) = (R_3\varepsilon|\boldsymbol{\tau}_3\tau_4)$, where R_3 is the 3×3 left upper block of R_s and $\boldsymbol{\tau}_3$ comprises the first three elements of $\boldsymbol{\tau}_s$. This symmetry operator gives rise to a symmetry operator in physical space if the following relation is fulfilled:

$$\mathbf{a}_4^* \cdot \boldsymbol{\tau}_3 = \tau_4. \qquad (6)$$

For example, for the lattice translations $(E1|n_1n_2n_3n_4)$, where n_i are integers, (6) gives $(12/11)n_1 = n_4$. It follows that n_1 must be a multiple of 11, *i.e.* the only lattice translations in physical space are those corresponding to the 11-fold supercell of the $TaSe_2$ subsystem. Application of (6) to all elements of G_s gives the supercell space group $G_c = Fm2m$ for $\tau_4 = (12/11)\tau_1 + (1/11)n$ (mod 1). Alternatively, $G_c = Fm2m$ follows for the sections $t = (6/11)\tau_1 + (1/22)n$ (mod 1) of superspace. All other values for τ_4 or t give rise to $G_c = F11m = Fm_z$. The orthorhombic symmetry of the diffraction pattern shows that the true supercell symmetry is *Fm*2*m*, which is one of the special sections of superspace.

Refinements

With respect to the subsystem lattice Λ_ν, the coordinates of atom j of subsystem ν in the superspace section t can be written as (van Smaalen, 1991*c*, 1992*a*)

$$x_{\nu i}(j) = \bar{x}_{\nu i}(j) + u^j_{\nu i}(\bar{x}_{\nu s4}) \tag{7}$$

for $\nu = 1$, 2 and $i = 1$, 2, 3. The basic structure coordinates $\bar{x}_{\nu i}$ are

$$\begin{aligned} \bar{x}_{1i}(j) &= n_{1i} + x^0_{1i}(j) \qquad i = 1, 2, 3, \\ \bar{x}_{21}(j) &= n_{21} + x^0_{21}(j) - t, \\ \bar{x}_{2i}(j) &= n_{2i} + x^0_{2i}(j) \qquad i = 2, 3, \end{aligned} \tag{8}$$

where $n_{\nu i}$ runs over all integers and $x^0_{\nu i}(j)$ are the coordinates of atom j with respect to the subsystem unit cell. These are the ones determined in the structure refinement. The modulation functions are periodic with periodicity one in their arguments $\bar{x}_{\nu s4}$. The latter are the fourth coordinates of the subsystem superspaces (van Smaalen, 1991*c*, 1992*a*),

$$\begin{aligned} \bar{x}_{1s4} &= \alpha_0 \bar{x}_{11}(j) + t, \\ \bar{x}_{2s4} &= \alpha_0^{-1}[\bar{x}_{21}(j) - t]. \end{aligned} \tag{9}$$

In the basic structure Bi and Se occupy the special position (0,0,z), each with probability one-half, and with slightly different z coordinates. The ordering as observed in the supercell ($A = 12a'_{21}$) can be designated as a block wave: only occupancies zero and one occur. For the present choice of the modulation wavevector, the corresponding occupational modulation functions are

$$P(\mathrm{Bi}) = \begin{cases} 1 \text{ for } 1/12 \leq \bar{x}_{2s4} \leq 2/12 \pmod{1/6}, \\ 0 \text{ for } 0 \leq \bar{x}_{2s4} \leq 1/12 \pmod{1/6}, \end{cases} \tag{10a}$$

$$P(\mathrm{Se2}) = 1 - P(\mathrm{Bi}). \tag{10b}$$

Since the modulation is commensurate, the modulation functions are described by a Fourier series with a finite number of terms. The coefficients can be used as independent parameters in the refinement procedure, thus providing a test for the square-wave ordering. Such refinements did not give a better fit than the model according to (10), while large correlations between the parameters did occur. Therefore, the structure determination was continued with the occupational modulation according to (10) employed without any free parameters.

All atoms are on special positions: Ta is on *m*2*m* and the other three atoms are in the mirror plane m_x.

