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A superspace group description of the misfit layer structure of $(SnS)_{1.17}(NbS_2)$

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Abstract. The misfit layer compound $(SnS)_{1.17}NbS_2$ belongs to the class of intergrowth compounds. In the simplest approximation, the structure can be described as that of two interpenetrating sublattices. The true structure consists of two interpenetrating, incommensurately modulated structures. In this paper the theory of superspace groups is applied to $(SnS)_{1.17}NbS_2$. It is shown that the symmetry is fully characterised by the (3 + 1)-dimensional superspace group $P\,^{Cm2m}_{1\,1s}$ ($\alpha\,0\,0$). Definitions of the component structure space groups and superspace groups are given. For the NbS_2 part they are found to be G_1 = Cm2m and $G_s^1 = P\,^{Cm2m}_{1\,1s}$. For the SnS part we obtain G_2 = Cm2*a* and $G_s^2 = P\,^{Cm2a}_{1\,1\,1}$. It is shown that this unified approach gives more information about the symmetry than when the subsystems are considered independently. One result is that in a structure refinement fewer possibilities have to be considered. Finally, the superspace group is used to derive the symmetry restrictions on the modulation functions of both subsystems.

1. Introduction

Compounds with a layered structure are characterised by strong chemical bonds within a planar layer of one atom (e.g., graphite) or a few atoms (e.g., transition metal dichalcogenides) thick, and weaker Van der Waals bonds between the atoms of adjacent layers. As this description suggests, it might be possible to design structures which consist of alternating layers of different chemical composition. The two different types of layers will have different intralayer lattice constants, which generally do not match. Consequently, it is not possible to define a unit cell and a space group with which these compounds can be described. Each component will have its own translational symmetry.

Indeed, compounds with a so-called composite crystal structure exist. In the case of layered compounds they are called misfit layer stuctures (Macovicky and Hyde 1981). One of such structures is defined by $LaCrS_3$. It consists of alternating layers of two-atom thick LaS and three-atom thick CrS_2 (Donohue 1975, Kato and Kawada 1977, Otera-Diaz *et al* 1985). The structure, described in a supercell by Kato and Kawada (1977), is probably incommensurate in one direction parallel to the layers.

Recently, compounds with this type of structure have been prepared and characterised by Wiegers *et al* (1988a, b), Meerschaut *et al* (1988), Meetsma *et al* (1988) and Guemas *et al* (1988). Electron microscopic studies were done by Kuypers *et al* (1988). Among those compounds was '$SnNbS_3$', with composition $(SnS)_{1.17}NbS_2$, whose crystal structure has been determined (Meetsma *et al* 1988). The diffraction pattern could be

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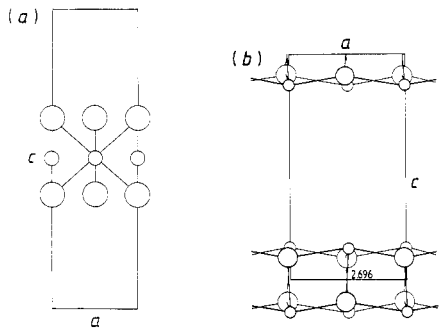

Figure 1. Projection of the structure along [010] for the NbS_2 part (*a*), and the SnS part (*b*). Large circles denote sulphur atoms; small circles correspond to Nb and Sn atoms, respectively.

described by two mutually incommensurate orthorhombic unit cells, with $b = 5.751(1)$ Å and $c = 11.762(1)$ Å. In the *a*-direction they were incommensurate with $a_1 = 3.321(1)$ Å and $a_2 = 5.673(1)$ Å. The structure was found to consist of layers of NbS_2 and SnS alternating perpendicular to the *c*-axis. The $(\boldsymbol{a}_1, \boldsymbol{b}, \boldsymbol{c})$ unit cell (cell 1) corresponds to the NbS_2 part of the structure. Cell 2 = $\{\boldsymbol{a}_2, \boldsymbol{b}, \boldsymbol{c}\}$ corresponds to the SnS part (figure 1).

Using the reflection data belonging to the separate unit cells, the two component structures were determined. From the reflections common to both cells, i.e., the $(0kl)$ plane, the relative position of the layers along $\boldsymbol{b}$ was determined (Meetsma *et al* 1988).

