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Abstract. The structure of the inorganic misfit layer compound $(LaS)_{1.14}NbS_2$ is reanalysed in the superspace-group formalism, using the recent single-crystal x-ray diffraction data obtained by Meerschaut, Rabu and Rouxel. Structure refinements make it possible to determine the values of the modulation functions of the various atoms. The largest modulation amplitudes are found on the La atoms and on the sulphur atoms of the NbS_2 subsystem. They mainly describe displacements in the plane of the layers. A detailed analysis is given of the coordination of various atoms by plotting interatomic distances as a function of the incommensurate phase parameter.

1. Introduction

Inorganic misfit layer compounds are one example of the so-called intergrowth structures. This type of crystal is characterized by the presence of two or more, mutually incommensurate, three-dimensional (3D) lattices. The structure is described by a finite fraction of the atoms being arranged periodically according to one lattice, while the remaining fraction has the periodicity of the second lattice.

The structures of the misfit layer compounds are characterized by an alternate stacking of layers MS_2 (with $M = Nb, Ta$, etc) and layers TS (with $T = Sn, La$, etc) [1, 2]. For $(LaS)_{1.14}NbS_2$ the NbS_2 subsystem forms an F-centred orthorhombic lattice, with the c axis perpendicular to the layers, and with lattice parameters given by $a_{11} = 3.310$ Å, $a_{12} = 5.793$ Å and $a_{13} = 23.043$ Å. The LaS subsystem is C-centred orthorhombic, with $a_{23} = \frac{1}{2}a_{13}$, $a_{22} = a_{12}$ and an a axis parallel to a_{11}, but with incommensurate length ratio: $a_{21} = 5.828$ Å (figures 1 and 2) [3, 4]. In this compound the intergrowth character is thus defined by the mutually incommensurate a axes of the two subsystems.

$(LaS)_{1.14}NbS_2$ has been synthesized by Meerschaut et al [3], who also performed a single-crystal x-ray diffraction measurement. Their structure determination was done using the same, large unit cell for both subsystems, defined by $a_s = 4a_{21} \simeq 7a_{11}$. However, they used the incorrect space group $Bbcb$ (note: the alternative setting used by Meerschaut et al has space group $Ccca$). Subsequently, it was shown [4] that the proper supercell space group is acentric: $Bb2b$. Recently, Meerschaut et al [5] have reinterpreted their data, giving new refinement results in the supercell description, using space group $Bb2b$.
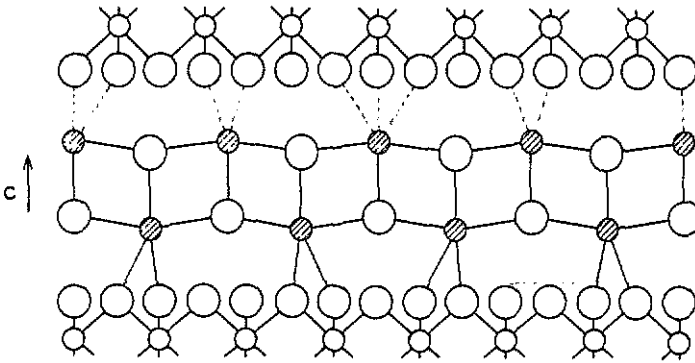
Figure 1. Projection of the structure of $LaS_{1.14}NbS_2$ along the *b* axis. Large open circles denote S atoms, small open circles denote Nb atoms, and hatched circles represent La atoms. Only half the unit cell along *b* is shown. The shortest distances between the two subsystems are indicated by broken lines.
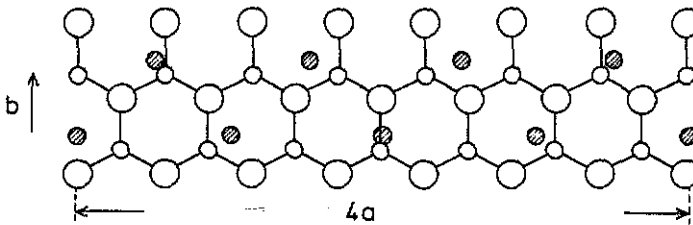
Figure 2. Projection of the structure along the *c* axis, showing the plane of contact between La atoms and S of the NbS_2 subsystem. Large open circles denote S atoms, small circles denote Nb atoms, and hatched circles represent La atoms. Only one-quarter of the unit cell along *c* is given. Sulphur atoms of the second subsystem (LaS) are omitted for clarity.

