Acta Cryst. (1995). B**51**, 271–275

Structure of Al–Mn Decagonal Quasicrystal. II. A High-Dimensional Description

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(*Received* 12 *August* 1994; *accepted* 9 *November* 1994)

Abstract

A high-dimensional description has been applied to a new structural model of decagonal Al–Mn, which is constructed on the basis of the structure of the Al_3Mn phase [Li (1995). *Acta Cryst.* B**51**, 265–270]. The structure of the Al–Mn decagonal quasicrystal consists of a sequence of six layers, involving two types of layers. Acceptance domains in a five-dimensional structure description are proposed for the structures of the layers. An ideal quasilattice of the Al–Mn decagonal quasicrystal can be referred to as a periodic stack of two-colour Penrose patterns in the sequence $T\bar{T}T\bar{T}$..., in which $\bar{T}$ is T in reverse colour.

1. Introduction

The structure of a decagonal quasicrystal (DQC) can be described by an irrational section of a high-dimensional periodic structure with physical space (Janssen, 1986). For instance, the Penrose pattern, an ideal quasiperiodic lattice, can be constructed from a four- or five-dimensional periodic lattice by a section or a projection method (Janssen, 1986; Jaric, 1986). The diffraction patterns of the DQCs taken with the incident beam along the tenfold axis are similar to that of the Penrose pattern. This implies that their structures possibly consist of several layers and the projection along the unique axis gives the Penrose pattern. Yamamoto & Ishihara (1988) proposed a model of the Al–Mn DQC formed by a stack of four types of subpatterns of the Penrose pattern, which originate from the four pentagonal acceptance domains in the four-dimensional description. This model shows how a lattice with the space group $P10_5/mmc$ can be constructed. However, it is a more hypothetical model for the Al–Mn DQC. A single-crystal X-ray analysis has been applied on the Al–Mn DQC by Steurer (1991) and a five-dimensional model of Al–Mn DQC was obtained. Note that this is an average structure since diffuse scattering was not considered. Recently, Niizeki (1993) proposed a structural model of the Al–Mn DQC on the basis of a modified pentagonal Penrose lattice and the structure of the Al_3Mn phase. The 10_5 screw axis in the Al–Mn DQC is interpreted by a periodic stack of the modified pentagonal Penrose lattice. We find that the model does not match the high-resolution electron microscopy (HREM) image of the Al–Mn DQC.

Structural models of DQCs constructed by decoration of a certain quasilattice with atoms face the problem of how to select the correct quasilattice. It seems to be rather difficult to choose the correct quasilattice, except *via* a structure determination through a diffraction experiment combined with the high-dimensional analysis (Steurer & Kuo, 1990). This is because an infinite number of different quasilattices exist which show only slightly different diffraction patterns (Steinhardt, 1987). In the previous paper (Li, 1995), a new structural model of the Al–Mn DQC was proposed. On the basis of the close relationship between the Al_3Mn phase and the Al–Mn DQCs, we firstly chose the atomic cluster in the Al_3Mn phase as the structural motif of the Al–Mn DQC. Secondly, the subunits for the Al–Mn DQC are constructed according to the HREM image of the Al–Mn DQC. The quasilattice forms by the aggregation of these subunits, in contrast to using a particular selected

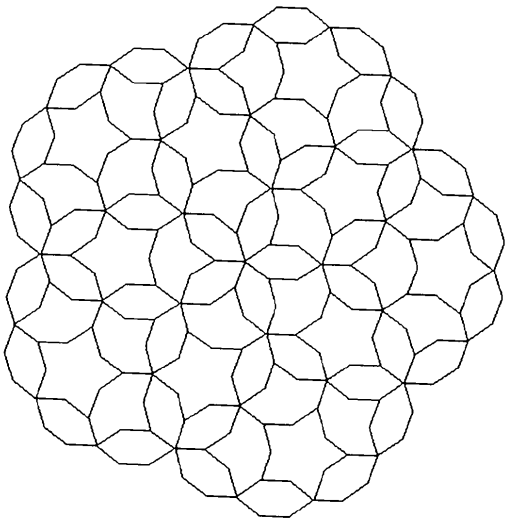

Fig. 1. The subpattern of the (original) Penrose pattern. It can be referred to as the grey Penrose pattern since it can be obtained as the projection of the two-colour Penrose patterns T and $\bar{T}$ ($\bar{T}$ is T with reverse colour).