Table 2. *Symmetry restrictions on the functions describing the displacive modulations*

The restrictions apply to the modulation functions as defined in (7)–(9), with symmetry operators from Table 1. For each atom it is stated whether the function is odd, even or zero.

	u_{11}	u_{22}	u_{33}
Ta ($\nu = 1$)	Odd	Even	Zero
Se1 ($\nu = 1$)	Odd	Even	Even
Bi ($\nu = 2$)	Odd	Even	Even
Se2 ($\nu = 2$)	Odd	Even	Even

Symmetry restrictions on the functions describing the displacive modulation follow from the corresponding superspace group elements. They are summarized in Table 2.

Refinement parameters for the modulation functions for displacements are their Fourier coefficients

$$u^j_{\nu i}(\bar{x}_{\nu s4}) = \sum_{n=1}^{n_m} A^j_{ni}\sin(2\pi n \bar{x}_{\nu s4}) + B^j_{ni}\cos(2\pi n \bar{x}_{\nu s4}). \tag{11}$$

As for the occupational modulation functions, the commensurability restricts the expansion to a finite number of terms, n_m, such that the number of independent parameters in the modulated-structure approach equals the number of parameters required in the supercell approach. Generally, the diffraction pattern shows the higher-order satellites to be very weak or absent. This means that the corresponding Fourier coefficients will be virtually zero and can be removed from the refinement. For the first subsystem, $n_m = 5$. Together with the symmetry restrictions this leads to 11 position parameters for Ta and 17 position parameters for Se1, the same number as is required in the supercell approach. In the refinements it appeared sufficient to include only harmonics up to $n = 2$, corresponding to 5 parameters for Ta and 8 parameters for Se1. This effectively reduced the number of refinement parameters in the superspace approach as compared to the supercell description.

For the second subsystem, $n_m = 6$. However, the special character of the occupational modulation requires that only 6 of the 12 possible positions are actually occupied. That means that the value of the displacement wave is only important for those 6 values of $\bar{x}_{2s4}$, thus reducing n_m to 3. Furthermore, one of the two parameters for $n = 3$ is redundant. Together with the effect of the site symmetry this leads to 9 position parameters each for Bi and Se2, the same number as is required in the supercell approach. All parameters were used in the refinements.

Refinements were performed with the computer program *COMPREF* (Petricek, Maly, Coppens *et al.*, 1991) of the program system *JANA* (Petricek,

Table 3. *Reliability factors for the final fit*

The R factors are defined as $R = \sum||F_{\rm obs}| - |F_{\rm calc}||/\sum|F_{\rm obs}|$ and $wR = [\sum w(|F_{\rm obs}| - |F_{\rm calc}|)^2/\sum w|F_{\rm obs}|^2]^{1/2}$, with weights w. Partial R factors are defined with a subset of the reflections. The $TaSe_2$ and BiS parts comprise the main reflections of the corresponding subsystem, excluding the common reflections $0KL0$. The BiSe main reflections pertain to a primitive unit cell with parameters $a'_{21} = 3.135$, $a'_{22} = 2.984$ and $a'_{23} = 12.171$ Å. Satellites of order m are defined as all $HKLM$ reflections with $m = \min(|H|,|M|)$.

Reflection subset	Number of reflections	R	wR
All	1614	0.050	0.062
$TaSe_2$ part	361	0.040	0.049
BiSe part	283	0.051	0.060
Common	105	0.041	0.050
$m = 1$	264	0.098	0.101
$m = 2$	133	0.069	0.091
$m = 3$	200	0.079	0.078
$m = 4$	268	0.050	0.057

Maly & Cisarova, 1991). The expression of the structure factor in the commensurate case is different from the expression for incommensurately modulated structures (Yamamoto, 1982). The integration over the fourth coordinate is replaced by a summation over a finite number of values of $\bar{x}_{s4}$. The refinement program was modified accordingly.

The starting model for the refinement was the structure as derived by Zhou, Meetsma, de Boer & Wiegers (1992), with the Bi/Se ordering described by the occupational modulation function (10). With the modulation parameters as described above and a single anisotropic temperature tensor for each of the four independent atoms, smooth convergence was obtained to a final $wR = 0.062$ with $R = 0.050$. Partial R factors for subsets of reflections are listed in Table 3.* Values for the basic structure coordinates, temperature factors and modulation parameters are given in Tables 4 and 5.