In this paper we use a superspace group to describe the symmetry of $(SnS)_{1.17}NbS_2$. In analogy with incommensurately modulated structures, as proposed by Janner and Janssen (1980), the reflections are indexed on the basis of a minimal set of rationally independent vectors in reciprocal space. Let this number be $(3 + d)$, then a $(3 + d)$-dimensional superspace group can be assigned to the structure. This superspace group then gives the complete symmetry of the structure. Following Janner and Janssen (1980) and van Smaalen (1989), this superspace group is used to derive the component space groups and the component superspace groups.

Furthermore, we derive the symmetry restrictions on the modulation functions. The latter, together with the basic structure as determined by Meetsma *et al* (1988), defines the complete structure.

2. The structure in superspace

Denote the two sublattices by $\Lambda_v = \{\boldsymbol{a}_{v1}, \boldsymbol{a}_{v2}, \boldsymbol{a}_{v3}\}$, with $v = 1, 2$ corresponding to the NbS_2 and SnS lattices, respectively. The reciprocal lattices are given by $\Lambda_v^* = \{\boldsymbol{a}_{v1}^*, \boldsymbol{a}_{v2}^*, \boldsymbol{a}_{v3}^*\}$. For $(SnS)_{1.17}(NbS_2)$, it was found that $\boldsymbol{a}_{12}^* = \boldsymbol{a}_{22}^*$ and $\boldsymbol{a}_{13}^* = \boldsymbol{a}_{23}^*$, whereas $\boldsymbol{a}_{11}^*$ and $\boldsymbol{a}_{21}^*$, are parallel, but have an incommensurate length ratio. This means that all reflections have integer indices with respect to a basis of only four vectors: $M^* = \{\boldsymbol{a}_1^*, \boldsymbol{a}_2^*, \boldsymbol{a}_3^*, \boldsymbol{a}_4^*\}$, with

$$\boldsymbol{a}_{vi}^* = \sum_{j=1}^{4} Z_{ij}^v \boldsymbol{a}_j^* \qquad v = 1, 2; i = 1, 2, 3. \tag{1}$$

The vectors $\boldsymbol{a}_j^*$ are to be chosen such that each (3×4) matrix $\mathbf{Z}^v$ is an integral matrix, thus ensuring the reflection indices to be integers. For $SnNbS_3$ a suitable choice is

$$\mathbf{Z}^1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad \mathbf{Z}^2 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}. \tag{2}$$

$\{\boldsymbol{a}_1^*, \boldsymbol{a}_2^*, \boldsymbol{a}_3^*\}$ define a basis in 3D space. Then $\boldsymbol{a}_4^*$ can be written as a linear combination of this set. In matrix notation this becomes

$$\boldsymbol{a}_4^* = \boldsymbol{\sigma}\begin{bmatrix}\boldsymbol{a}_1^*\\ \boldsymbol{a}_2^*\\ \boldsymbol{a}_3^*\end{bmatrix} \tag{3}$$

with $\boldsymbol{\sigma} = (\alpha\, 0\, 0)$ is a 1×3 matrix defining the incommensurate vectors. From the experiment it follows that $\alpha = a_{11}/a_{21} = 0.585 = 1/1.708$.

The set M^* can be considered as the projection of a lattice, Σ^*, in four-dimensional superspace (Janner and Janssen 1980):

$$\begin{aligned}\boldsymbol{a}_{si}^* &= \boldsymbol{a}_i^* \\ \boldsymbol{a}_{s4}^* &= \boldsymbol{a}_4^* + \boldsymbol{b}^*\end{aligned} \qquad i = 1, 2, 3 \tag{4}$$

where $\boldsymbol{b}^*$ is a vector perpendicular to physical, three-dimensional space. The reciprocal to equation (4) is Σ, given by the vectors

$$\begin{aligned}\boldsymbol{a}_{s1} &= \boldsymbol{a}_1 - \alpha\boldsymbol{b} \\ \boldsymbol{a}_{si} &= \boldsymbol{a}_i \qquad\qquad i = 1, 2 \\ \boldsymbol{a}_{s4} &= \boldsymbol{b}\end{aligned} \tag{5}$$