One question to be answered for $(LaS)_{1.14}NbS_2$ is whether the true *a*-axes ratio is incommensurate or equal to $4/7$. The lattice parameters determined for the individual subsystem lattices indicate that $4/7$ is too crude an approximation [4]. Therefore, the supercell approach can only lead to an approximate description of the real structure. A more important drawback of the supercell approach is that it cannot fully employ the symmetry present in the system. This is expressed by the need to specify and refine a large number of structural parameters in that approach [3, 5].

This problem is resolved by the composite structure approach, as given by Wiegers *et al* [4] for $(LaS)_{1.14}NbS_2$. Each subsystem is then described by a few independent atoms with coordinates with respect to the subsystem's own unit cell (compare figures 1 and 2). The advantage of this approach is that it makes an analysis of the building properties easier. A disadvantage is that the symmetry is still not being used completely. A problem that becomes even more important is when not only the basic structure (translationally symmetric subsystems) is analysed, but also the modulation (modulated subsystems) is taken into account. The superspace-group approach then becomes unavoidable.

The superspace-group description of the orthorhombic misfit layer compound $(SnS)_{1.17}NbS_2$ has been given previously [6]. The first result, which is of more philosophical importance, is that the superspace-group approach shows that intergrowth

compounds indeed have space-group symmetry. For the basic structure, its principal result was to define a relation between the space groups of the individual subsystems. This allowed for the determination of the proper acentric space group for the SnS subsystem [6]. Subsequently, this principle was applied to other misfit compounds, among which was (LaS)$_{1.14}$NbS$_2$ [1, 4, 7]. The symmetry restrictions for the modulation functions were also given, but values for the remaining independent parameters were not determined. Recently, refinements of the modulated structure of LaCrS$_3$ and (PbS)$_{1.12}$VS$_2$ were published by Kato and coworkers [8, 9].

In this paper we will give the complete superspace-group description for (LaS)$_{1.14}$NbS$_2$, including a determination of the modulation parameters. Refinements were performed with the computer program COMPREF [10] and using the x-ray data by Meerschaut *et al* [3]. In the second half of the paper the coordination of the various atoms is studied, both with respect to atoms in the same subsystem and with respect to the atoms of the other subsystem.

2. Superspace-group symmetry

The superspace-group analysis of intergrowth crystals has been given by Janner and Janssen [11] and was further developed by van Smaalen [12]. The starting point of this approach is the description of the diffraction pattern with a finite set of integral indices. For (LaS)$_{1.14}$NbS$_2$ it was shown previously that four reciprocal vectors are sufficient [4]. This set, $M = \{a_1^*, \ldots, a_4^*\}$, can be defined as $a_1^* = a_{11}^*, a_2^* = a_{12}^*, a_3^* = a_{13}^*$ and $a_4^* = a_{21}^*$. The $a_{\nu i}^*$ ($\nu = 1, 2; i = 1, 2, 3$) are the reciprocal lattice vectors of the subsystem unit cells as defined in the introduction, with $\nu = 1$ describing the NbS$_2$ subsystem. Now, the basis vectors of the subsystem reciprocal lattice, Λ_ν^*, can be written as an integral linear combination of the basis vectors in M [11]:

$$a_{\nu i}^* = \sum_{k=1}^{4} Z_{ik}^\nu a_k^*. \tag{1}$$

Because a_{11}^* and a_{21}^* are parallel, the matrix defining the components of the fourth reciprocal vector in M with respect to the first three is given by

$$\sigma = (\alpha, 0, 0) \tag{2}$$

with $\alpha = a_{11}/a_{21} = 0.568$.

Owing to the interaction between the subsystems, each one will be modulated, with a modulation wavevector given by the periodicities of the reciprocal lattice of the other subsystem. This means that the modulation wavevectors are given by the vectors in M that are absent in Λ_ν^*. So, the $3 \times (3 + 1)$ matrix Z can be extended to a $(3 + 1) \times (3 + 1)$ matrix W by juxtaposition with an integer matrix V [12]:

$$W^\nu = \begin{pmatrix} Z^\nu \\ V^\nu \end{pmatrix}. \tag{3}$$

Requirements for V^ν are that: (i) W^ν is non-singular and (ii) the entire diffraction pattern

can be described. V^ν defines the modulation wavevector in subsystem ν in terms of the vectors present in M:

$$q^\nu = \sum_{k=1}^{4} V_{lk}^\nu a_k^*. \tag{4}$$

It is not dificult to show that any main reflection or satellite of subsystem ν with indices $(h_\nu, k_\nu, l_\nu, m_\nu)$ with respect to Λ_ν^* and the vector q^ν has integer indices with respect to M given by

$$(H, K, L, M) = (h_\nu, k_\nu, l_\nu, m_\nu) W^\nu. \tag{5}$$

Previously, we have given the matrix

$$Z^2 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{bmatrix} \tag{6}$$

for the LaS subsystem ($\nu = 2$). This would lead to the V^2 matrix $(1, 0, 1, 0)$. To facilitate the analysis we will now use the matrices

$$W^1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad W^2 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \tag{7}$$

for the NbS$_2$ subsystem ($\nu = 1$) and the LaS subsystem ($\nu = 2$), respectively. This means that we will use $a_{23} = a_{13}$, instead of $a_{23} = \frac{1}{2} a_{13}$ as defined in the introduction, together with a new centring translation for the second subsystem.

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 [11, 13]. With e and e^* a pair of mutually reciprocal vectors, perpendicular to physical space, the superspace lattice basis Σ and its reciprocal Σ^* are defined as

$$\Sigma: \begin{cases} a_{s1} = (a_1, -\alpha e) \\ a_{s2} = (a_2, 0) \\ a_{s3} = (a_3, 0) \\ a_{s4} = (0, e) \end{cases} \tag{8a}$$

$$\Sigma^*: \begin{cases} a_{s1}^* = (a_1^*, 0) \\ a_{s2}^* = (a_2^*, 0) \\ a_{s3}^* = (a_3^*, 0) \\ a_{s4}^* = (a_4^*, e^*). \end{cases} \tag{8b}$$

From the relation between the subsystem unit cells and the supercell it follows that

the relation between the four-integer indexing and the supercell indexing (h_s, k_s, l_s) by Meerschaut *et al* [3] is given by [4]

$$h_s = 7H + 4M$$
$$k_s = K \qquad\qquad\qquad (9)$$
$$l_s = L.$$

Obviously, for given (h_s, k_s, l_s), equation (9) has infinitely many solutions. Except for a very few, these solutions have high values for both $|H|$ and $|M|$. Such indices describe higher-order satellites in each subsystem, and thus will have negligible intensity. There is always one solution that has either $|H|$ or $|M|$ less than $|H|$ and $|M|$ of all other solutions (note: H may be equal to either M or $-M$). This set of indices is used as the reflection indices in the analysis in this paper. For most reflections, the next solution is a satellite of at least two orders higher, and it is indeed a good approximation to neglect its intensity. Only for a few reflections is the next solution but one reflection order higher. For example, the (4, K, L, -1) and the (0, K, L, 6) reflections coincide. In these instances the error made by neglecting this reflection will be somewhat larger. Unfortunately, computational difficulties prevented us from correcting for this effect.

After extraction of the four-integer indexing from the supercell indexing, 860 reflections with $I > 2.5\sigma(I)$ were obtained. This set divided into 584 main reflections, 226 first-order satellites and 50 second-order satellites. Analysis of missing reflections showed that the extinction conditions $H + K + M = $ odd, $H + L = $ odd and $K + L + M = $ odd are absent for the general (H, K, L, M) reflections; and $H + K = $ odd and $M = $ odd are absent for the ($H, K, 0, M$) reflections. Only five reflections violating these conditions were found with intensity just above the $2.5\sigma(I)$ threshold. The former three conditions point towards F-centring, with centring translations

$$(\tfrac{1}{2}, 0, \tfrac{1}{2}, 0) \qquad\qquad\qquad (10a)$$
$$(\tfrac{1}{2}, \tfrac{1}{2}, 0, \tfrac{1}{2}) \qquad\qquad\qquad (10b)$$
$$(0, \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}). \qquad\qquad\qquad (10c)$$

The latter two conditions correspond to a mirror plane perpendicular to the *c* axis, with a translation of either $\tfrac{1}{2}a_4$ or $\tfrac{1}{2}a_1 + \tfrac{1}{2}a_2$. Both glide planes are present in the superspace group.