With the structure obtained by Zhou, Meetsma, de Boer & Wiegers (1992) again used as a starting point, a refinement in the supercell was performed of all appropriate position parameters but with equal temperature tensors for atoms equivalent in the subsystem unit cell. This refinement converged to $wR = 0.061$ and $R = 0.049$. Comparison of the coordinates from the supercell refinement with the supercell coordinates obtained from the superspace refinement showed them to be equal within standard deviations. This shows that the superspace and supercell approaches lead to the same structure model. Furthermore, it illustrates the power of the superspace approach for commensurate modulations, as it uses less parameters to describe the same structure as given in the supercell.

Table 4. *Basic structure coordinates and temperature parameters* (Å^2) *as obtained by the refinement of the modulated structure*

Coordinates refer to the subsystem lattices. Standard deviations in the last digits are in parentheses. The temperature factor that appears in the expression for the structure factor is defined by $T = \exp(-2\pi^2\sum_{i,j=1}^{3}U_{ij}a^*_{\nu i}a^*_{\nu j}h_{\nu i}h_{\nu j})$. U_{12} and U_{13} are zero as a consequence of the symmetry.

	ν	$x^0_{\nu 1}$	$x^0_{\nu 2}$	$x^0_{\nu 3}$
Ta	1	0	0	0
Se1	1	0.0	0.3340 (2)	−0.06837 (5)
Bi	2	0.0	0.0810 (5)	0.31307 (3)
Se2	2	0.0	0.0850 (9)	0.30110 (7)

		U_{11}	U_{22}	U_{33}	U_{12}
Ta	1	0.0072 (2)	0.0034 (2)	0.0057 (2)	0
Se1	1	0.0079 (4)	0.0037 (4)	0.0071 (4)	0.0000 (3)
Bi	2	0.0259 (3)	0.0167 (3)	0.0183 (3)	0.0006 (6)
Se2	2	0.0238 (8)	0.0108 (6)	0.0139 (6)	0.0005 (14)

Table 5. *Modulation parameters*

Values are given for $A^j_{n1}a_{\nu 1}$, $B^j_{n2}a_{\nu 2}$ and $B^j_{n3}a_{\nu 3}$ (Å), for j = Ta, Se1 ($\nu = 1$) and for j = Bi, Se2 ($\nu = 2$) [equation (11) and Table 2]. Standard deviations in the last digits are in parentheses.

j	A^j_{11}	B^j_{12}	B^j_{13}	A^j_{21}	B^j_{22}	A^j_{23}	A^j_{31}
Ta	−0.014 (1)	−0.0303 (7)	0.0	0.000 (1)	0.0040 (12)	0.0	
Se1	0.009 (2)	−0.0058 (13)	0.023 (2)	−0.004 (4)	0.006 (2)	0.002 (3)	
Bi	−0.044 (1)	0.056 (3)	0.011 (2)	0.032 (1)	−0.057 (2)	0.021 (1)	0.013 (1)
Se2	0.003 (5)	−0.042 (7)	−0.001 (4)	−0.298 (3)	−0.028 (5)	−0.016 (3)	0.124 (3)

Superspace refinements were also performed with the expression for the structure factor that applies to incommensurate structures. Significant differences, in particular higher R factors, were observed. The reason is probably the block-wave character of the occupational modulation, which leads to quite different Fourier components in the commensurate and incommensurate cases.

The refinements easily converged to a secondary minimum, with only a slightly higher R factor of 0.053 as compared with 0.050 in the true minimum. Between these two solutions differences in distances were found up to 0.1 Å. In particular the short Bi—Bi distance was found as 3.18 Å in the secondary minimum, instead of 3.10 Å in the true minimum. Zhou, Meetsma, de Boer & Wiegers (1992) obtained 3.18 Å as the Bi—Bi distance, which we believe to be a secondary minimum too.

Discussion

Two major differences are found between $(BiSe)_{1.09}TaSe_2$ and the presently known incommensurate misfit-layer compounds. In $(BiSe)_{1.09}TaSe_2$ the ordering within the BiSe subsystem is different from the rock-salt-type structure (Figs. 1 and 2), and the ratio of the a axes of the two subsystems is now commensurate instead of incommensurate, $\alpha_0 = 12/11$.