with again $\boldsymbol{b}$ perpendicular to physical space. By construction, physical space is any section of superspace, perpendicular to the additional dimension $\boldsymbol{b}^*$. That is, a point

$$\boldsymbol{r}_s = \sum_{i=1}^{4} x_{si}\boldsymbol{a}_{si}$$

in superspace is also in physical space if

$$\boldsymbol{b}^* \cdot \boldsymbol{r}_s = t \tag{6}$$

where $t \in \mathbb{R}$ is a constant determining the particular section chosen. With equation (5) this becomes

$$x_{s4} = t + \alpha x_{s1}. \tag{7}$$

Let $\boldsymbol{r}_s$ be a superspace vector lying in physical space. Then it is easy to derive that equation (1) also gives the relation between its coordinates with respect to Σ and the coordinates with respect to Λ_v,

$$\begin{bmatrix}x_{v1}\\ x_{v2}\\ x_{v3}\end{bmatrix} = \mathbf{Z}^v\begin{bmatrix}x_{s1}\\ x_{s2}\\ x_{s3}\\ x_{s4}\end{bmatrix}. \tag{8}$$

Consider an atom in the vth subsystem. The position is

$$\boldsymbol{r}(nv_j) = \sum_{i=1}^{3}(n_i + x_{vi}^j)\boldsymbol{a}_{vi} \tag{9}$$

where $n_i \in \mathbb{Z}$, and $\{x_{vi}^j\}$ defines the position of atom j in subsystem v within the unit cell

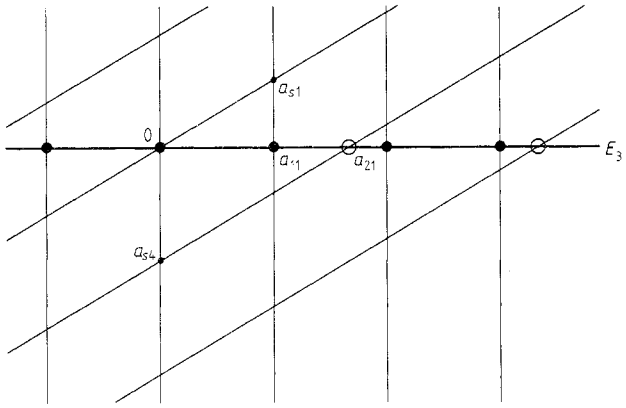

Figure 2. A two-dimensional section of superspace. Physical space (E^3) shows up as a one-dimensional section. The direction shown is that where the two subsystem lattices have incommensurate periodicities, a_{11} and a_{21}. The four-dimensional equivalent of the atoms are straight lines (equation (10)). For Λ_1 they are parallel to a_{s4}, for Λ_2 they are parallel to a_{s1}. Because atoms cannot intersect, the two sets of lines have to have different positions along at least one of the other two directions. For example, with c perpendicular to the plane, the lines parallel to a_{s1} can be at $z = 0$, whereas the others are at $z = \frac{1}{2}$. The intersection of the 4D atoms with E^3 gives the atomic positions of the two incommensurate lattices. Points of Λ_1 are denoted by small filled circles, points of Λ_2 are larger open circles.

of Λ_v.

To ensure the periodicity of subsystem v, equivalent atoms are found for all $n_i \in \mathbb{Z}$. We now seek to find the four-dimensional equivalent of this set of atoms, such that: (1) the section with physical space (equation (7)) gives the set of positions in equation (9); (2) the four-dimensional density function is periodic with Σ. It follows that the superspace analogue of a point-like atom in E^3 is a d-dimensional subspace (for $SnNbS_3$, $d = 1$). For $v = 1, 2$ we obtain (see figure 2)

$$A_1(n;j) = \left\{ \boldsymbol{r}_s = \sum_{i=1}^{4} x_{si}\boldsymbol{a}_{si} \,|\, x_{si} = n_i + x^j_{1i},\ i = 1,2,3,\ n_i \in \mathbb{Z} \right\}$$
$$A_2(n;j) = \left\{ \boldsymbol{r}_s = \sum_{i=1}^{4} x_{si}\boldsymbol{a}_{si} \,|\, x_{si} = n_i + x^j_{2i},\ i = 2,3,\ x_{s4} = n_1 + x^j_{21},\ n_i \in \mathbb{Z} \right\} \qquad (10)$$

Because the atoms are continuous in one dimension, equation (7) gives a solution for any $t \in \mathbb{R}$. Applying equations (7) and (8) to (10) then shows that $A_v(n;j)$ defines an atom in physical space, exactly at the positions given in equation (9).