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ISSN 0108-7681

quasilattice. On the other hand, an ideal quasiperiodic lattice can be formed by these subunits, which appear as a two-colour Penrose pattern in the puckered and flat layers in the model.

The high-dimensional description of the structure of the DQC is more concise and concrete than the description by subunits in three-dimensional space. In the present paper, we describe this model (Li, 1995) in a high-dimensional description. A decagonal coordinate system in five-dimensional space is adapted, which was used by Yamamoto & Ishihara (1988). The unit vectors of the decagonal system $\mathbf{d}_i^*$ $(i = 1, 2, 3, ...5)$ in reciprocal space are defined by $\mathbf{d}_i^* = \sum_j \tilde{M}_{ij}^{-1}\mathbf{a}_j$, where a tilde means the transposition of the matrix and $\mathbf{a}_i$ $(i = 1, 2, 3...5)$ are the orthogonal basic vectors with unit length, three of which span the external (physical) space and the remaining two the internal (complementary) space. We take $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_5$ for the basic vectors of the external space ($\mathbf{a}_5$ along the unique axis) and $\mathbf{a}_3$, $\mathbf{a}_4$ for those of the internal one. The matrix $\tilde{M}^{-1}$ is defined by

$$a^*/5^{1/2}\begin{pmatrix} c_1 & s_1 & c_2 & s_2 & 0 \\ c_2 & s_2 & c_4 & s_4 & 0 \\ c_3 & s_3 & c_1 & s_1 & 0 \\ c_4 & s_4 & c_3 & s_3 & 0 \\ 0 & 0 & 0 & 0 & (5^{1/2}c^*)/a^* \end{pmatrix},$$

where $c_j = \cos(2\pi j/5)$, $s_j = \sin(2\pi j/5)$ $(j = 1, 2, ..., 4)$ and a^* and c^* are the reciprocal lattice constants. The unit vectors $\mathbf{d}_i$ reciprocal to $\mathbf{d}_i^*$ are given by $\mathbf{d}_i = \sum_j M_{ij}a_j$. M is written as

$$2a/5^{1/2}\begin{pmatrix} c_1 - 1 & s_1 & c_2 - 1 & s_2 & 0 \\ c_2 - 1 & s_2 & c_4 - 1 & s_4 & 0 \\ c_3 - 1 & s_3 & c_1 - 1 & s_1 & 0 \\ c_4 - 1 & s_4 & c_3 - 1 & s_3 & 0 \\ 0 & 0 & 0 & 0 & (5^{1/2}c)/2a \end{pmatrix},$$

where $a = 1/a^*$, $c = 1/c^*$. Here the parameters a and c are 2.77 and 12.4 Å, respectively.

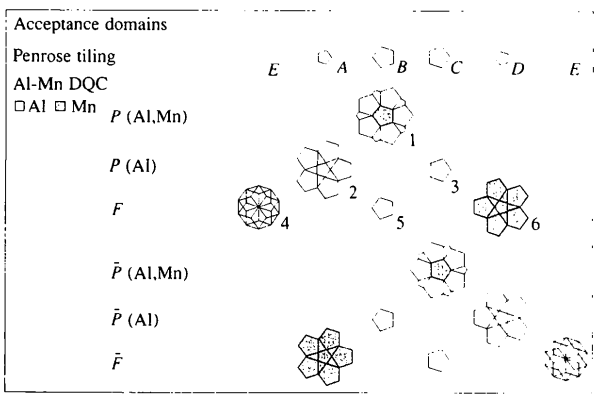

Fig. 2. The acceptance domains for the Penrose pattern and for the Al–Mn decagonal quasicrystal.