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* Lists of calculated and observed structure factors, supercell coordinates calculated from the modulation functions and coordinates from the supercell refinement have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55714 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Nevertheless, the features displaying the interactions between the subsystems of $(BiSe)_{1.09}TaSe_2$ closely resemble the structures of the incommensurate misfit-layer compounds. Like the incommensurate compounds, the metal atoms of the BiSe subsystem protrude outwards such that they are responsible for the shortest interatomic distances between the subsystems. Owing to the commensurability, the infinite number of different metal-atom to chalcogenide distances observed in the incommensurate compounds is replaced by three different Bi coordinations in $(BiSe)_{1.09}TaSe_2$.

The variation due to the modulation in the bonding distances between the six crystallographically independent Ta atoms and their coordinating Se atoms is very small. The variation in the shortest Ta—Ta distances is greater, as is to be expected, since these distances are longer than for a true metal bonding (Table 6).

The shortest distance from a Bi atom to an Se atom of the other subsystem is several tenths of an ångstrom longer than the Bi to Se distance within the second subsystem (Table 7). A similar effect was observed in the Pb- and Sn-containing misfit-layer compounds. This is different from the rare-earth misfit-layer compounds, where the intra- and inter-subsystem distances are of equal magnitude. It shows that the inter-subsystem interaction in the Bi, Pb and Sn compounds should be considerably weaker than in the other compounds. It thus explains the absence of charge transfer between the subsystems as measured for $(SnS)_{1.20}TiS_2$ (Ettema, Wiegers, Haas & Turner, 1992), and inferred from transport properties for the present compound and isostructural $(BiSe)_{1.10}NbSe_2$ (Zhou, Meetsma, de Boer & Wiegers, 1992).

The bond-valence method can be used to obtain a quantitative measure for the valences of the atoms (Brown, 1981; O'Keeffe, 1989). Valences were calculated for the three crystallographically independent Bi atoms. Within the error boundaries, they were found to be equal (Table 8). Note that this includes a contribution to the valence of the Bi1 atom of a Bi—Bi bond valence of almost 1. Even more pronounced than for the incommensurate misfit-layer compounds, the effect of the modulation is to make the valences, *i.e.* the average environment, of the independent Bi atoms more equal (Table 8).

For the incommensurate misfit-layer compounds there are an infinite number of valence values, corresponding to the infinite number of different coordinations (Coppens, Cisarova, Bu & Sommer-Larsen, 1991; van Smaalen, 1992*b*). These values appeared to lie within a narrow range. Furthermore, the average over one period of the modulation can be calculated and a value obtained that can be compared with the Bi valences in the present compound (Table 9).

Table 6. *Coordination distances* (Å) *of the six crystallographically independent* Ta *atoms*

Distances are given only within the $TaSe_2$ subsystem. In the first column the approximate directions of the bonds are given.

Direction	Ta1 atom		Ta2 atom		Ta3 atom	
−**a**	Se6	2.578	Se5	2.579	Se4	2.582
a	Se6	2.578	Se6	2.580	Se5	2.583
b	Se1	2.588	Se2	2.589	Se3	2.591
−**a**	Ta2	3.429	Ta3	3.426	Ta4	3.422
a	Ta2	3.429	Ta1	3.429	Ta2	3.426
b	Ta6	3.386	Ta5	3.389	Ta4	3.411
b	Ta6	3.386	Ta6	3.390	Ta5	3.425
−**b**	Ta6	3.490	Ta5	3.472	Ta4	3.442
−**b**	Ta6	3.490	Ta6	3.491	Ta5	3.477

Direction	Ta4 atom		Ta5 atom		Ta6 atom	
−**a**	Se4	2.582	Se3	2.579	Se2	2.576
a	Se3	2.583	Se2	2.580	Se1	2.576
b	Se4	2.593	Se5	2.595	Se6	2.597
−**a**	Ta3	3.422	Ta4	3.418	Ta5	3.415
a	Ta5	3.418	Ta6	3.415	Ta6	3.414
b	Ta3	3.442	Ta3	3.477	Ta2	3.491
b	Ta4	3.453	Ta2	3.472	Ta1	3.490
−**b**	Ta4	3.453	Ta3	3.425	Ta2	3.400
−**b**	Ta3	3.411	Ta2	3.389	Ta1	3.386

Table 7. *Interatomic distances* (Å) *for the coordinations around the three crystallographically independent* Bi *atoms*

Se atoms with two-digit numbers are from the second subsystem; Se atoms with single-digit numbers are from the $TaSe_2$ subsystem (Fig. 4). In the first column the approximate directions of the bonds are given.