3. The symmetry

In the description of '$SnNbS_3$' as a structure consisting of two subsystems, each with its own periodicity, two space groups are assigned to the compound, neither of which gives the symmetry of the complete structure. In § 2 a four-dimensional periodic density function is defined of which the three-dimensional section gives the density function of the crystal. Because of this periodicity, there is a four-dimensional space group, i.e., a superspace group, defining the symmetry of the superspace density function. This superspace group gives all the symmetry of the incommensurate composite structure.

To a large extent, the determination of the symmetry can be done by analysing the diffraction pattern. The analysis is completely analogous to that for incommensurately modulated crystals, with $\boldsymbol{a}_4^*$ taking up the role of the modulation wavevector $\boldsymbol{q}$ (De Wolff *et al* 1981).

From Meetsma *et al* (1988) it follows that the diffraction pattern has (mmm) symmetry. The corresponding point group elements $(R\varepsilon)$ in superspace are (2^x1), $(2^y\bar{1})$, $(2^z\bar{1})$, $(m_x\bar{1})$, (m_y1) and (m_z1). Denote the subsystem reflection indices with respect to Λ_v^* by $(h_vk_vl_v)$. Then, the systematic absences observed are (Meetsma *et al* 1988),

$$v = 1: \qquad (h_1k_1l_1)\text{: } h_1 + k_1 = \text{odd is absent} \tag{11a}$$

$$v = 2: \qquad (h_2k_2l_2)\text{: } h_2 + k_2 = \text{odd is absent} \tag{11b}$$

$$v = 2: \qquad (h_2k_20)\text{: } k_2 = \text{odd; } h_2 = \text{odd is absent.} \tag{11c}$$

Conditions (11*a*, *b*) represent a C-centring in each lattice; condition (11*c*) indicates the presence of an $\boldsymbol{a}$-glide and a $\boldsymbol{b}$-glide in Λ_2. With respect to M^*, and thus also with respect to Σ^*, the reflection positions have integer indices $(HKLM)$. The relation between M^* and Λ_v^* gives:

$$\begin{aligned}(HKLM) &= (h_1k_1l_10) \qquad \text{for } v = 1\\ (HKLM) &= (0k_2l_2h_2) \qquad \text{for } v = 2.\end{aligned} \tag{12}$$

It follows that all reflections with both H and M not zero are absent. The systematic absences, with respect to this new basis, are

$$(HKL0)\text{: } H + K = \text{odd is absent} \tag{13a}$$

$$(0KLM)\text{: } K + M = \text{odd is absent} \tag{13b}$$

$$(0K0M)\text{: } K = \text{odd; } M = \text{odd is absent.} \tag{13c}$$

Conditions (13*a*, *b*) can be combined into

$$(HKLM)\text{: } H + K + M = \text{odd is absent} \tag{14}$$

which represents a centring in superspace of the form

$$\bar{\boldsymbol{c}}\boldsymbol{t} = (\tfrac{1}{2}\tfrac{1}{2}0\tfrac{1}{2}). \tag{15}$$

Combining (13*a*) and (13*c*) gives

$$(HK0M)\text{: } H + K = \text{odd; } M = \text{odd is absent.} \tag{16}$$

The absences in equation (16) indicate the presence of the glide planes $(m_z1|\tfrac{1}{2}\tfrac{1}{2}00)$ and $(m_z1|000\tfrac{1}{2})$.

From equation (15) we determine the Bravais class $P^{Cmmm}_{\bar{1}\,1\,1}$ $(\alpha 00)$, no. 13 of De Wolff *et al* (1981), but in a different setting. Together with equation (16) this shows that the possible superspace groups are $P^{Cmmm}_{\bar{1}\,1\,s}$ and any of its acentric maximal subgroups. Because the two component structures have translational periodicity Λ_v in 3D, their symmetry can be characterised by a 3D space group. These space groups can be derived from the superspace group in the following way.