2. The structures of the layers

2.1. *Varieties of the Penrose pattern*

A periodic stack of the two-colour Penrose pattern (Li, Dubois & Kuo, 1994) is shown in Fig. 5 of the previous paper (Li, 1995). Fig. 1 shows the projection of these two-colour Penrose patterns, which is referred to as a grey Penrose pattern. This is a subpattern of the Penrose pattern composed of two kinds of rhombuses. The acceptance domains (A, B, C, D and E) for the Penrose pattern are shown in the upper part of Fig. 2 and the use of the acceptance domains B and C will give the grey Penrose pattern.

2.2. *The structures of the layers*

As stated in the previous paper (Li, 1995), there are two types of layers in the structure of the Al–Mn DQC, a puckered (P) and a flat (F) layer. Six layers in the sequence $PFp\bar{P}\bar{F}\bar{p}$... form a period of 12.4 Å along the tenfold axis. The $p(\bar{p})$ layer relates to the $P(\bar{P})$ layer by a mirror plane coinciding with the $F(\bar{F})$ layer. The $\bar{P}(\bar{F})$ layer is related to the $P(F)$ layer in a reverse mode. Fig. 2 (lower part) shows the acceptance domains in the five-dimensional description for the puckered and flat layers in the structural model of the Al–Mn DQC, in which the white colour denotes the Al area and the black colour the Mn area. The P layer is composed of two almost flat layers, which nearer to the F layer is comprised of only Al atoms and referred to as the P(Al) layer, while the other is composed of Al and Mn atoms and referred to as the P(Al,Mn) layer. It is clear that these acceptance domains are derived from those for the Penrose pattern. Fig. 3 shows the atomic arrangements obtained from the corresponding acceptance domains: (*a*) P(Al,Mn), (*b*) $\bar{P}$(Al,Mn), (*c*) P(Al), (*d*) $\bar{P}$(Al), (*e*) F and (*f*) $\bar{F}$ layers. They are composed of the subunits discussed in the previous paper (Li, 1995) and appear as the two-colour Penrose pattern, as indicated by the solid lines. Note that the $\bar{P}$ and $\bar{F}$ layers are related to P and F layers by exchanging the motives in the subunits. The puckered layers p and $\bar{p}$ are not shown because they are the mirror images of the P and $\bar{P}$ layers, respectively.

3. The three-dimensional structure

3.1. *Structure and properties*

The three-dimensional structure can easily be constructed from the structures of the layers discussed above. The Penrose pattern can be obtained by placing the acceptance domains A, B, C, D and E at $(-p, -p, -p, -p, x_5)$ and $p = 3, 4, 0, 1$ and 2, respectively, where $(x_1, x_2, x_3, x_4, x_5)$, x_j are the coordinates with respect to $\mathbf{d}_j$ (x_5 is irrelevant for the description of the Penrose pattern). Following the construction of the Penrose pattern, the atomic coordinates of the indepen-

dent atoms in the model for the Al–Mn DQC can be obtained, see Table 1.

As discussed by Li, Duneau & Kuo (1994), a periodic stack of two-colour Penrose patterns in the sequence $T\bar{T}T\bar{T}...$ ($\bar{T}$ is T with reverse colours) produces a three-dimensional lattice with space group $P10_5/mmc$. Unlike the tiles of the original Penrose pattern, each tile in the two-colour Penrose pattern has two types of states, denoted by white or black. The distributions of the white/black and black/white are the same except in opposite orientations, *i.e.* the distribution of the white tiles can be transformed to those of the black tiles by a 36° rotation in the high-dimensional space. In the projection scheme, one can easily check that the distributions of the white and black tiles are specified by two related acceptance domains, which are pentagons in opposite directions (the pentagons A and D in Fig. 2). It is obvious that the symmetry in the two-colour Penrose pattern decreases from the tenfold of the original Penrose pattern to fivefold. This can be referred to as a colour symmetry in the two-dimensional quasiperiodic lattice. Two such patterns with reverse colours are related by 36° rotational symmetry in high-dimensional space. Therefore, the space group of the three-dimensional lattice is $P10_5/mmc$, which satisfies the structural model of the Al–Mn DQC discussed above.