Direction	Bi1 atom		Bi2 atom		Bi3 atom	
−**a**	Bi1	3.109	Se21	2.977	Se61	2.861
a	Se21	3.373	Se41	3.048	Se41	3.267
−**b**	Se61	2.978	Se41	3.002	Se21	2.975
b	Se61	3.048	Se41	2.990	Se21	3.043
c	Se61	2.795	Se41	2.767	Se21	2.772
	Se6	3.232	Se4	3.348	Se5	3.318
	Se1	3.564	Se3	3.385	Se2	3.431
	Se2	3.706			Se3	3.881

According to the valences of the metal atom *M*, the misfit-layer compounds $(MX)_xTX_2$ ($X = $ S, Se) can be divided into three classes. If *M* is a rare-earth element there is a tendency toward a valence of 3. This can be achieved by electron transfer from *M* to the d_{z^2} band of the *T* atoms, a model in accordance with measured transport properties (Wiegers & Meerschaut, 1992). In addition, the more highly charged metal atom will form a bond with the S1 (Se1) atoms of the TX_2 subsystem, as is expressed by the contribution of about 1 of the inter-subsystem interactions to the total valence of *M* (Table 9).

The second class is formed by the $M = $ Sn, Pb misfit compounds. A valence slightly larger than 2 is calculated, with only a minor contribution from the inter-subsystem bonding, indicating only a weak interaction between the subsystems. This is in accordance with no significant charge transfer, as was found by X-ray photoelectron spectroscopy (Ettema, Wiegers, Haas & Turner, 1992).

Table 8. *Valences of* Bi *as calculated with the bond-valence method from the distances in Table* 7

Valences are calculated with use of Bi to Se distances, for Se within the BiSe subsystem and Se in the other subsystem, and the total valence. For Bi1, the valence is calculated (*a*) without and (*b*) including the contribution of the short Bi1—Bi1 distance. Parameters used are $R_{ij} = 2.720$ Å for Bi—Se and $R_{ij} = 3.060$ Å for Bi—Bi (Brese & O'Keeffe, 1991; O'Keeffe & Brese, 1992). The last column gives the valences for a fictitious structure with the displacement modulations set to zero but with the occupational ordering retained.

	Own subsystem	Other subsystem	Total	Basic structure
Bi1 (*a*)	1.90	0.42	2.32	2.54
Bi1 (*b*)	2.77	0.42	3.19	3.36
Bi2	2.74	0.35	3.09	2.82
Bi3	2.70	0.39	3.09	2.85

Table 9. *Average value for the valence of the metal atom M in three misfit-layer compounds*

References: (*a*) van Smaalen (1991*c*); (*b*) van Smaalen, Meetsma, Wiegers & de Boer (1991); (*c*) this paper, Table 8.

	Own subsystem	Other subsystem	Total
$(LaS)_{1.14}NbS_2$ (*a*)	2.20	0.93	3.13
$(PbS)_{1.18}TiS_2$ (*b*)	1.96	0.29	2.21
$(BiSe)_{1.09}TaSe_2$ (*c*)	2.74	0.39	3.13

The bismuth-containing compounds form a separate class. The small inter-subsystem contribution to the valence resembles that in the Pb- and Sn-containing compounds. It points towards a weak inter-subsystem interaction and the absence of charge transfer, in accordance with electrical-transport properties (Zhou, Meetsma, de Boer & Wiegers, 1992). Yet the valence of Bi is calculated to be 3 (Table 9), resembling the rare-earth compounds. Apparently, this discrepancy is resolved by the strong Bi—Bi bonding within the second subsystem.

Concluding remarks

$(BiSe)_{1.09}TaSe_2$ is found to be a commensurate misfit-layer compound. The most convincing proof comes from the structure-factor calculation. The commensurate approach gives a better fit to the experimental intensities than the incommensurate formalism. The relative position of the subsystems along their co-parallel $\mathbf{a}_{\nu 1}$ axes could be determined and was fixed to give a supercell symmetry by the space group *Fm*2*m*. This contrasts with the incommensurate misfit-layer compounds, for which the relative position along the $\mathbf{a}_{\nu 1}$ axes is a meaningless parameter.