Let $(\mathbf{R}\varepsilon\,|\,\tau_1\tau_2\tau_3\tau_4)$ be the matrix representation on Σ of a superspace group element. Then, the matrix representation of this operator on Λ_v is given by (van Smaalen 1989)

$$\mathbf{R}^v = \mathbf{Z}^v \begin{pmatrix} R & 0 \\ M & \varepsilon \end{pmatrix} \begin{bmatrix} (Z_3^v + Z_d^v\sigma)^{\text{inv}} \\ \sigma(Z_3^v + Z_d^v\sigma)^{\text{inv}} \end{bmatrix} \qquad \boldsymbol{\tau}^v = \mathbf{Z}^v \begin{bmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \\ \tau_4 \end{bmatrix} \tag{17}$$

where $\mathbf{Z}^v = (Z_3^v Z_d^v)$ is the juxtaposition of a 3×3 and a $3 \times d$ ($d = 1$) matrix, and

$$\begin{bmatrix} (Z_3^v + Z_d^v \sigma)^{\text{inv}} \\ \sigma(Z_3^v + Z_d^v \sigma)^{\text{inv}} \end{bmatrix}$$

is the inverse of $\mathbf{Z}^v$ (van Smaalen 1989). For $(\mathbf{R}^v | \boldsymbol{\tau}^v)$ to be a symmetry operator of the subsystem v, it is required that (van Smaalen 1989, Janner and Janssen 1980)

$$\mathbf{R}^v \boldsymbol{\Lambda}_v = \boldsymbol{\Lambda}_v. \tag{18}$$

In components, this means that for any set of integers $\boldsymbol{n} = (n_1, n_2, n_3)$, $\mathbf{R}^v \boldsymbol{n}$ has to be a triplet of integers again. If this is not the case, it follows that $\mathbf{R}^v \boldsymbol{\Lambda}_v$ gives any of the other subsystem lattices $v' \neq v$. This last condition shows that for '$SnNbS_3$', with only two subsystems, $\mathbf{R}^v \boldsymbol{\Lambda}_v = \boldsymbol{\Lambda}_v$ either for both subsystems or for neither one of the two.

For '$SnNbS_3$', we obtain from equations (2) and (17) for a superspace group operator $(R\varepsilon | \boldsymbol{\tau})$

$$R^1 = R \qquad \boldsymbol{\tau}^1 = (\tau_1 \tau_2 \tau_3) \tag{19}$$

$$R^2 = \begin{bmatrix} \varepsilon & 0 & 0 \\ (1/\alpha) r_{21} & r_{22} & r_{23} \\ (1/\alpha) r_{31} & r_{32} & r_{33} \end{bmatrix} \qquad \boldsymbol{\tau}^2 = (\tau_4 \tau_2 \tau_3).$$

It follows that only operators with $r_{21} = r_{31} = 0$ can be part of the space group G_2. All elements fulfil this requirement, so that all elements of the superspace group give rise to an element of the subsystem space groups.

For the superspace group $G_s' = \mathrm{P}\,{}^{\mathrm{Cmmm}}_{1\,1\,\mathrm{s}}$, the two subsystem space groups thus are:

$$G_1' = \mathrm{Cmmm} \qquad G_2' = \mathrm{Cmm}a. \tag{20}$$

From the structure refinement of Meetsma *et al* (1988) it follows that the NbS_2 part of the structure has a symmetry according to the space group Cm2m, which is an acentric subgroup of G_1'. The superspace group analysis given above now shows that the SnS part space group cannot be anything but $G_2 = \mathrm{Cm}2a$. This is contradictory to the result of Meetsma *et al* (1988), who obtained a slightly lower R-factor for a structure model according to C2m*b* than one for Cm2*a*. It may be noted that the difference is only due to a small deviation of the coordinates from their centrosymmetry values.

The explanation for this discrepancy lies in the fact that the NbS_2 part of the structure is described very well by the periodic atomic arrangement ($R_F 2 = 3.6\%$). For SnS, however, an R-factor of only 8.5% was obtained. This indicates that the data are not fitted as well as possible. The model lacks the modulation of the atomic positions in SnS with the incommensurate periodicity of the NbS_2 lattice. Apparently the error introduced by the absence of this modulation is better fitted by the C2m*b* model, rather than by the true symmetry Cm2*a*.