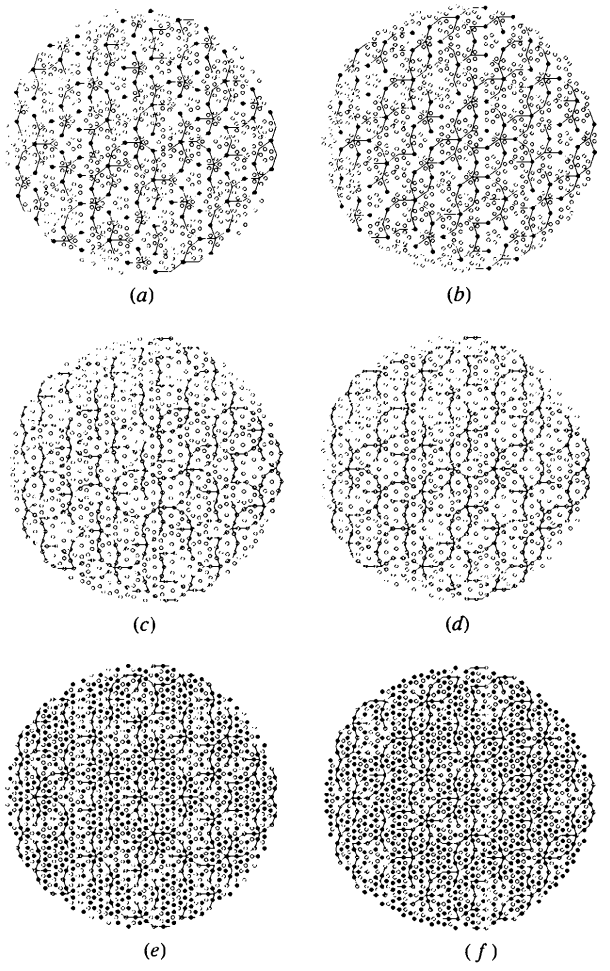

Fig. 3. The structures in the layers of the Al–Mn decagonal quasicrystal. The puckered layer is separated into two almost flat layers. Structures: (*a*) P(Al,Mn), (*b*) $\bar{P}$(Al,Mn), (*c*) P(Al), (*d*) $\bar{P}$(Al), (*e*) F and (*f*) $\bar{F}$ layers.

Table 1. *Coordinates of the five-dimensional atoms of the* Al–Mn *decagonal quasicrystal*

Acceptance domain	Coordinates x_1	x_2	x_3	x_4	x_5	Occupancy
1	−4/5	−4/5	−4/5	−4/5	0.06~0.08	Al + Mn
2	−3/5	−3/5	−3/5	−3/5	0.12~0.15	Al
3	0	0	0	0	0.12~0.15	Al
4	−2/5	−2/5	−2/5	−2/5	1/4	Al
5	−4/5	−4/5	−4/5	−4/5	1/4	Al
6	−1/5	−1/5	−1/5	−1/5	1/4	Mn

The composition and density of the model can be calculated in the following way. In the ideal quasiperiodic packing case, the frequencies of the three subunits are, $F_H : F_C : F_S = 5\tau : 5 : (2\tau - 1)$, $\tau = (5^{1/2} + 1)/2 = 1.618...$ is the usual golden mean. The numbers of Al and Mn atoms in the three subunits are H(Al) = 62 and H(Mn) = 16 in the subunit H, C(Al) = 97 and C(Mn) = 25 in the subunit C and S(Al) = 134 and S(Mn) = 34 in the subunit S. Therefore, the composition of the model (Al_xMn) is

$$x = \frac{[H(\mathrm{Al})F_H + C(\mathrm{Al})F_C + S(\mathrm{Al})F_S]}{[H(\mathrm{Mn})F_H + C(\mathrm{Mn})F_C + S(\mathrm{Mn})F_S]^{-1}} = 3.897.$$