The structure was separated into two short-period basic structures and a modulation, together defining the true long-period structure. Both the basic structures and the modulations were determined. It was shown that refinements easily converged to a secondary minimum, characterized by a different modulation but with an only slightly higher *R* factor. The superspace approach required less parameters to describe the same structure model as the supercell approach. Furthermore, refinements starting with small values for the modulation parameters always converged to the proper minimum. The power of the superspace method for commensurate modulations thus shows up both in the description of the structure and in the solution for the structure.

The Bi/Se ordering differs from the rock-salt-type structure as found in the other misfit compounds (Zhou, Meetsma, de Boer & Wiegers, 1992). One-third of the Bi atoms are involved in a Bi—Bi bond of order 1. Together with the Bi—Se bonds, this allows for a bismuth valence of 3, while there is no charge transfer and there is only a weak inter-subsystem interaction. Through the bond-valence method it was shown that the effect of the modulation is towards an equal valence for all Bi atoms, of value about 3 (Table 8).

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Tables of Coincidence Orientations for Ordered Tetragonal $L1_0$ Alloys for a Range of Axial Ratios

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Abstract

In this paper we develop and apply techniques for computation of CSL, DSCL and step-vector data for grain boundaries in tetragonal materials for a range of axial ratios. This has application to $L1_0$ alloys including TiAl, which is a candidate for lightweight high-temperature structural applications. Our results are compared with others and found to be more accurate and complete. We provide data for a wider range of axial ratios than those considered by previous workers. We have also derived equivalent quaternions for tetragonal crystals in tetragonal-crystal coordinates and listed conditions for selecting a unique reduced rotation in tetragonal-crystal coordinates so that a disorientation description becomes available.

Introduction

Coincidence-site lattices (CSLs) are geometrical models of grain-boundary structure that are formed by relative rotations of two congruent lattices, with a lattice site used as the origin. The ratio of the unit-cell volume of the CSL to that of the original lattice is usually denoted by Σ. Grain boundaries corresponding to relatively low Σ values have been found to exhibit special behaviors, leading Watanabe (1984) to introduce the concept of grain-boundary design as a means of improving various properties in polycrystalline materials.

In grain-bounday geometry, the displacement-shift-complete lattice (DSCL), which is a lattice of vectors representing the 'complete' displacements of one crystal with respect to the other and leaving the boundary structure shifted, is also of importance. If the relative orientation between two grains deviates by only a few degrees from a coincidence orientation with a low value of Σ, then it has often been observed that the deviation from exact coincidence is accommodated by arrays of DSC dislocations in the boundary. Knowledge of the DSCL is essential, for example, for the application of modern theories of slip transmission (Clark, Wagoner, Chen, Lee, Robertson & Birnbaum, 1992).

Knowledge of the step vector associated with a DSC dislocation is essential in determination of the height of the step in the grain boundary that is associated with the core of a grain-boundary dislocation. The step vectors for grain-boundary dislocations in cubic crystals were determined by King (1982) and in h.c.p. materials by Chen & King (1987). Quantitative confirmation of the importance of step vectors in determination of the behaviors of grain boundaries has been given by Fukutomi, Kamijo & Horiuchi (1986).

Bruggeman, Bishop & Hartt (1972) pointed out that three-dimensional CSLs can only be obtained in h.c.p. crystals when $(c/a)^2$ is a rational fraction, except for rotations about the [0001] axis. Hence it is necessary to constrain the real $(c/a)^2$ value to some proximate rational value to obtain a three-dimensional CSL, which Chen & King (1988) called a constrained CSL (CCSL), in order that a DSC lattice becomes available. The CSLs that are associated with the [0001] rotation axis are exact CSLs (ECSLs). Grain-boundary dislocations whose Burgers vectors are appropriate DSC lattice vectors will accommodate deviation from a CCSL in constraint as well as misorientation. The idea of constrained coincidence lattices extends to all non-cubic lattices. In tetragonal crystals, the CSLs that are obtained by rotations about the [001] axis are ECSLs and the CSLs that are obtained for axes other than [001] are CCSLs. Grimmer (1989) called rotations

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