4. The complete structure

The structure determination of Meetsma *et al* (1988), and the analysis in § 3 pertains to a structure consisting of two periodic subsystems. Since these subsystems coexist in the same compound (figure 1), it is natural to assume that each subsystem will be modulated

Table 1. Elements of the superspace group G_s, together with the corresponding elements of the subsystem space groups G_v, $v = 1, 2$. The operators shown have to be combined with the lattice translations.

$G_s = P^{Cm2m}_{11s}$	G_1 = Cm2m	G_2 = Cm2*a*
$(E1\vert\frac{1}{2}\frac{1}{2}0\frac{1}{2})$	$(E\vert\frac{1}{2}\frac{1}{2}0)$	$(E\vert\frac{1}{2}\frac{1}{2}0)$
$(m_x\bar{1}\vert000\frac{1}{2}+\tau_4)$	$(m_x\vert000)$	$m_x\vert\frac{1}{2}+\tau_400)$
$(2_y\bar{1}\vert000\tau_4)$	$(2_y\vert000)$	$(2_y\vert\tau_400)$
$(m_z1\vert000\frac{1}{2})$	$(m_z\vert000)$	$(m_z\vert\frac{1}{2}00)$

with the periodicities of the other subsystem with which it is incommensurate. In this way, a structure is obtained which comprises two incommensurate subsystems, instead of two periodic subsystems.

Experimentally, these modulations would show up in the diffraction pattern through the occurrence of 'satellites' at the positions $S = (HKLM)$, with both H and M unequal to zero. Indeed, such reflections have been observed in electron diffraction (Kuypers *et al* 1988). However, in x-ray diffraction they could not be measured (De Boer 1988), thus making a quantitative analysis of the modulation impossible.

It is noted that the satellites do not add new diffraction positions to the originally defined set M^* and the lattice Σ^*. Therefore, the real, modulated structure is described by the same superspace group as derived in § 3.

Now, the three-dimensional section of the superspace atoms need no longer give a 3D periodic structure; the only requirement remaining is the periodicity in superspace. The one-dimensional subspaces (straight lines) representing the atoms in superspace (equation 10) have to be replaced by wavy lines, on the average parallel to a subspace. The period of this wave has to be equal to the period of Σ in the corresponding direction. This waviness then defines the modulation function, in the same way as it does for ordinary modulated structures.

The condition for $(\mathbf{R}^v\vert\boldsymbol{\tau}^v)$ (equation (17)) to be a 3D symmetry operator has to be supplied by the condition (Yamamoto and Nakazawa 1982, van Smaalen 1987)

$$\sigma\boldsymbol{\tau}' = \tau_4 \qquad \text{with } \boldsymbol{\tau}' = \begin{bmatrix}\tau_1\\ \tau_2\\ \tau_3\end{bmatrix}. \tag{21}$$

Generally the set of $(\mathbf{R}^v\vert\boldsymbol{\tau}^v)$ fulfulling equation (21) will not constitute a space group. In particular, for 'SnNbS$_3$' translations along $\boldsymbol{a}_{v1}$ will not be part of the 3D groups of the subsystems.

To characterise the symmetry of each subsystem, the complete superspace group is now required. The superspace group as derived in this paper is defined on the basis of the $(3 + d)$ vectors M^* in 3D space, corresponding to a reciprocal basis Σ^* in superspace.

It is useful to introduce the concept of a subsystem superspace group, G_s^v. The vectors $\boldsymbol{a}_{vi} \in \Lambda_v$ are supplied with d-wave vectors $\boldsymbol{q}^{vj}$, describing the modulation in the vth subsystem. From the above discussion it follows that these $(3 + d)$ vectors are merely a rearrangement of the vectors, $\boldsymbol{a}_i^* \in M^*$. The 3-vectors $\boldsymbol{a}_i^*$ are obtained through equation (1). The remaining d-vectors can be defined by

$$\boldsymbol{q}^{vj} = \sum_{j=1}^{3+d} \mathbf{W}_{ij}^v \boldsymbol{a}_j^* \tag{22}$$

with $\mathbf{W}^v$ an integral $d \times (3 + d)$ matrix, for which the only requirement is that