The Al–Mn DQC was firstly found in a rapidly solidified Al_4Mn (Bendersky, 1985), which matches the composition of the model closely. The density of the model is calculated in a similar way

$$D_X = \frac{(M_H F_H + M_C F_C + M_S F_S)}{(V_H F_H + V_C F_C + V_S F_S)} = 3.72 \text{ Mg m}^{-3},$$

in which M_H, M_C and M_S are the mass in the subunits H, C and S and V_H, V_C and V_S are the volumes of the subunits H, C and S. The density of the Al–Mn DQC has not been measured experimentally, but some values of the Al–Mn phases of similar composition are given for comparison: the density of hexagonal φ-$Al_{10}Mn_3$ is 3.65 (5) (Taylor, 1959), hexagonal μ-Al_4Mn 3.556 (2) (Shoemaker, Keszler & Shoemaker, 1989), δ-$Al_{11}Mn_4$ 3.88 (Kontio, Stevens, Coppens, Brown, Dwight & Williams, 1978), and orthorhombic Al_3Mn 3.90 Mg m^{-3} (Shi, Li, Ma & Kuo, 1994).

The composition of the model can also be calculated from the acceptance domains. The proportions of Al and Mn in puckered and flat layers are 80.484:6.225 and 34.063:36.565. Therefore, the composition of the model is Al_xMn, $x = (80.484 \times 2 + 34.063)/(6.225 \times 2 + 36.565) = 3.897$.

A projection of the model along the tenfold axis is shown in Fig. 4, and a quasilattice is outlined by solid

lines. It is obvious that the projection can be referred to as a grey Penrose pattern and there are decagonal channels distributed at the vertices of the subunits. Therefore, the projections are comparable to the high-resolution electron microscopy (HREM) image of the Al–Mn DQC [Fig. 2 in the previous paper (Li, 1995)], except the subunits in the projection are packed quasiperiodically while the subunits in the HREM image of the (true) Al–Mn DQC (Hirabayashi & Hiraga, 1987) are packed randomly.

3.2. *Comparison with Niizeki's model*

A model for the Al–Mn DQC has been recently proposed by Niizeki (1993). The main feature of this model is to use a modified pentagonal Penrose pattern as the quasilattice of the Al–Mn DQC. In contrast to the original Penrose pattern with tenfold rotational symmetry, the modified pattern is a quasiperiodic lattice composed of the same tiles, but with fivefold rotational symmetry, see (*a*) Q_0 and (*b*) $\bar{Q}_0$ in Fig. 5 ($\bar{Q}_0$ is Q_0 in a negative direction). A 10_5 rotational symmetry can be achieved by stacking two pentagonal Penrose quasilattices Q_0 and $\bar{Q}_0$ along the fivefold axis (Niizeki, 1993). To construct a structural model, Niizeki suggests that the local atomic arrangements in the layers of the Al_3Mn structure can be used to decorate the modified pentagonal Penrose quasilattice.

Although both Niizeki's model and the present one are constructed on the basis of the structure of the Al_3Mn phase, they are quite different. Firstly, the superposition of Q_0 and $\bar{Q}_0$ shows that many vertices of the two modified pentagonal Penrose patterns do not coincide, see Fig. 5(*c*), indicating that the columns of atomic clusters in the Al_3Mn phase cannot be rebuilt in these areas. In contrast to the present model, Niizeki's model is not really composed of the atom cluster of the Al_3Mn phase, despite the layer structures in Niizeki's model being related to those of the Al_3Mn phase. Secondly, the HREM image of the Al–Mn DQC shows that the structure of the (true) Al–Mn DQC consists of randomly packed subunits. As an ideal model with quasiperiodic lattices, these subunits should appear in the structural model, but they cannot be found in Niizeki's model. Thirdly, the space group of the Al–Mn DQC ($P10_5/mmc$) is explained by a periodic stacking of the modified pentagonal Penrose quasilattices in Niizeki's model instead of the periodic stacking of the two-colour Penrose quasilattices in the present model.

4. Concluding remarks

In conclusion, a five-dimensional description can be applied to the structural model of the Al–Mn DQC, which is constructed on the basis of the structure of the Al_3Mn phase. The structures of the layers in the model of the Al–Mn DQC can be defined by the acceptance domains in a five-dimensional description. The model satisfies the space group of $P10_5/mmc$ and suggests a reasonable composition and density. Comparison of our model with other models for Al–Mn DQCs indicates, in our belief, some preference for the present model.

One of the authors, XZL, is grateful to the Alexander von Humboldt Foundation for financial support.

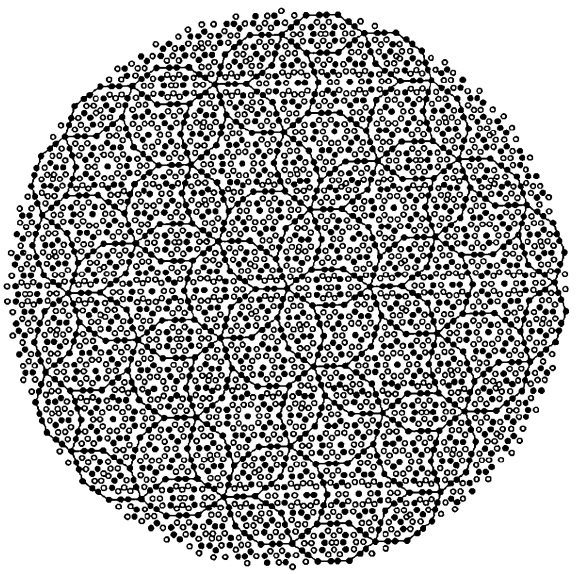

Fig. 4. Projection of the present model of the Al–Mn decagonal quasicrystal along the periodic axis.

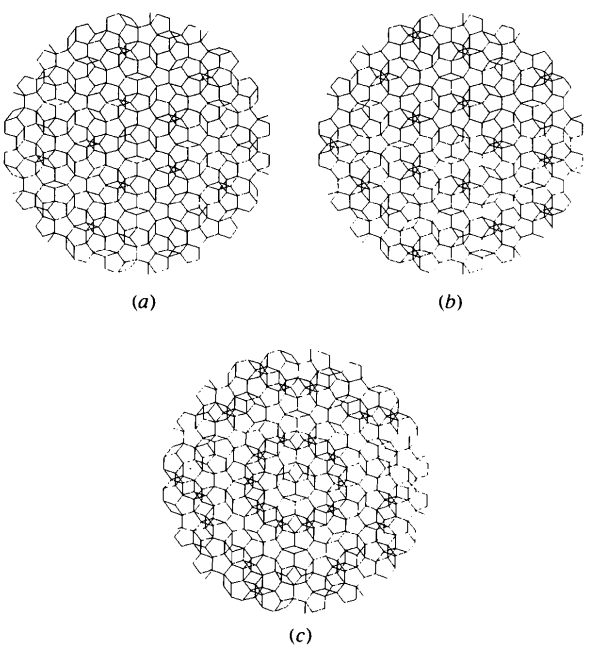

Fig. 5. Modified pentagonal Penrose patterns: (*a*) Q_0 and (*b*) $\bar{Q}_0$ ($\bar{Q}_0$ is Q_0 in a negative direction). (*c*) The superposition of Q_0 and $\bar{Q}_0$.