Table 2. Average positions and symmetry restrictions for the independent atoms in $SnNbS_3$. The model of Meetsma *et al* (1988) corresponds to a value of $\tau_4 = -\frac{1}{2}$. The modulation function is defined by

$$u^{\mu}_{\alpha}(\bar{x}^{v}_{4}) = \sum_{n=1}^{\infty} \{A^{\mu}_{n\alpha} \cos(2\pi n \bar{x}^{v}_{4}) + B^{\mu}_{n\alpha} \sin(2\pi n \bar{x}^{v}_{4})\}$$

for $\alpha = x, y, z$ and atom μ. $\bar{x}^{v}_{4}$ is defined by: $\bar{x}^{1}_{4} = \alpha\bar{x}_1 - \frac{1}{2}\tau_4 = \alpha n_1 - \frac{1}{2}\tau_4$ and $\bar{x}^{2}_{4} = \alpha\bar{x}_1 = \alpha(n_1 + \frac{1}{4} + \frac{1}{2}\tau_4)$, where n_1 is an integer defining the unit cell along $\boldsymbol{a}_{v1}$. Note that depending on whether an odd or an even harmonic is considered, either A_n or B_n is zero, or even both are zero.

		Average position	n is odd		n is even	
			$\cos(2\pi n\bar{x}^{v}_{4})$	$\sin(2\pi n\bar{x}^{v}_{4})$	$\cos(2\pi n\bar{x}^{v}_{4})$	$\sin(2\pi n\bar{x}^{v}_{n})$
Nb	x	0	—	B^{1}_{nx}	—	—
	y	0.083	—	—	A^{1}_{ny}	—
($v = 1$)	z	$\frac{1}{2}$	—	—	A^{1}_{nz}	—
S	x	0	A^{2}_{nx}	—	—	B^{2}_{nx}
	y	0.75	—	B^{2}_{ny}	A^{2}_{ny}	—
	z	0.6328	—	B^{2}_{nz}	A^{2}_{nz}	—
Sn	x	$\frac{1}{4} + \frac{1}{2}\tau_4$	—	B^{3}_{nx}	—	B^{3}_{nx}
	y	0.25	A^{3}_{ny}	—	A^{3}_{ny}	—
($v = 2$)	z	0.134	A^{3}_{nz}	—	A^{3}_{nz}	—
S	x	$\frac{1}{4} + \frac{1}{2}\tau_4$	—	B^{4}_{nx}	—	B^{4}_{nx}
	y	0.75	A^{4}_{ny}	—	A^{4}_{ny}	—
	z	0.0954	A^{4}_{nz}	—	A^{4}_{nz}	—

$$\mathbf{Y}^{v} = \begin{bmatrix} Z^{v} \\ W^{v} \end{bmatrix}$$

is invertable. For $SnNbS_3$ the two $\mathbf{Y}^{v}$ matrices can be chosen as

$$\mathbf{Y}^{1} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad \mathbf{Y}^{2} = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}. \tag{23}$$

The symmetry operators of G^{v}_{s} are now obtained from those of G_s through a similarity transform:

$$(\mathbf{R}\varepsilon)^{v} = \mathbf{Y}^{v}(\mathbf{R}\varepsilon)\mathbf{Y}^{v,\mathrm{inv}} \tag{24}$$

and

$$\boldsymbol{\tau}^{v} = \mathbf{Y}^{v}\boldsymbol{\tau}. \tag{25}$$

Applying equations (24) and (25) to $G_s = \mathrm{P}^{\mathrm{Cm2m}}_{\bar{1}\,1\,\mathrm{s}}(\alpha 00)$ gives the subsystem superspace groups:

$$G^{1}_{s} = \mathrm{P}^{\mathrm{Cm2m}}_{\bar{1}\,1\,\mathrm{s}}(\alpha 00) \equiv G_s \qquad G^{2}_{s} = \mathrm{P}^{\mathrm{Cm2}a}_{\bar{1}\,1\,1}(\alpha^{-1} 00). \tag{26}$$

Now G^{v}_{s}, $v = 1, 2$ define an exact symmetry of the corresponding subsystem; in fact, they could have been derived without the complete system superspace group. The usefulness of the latter is that it defines the phase relation between those two subsystems.