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Acta Cryst. (1995). B**51**, 275–287

(3 + 2)-Dimensional Superspace Approach to the Structure of the Incommensurate Intergrowth Compound: $(SbS)_{1.15}TiS_2$

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(*Received* 8 *August* 1994; *accepted* 1 *December* 1994)

Abstract

The inorganic misfit-layer compound $(SbS)_{1.15}TiS_2$ was prepared by high-temperature reaction of the elements. The structure, determined by single-crystal X-ray diffraction, is described by two interpenetrating incommensurately modulated subsystems. The first subsystem comprises TiS_2 sandwiches, with Ti atoms in trigonal-antiprisms of S atoms. The lattice parameters are $a'_{11} = 3.403\,(1)$, $a'_{12} = 3.410\,(1)$, $a_{13}' = 11.385\,(1)$ Å, $\alpha'_1 = 81.544\,(7)$, $\beta'_1 = 82.817\,(8)$ and $\gamma'_1 = 60.08\,(1)°$. The second subsystem is built of intrinsically interface-modulated double layers of SbS. The basic structure unit-cell dimensions are given by $a'_{21} = 2.954\,(1)$, $a'_{22} = 2.968\,(1)$, $a'_{23} = 11.311\,(1)$ Å, $\alpha_2 = 83.973\,(8)$, $\beta_2 = 85.87\,(1)$, $\gamma_2 = 84.06\,(1)°$. The interface modulation wavevector of SbS is given by $\mathbf{q} = 0.409(\mathbf{a}^{*\prime}_{21} + \mathbf{a}^{*\prime}_{22})$. The two subsystems have the common $(\mathbf{a}^{*\prime}_{\nu 2}, \mathbf{a}^{*\prime}_{\nu 3})$ plane. The whole X-ray diffraction pattern is indexed with five integer indices, thus a (3 + 2)-dimensional superspace group is used to analyse the complete structure. Both the superspace-group symmetry and the subsystem symmetries are centrosymmetric triclinic, belonging to the superspace group $P\bar{1}$. Refinement on 2483 reflections with $I > 2.5\sigma(I)$ converged to $wR = 0.069$ ($R = 0.062$). The final structure model consists of both occupational and displacive modulations for the atoms in the SbS subsystem, which results in zigzag clusters of –Sb–Sb– and –S–S– parallel to the $[1\bar{1}0]$ direction of SbS. The shortest Sb—Sb and S—S distances are 2.84 and 3.43 Å, respectively. The average valence of Sb was calculated as 3.13. The distinguishing feature is the incommensurate ordering of Sb/S atoms on the rock-salt structure, with a modulation wavevector apparently unrelated to the periodicities of the TiS_2 subsystem.

1. Introduction

Recently, 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; $0.09 < \delta < 0.23$; $n = 1$ or 2) have attracted much attention, because of their special crystallographical features as well as many interesting physical properties (Wiegers *et al.*, 1989; Wiegers & Meerschaut, 1992; van Smaalen, 1992*a*). These compounds are built of two different types of layers: two-atom-thick ($\mathcal{MX}$) layers with a distorted NaCl-type structure and $(\mathcal{TX}_2)_n$ ($n = 1, 2$) sandwiches with a NbS_2- or TiS_2-type structure. Commonly, the layers $\mathcal{MX}$ and $\mathcal{TX}_2$ are stacked alternately, but also compounds have been found with paired sandwiches of $\mathcal{TX}_2$ (Meerschaut, Auriel & Rouxel, 1992). Structures of misfit compounds can be described by assigning different unit cells to the $\mathcal{MX}$ and $\mathcal{TX}_2$ layer types. Both unit cells have $\mathbf{c}^*$ axes in common, perpendicular to the layers, and one common $\mathbf{b}^*$ axis. The two unit cells are mutually incommensurate, as expressed by the collinear $\mathbf{a}$ axes with incommensurate length ratio. The interaction of the subsystems induces a mutual modulation, where $\mathbf{a}^*_{11}$ is the modulation wavevector of the second subsystem, and $\mathbf{a}^*_{21}$ the modulation

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