The groups G_s^v are higher-dimensional space groups equivalent to G_s, as they are obtained through a coordinate transformation $\mathbf{Y}^v$ (equations (23), (24)). However, they do not constitute equivalent superspace groups, because at least one of the $\mathbf{Y}^v$ involves a mixing of the first 3-coordinates with the d additional coordinates. Such an operation is part of the $(3 + d)$-dimensional space groups, but is not allowed for superspace groups.

The superspace group G_s and/or the subsystem superspace groups can now be employed to derive the symmetry restrictions on the modulation function of each atom. In table 1 we list the elements of the superspace group and the subsystem space groups. Note that τ_4 defines the position of the origin in Λ_2. In table 2 the average structure coordinates as determined by Meetsma *et al* (1988) are given, together with the symmetry restrictions on the modulation functions (SnS positions are changed to values with Cmm*a* symmetry). Note that τ_4 now defines the relative position of the two lattices, as well as the relative phase of the modulation functions.

5. Discussion

With the results of the previous sections we are in a position to give a full description of the structure of $SnNbS_3$. In the first stage, we recognise that the structure is built of crystalline layers. Layers of different chemical compositions alternate along the ***c***-axis. For $SnNbS_3$ the orientation is such that there is a true translational order perpendicular to the layers, which is one layer of each kind thick. Taking into account only one type of layer, a spacegroup can be assigned to that part of the structure. This can be done for each layer type, and the corresponding space groups were designated as the subsystem space groups G_v (equation (20)).

The second feature to be recognised is the relation between the periodicities of different types of layers. For $SnNbS_3$, the periodicities match in one direction (***b***-axis), but are incommensurate in the other ($\boldsymbol{a}_v$-axis). This means that layers can be shifted with respect to each other parallel to ***a*** without altering the structure. Such a shift merely corresponds to a different choice of the origin. Along ***b***, the two types of layers do have a specific orientation. This was already determined by Meetsma *et al* (1988).

In principle the basic, non-modulated structure has now been determined. However, as the results of Meetsma *et al* (1988) show, from the x-ray diffraction there is much ambiguity as to whether the space group of the SnS subsystem is Cmm*a*, Cmm*b*, C2m*a* or Cm2*b*. Now the superspace group comes into play. As shown in this paper the superspace group uniquely defines the symmetry of a misfit structure. Both subsystem space groups can be derived from the superspace group (equations (17), (18)). Thus the superspace group provides a relation between the two subsystem space groups. The diffraction results unequivocally show the NbS_2 subsystem space group to be Cm2m, thus leading to Cm2*a* as the only possible subsystem space group for SnS (§ 3).

Through their mutual interaction, the real structure of each layer is modulated with the incommensurate period of the other. Now the superspace group is already necessary to describe the symmetry of each individual subsystem. In § 4 we have defined the subsystem superspace groups, G_s^v, and we have shown how they can be derived from the complete structure superspace group. In fact, the subsystem superspace groups are obtained from the superspace group by only a change of basis in superspace (equations (23)–(26)).

Either the subsystem superspace group or the complete system superspace group can now be used to derive symmetry restrictions on the modulation functions of the

subsystems. When using G_s^v, this leads to a set of restrictions on subsystem v parameters which are independent of the other subsystem. However, it will be clear that the displacements of the atoms in v depend on the relative position of lattice v' with respect to v. This can only be achieved by adjusting the phase of the modulation functions in both subsystems. This relation between the phases of the modulation functions and the relative positions of the subsystem lattices is given by the complete system superspace group. For '$SnNbS_3$', the modulation functions are given in table 2. Different relative positions of the lattices Λ_1 and Λ_2 correspond to different values of τ_4 (compare the position of m_x in Λ_2, table 1). From table 2 it follows that a different choice of τ_4 corresponds with an appropriate change of the phase of the modulation functions.

6. Conclusion

In this paper we have applied the theory of superspace groups to the misfit layer structure '$SnNbS_3$'. It is shown that the symmetry of the structure of each subsystem of this compound is completely described by a subsystem space group G_v (basic structure) and a subsystem superspace group G_s^v (real structure).

A superspace group could be assigned to the complete structure. It defines a relation between both G_v and both G_s^v, and thus provides a means to assert the phase relation between the two subsystem lattices.

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