The extinctions found are compatible with the centrosymmetric superspace group $P{:}Fmmm{:}\bar{1}1s(\alpha, 0, 0)$. As described earlier, only the acentric superspace group $P{:}Fm2m{:}\bar{1}1s(\alpha, 0, 0)$ is compatible with the basic structure [4]. In this paper we will show that this superspace group also describes the modulation correctly.

3. Embedding in superspace

There are two alternative approaches to the superspace-group analysis of intergrowth compounds. The first is where the structure is described through its coordinates with respect to the superspace basis. After computations (structure factor, distances) a 3D picture can be obtained by taking the appropriate section of superspace. This approach was adopted in earlier publications [6, 12]. The disadvantage of this description is that it obscures the component character of the structure. In the second approach, adopted in this paper, each subsystem is described as a modulated structure with respect to its

own subsystem basis. The symmetry is still given by the superspace group. The problem to be solved then is to derive the effect of the superspace-group operators on the coordinates with respect to the subsystem lattices, and to obtain the phase relation between the various subsystems. In this paper we will give the resulting equations of that analysis, which are of interest for $(LaS)_{1.14}NbS_2$. The general derivation will be given elsewhere [14].

First, we give some definitions that are needed in the remainder of the paper. The embedding of physical space in superspace is defined by equations (1), (2), (3), (7) and (8). Analogously, for each subsystem, a different embedding in superspace can be defined, using the vectors of Λ_ν^* (equation (1)) together with the vector q^ν (equation (4)). It is easy to derive that the subsystem sigma matrix (the components of q^ν) is given by [12]

$$\sigma_\nu = (V_3^\nu + V_d^\nu \sigma)(Z_3^\nu + Z_d^\nu \sigma)^{-1} \tag{11}$$

where the matrix Z^ν is written as the juxtaposition of a 3×3 matrix Z_3^ν and a $3 \times d$ matrix Z_d^ν. Analogously, $V^\nu = (V_3^\nu, V_d^\nu)$. This embedding can be considered as the standard embedding of a modulated structure in superspace. It is different for each subsystem, and will be called the subsystem superspace embedding. It can be shown that W^ν (equation (7)) is precisely the coordinate transformation in superspace between Σ (equation (8)) and the subsystem superspace embedding Σ_ν, thus defining the latter:

$$\begin{pmatrix} x_{\nu s 1} \\ \vdots \\ x_{\nu s, 3+d} \end{pmatrix} = W^\nu \begin{pmatrix} x_{s 1} \\ \vdots \\ x_{s, 3+d} \end{pmatrix}. \tag{12}$$

A point in superspace ($\mathbb{E}^s$) is given by the position vector

$$r_s = \sum_{k=1}^{4} (x_{sk} a_{sk}) \tag{13a}$$

or equivalently by

$$r_s = \sum_{k=1}^{4} (x_{\nu s k} a_{\nu s k}). \tag{13b}$$

Then physical space ($\mathbb{E}^3$) is a subspace of $\mathbb{E}^s$, given by the collection of points $((0, e^*) \cdot r_s) = 0$. Equivalent descriptions of physical space, $\mathbb{E}^3(t)$, are obtained as the collection of points given by $((0, e^*) \cdot r_s) = t$. Because Σ and Σ_ν have different basis vectors, selecting a single section $\mathbb{E}^3(t)$ will correspond to different values for t when using either equation (13a) or (13b). These values are denoted by t and t_ν, respectively.

The relation between the two subsystems is given by the relation between t and the two parameters t_ν. Furthermore, the basic structure coordinates of each subsystem may depend on t, owing to a t-dependent shift of the origin. The derivation of these relations for the general case of a $(3 + d)$-dimensional superspace and an arbitrary number of subsystems will be given elsewhere [14]. Here we give the results for $(LaS)_{1.14}NbS_2$.

The coordinates of the atoms in subsystem ν with respect to the subsystem lattice basis Λ_ν are ($i = 1, 2, 3$)

$$x_{\nu i} = n_{\nu i} + x_{\nu i}^0(j) + u_{\nu i}^j(x_{\nu s 4}^0) \tag{14}$$

where $n_{\nu i}$ runs over all integers, defining the periodicity of the subsystem; $x_{\nu i}^0(j)$ is the

basic structure position within one unit cell; the optional argument j denotes a particular atom in the unit cell; and $u^j_{\nu i}(x^0_{\nu s4})$ is the periodic modulation function for that atom. The argument of the modulation function is the fourth coordinate of the subsystem superspace embedding Σ_ν, defined by

$$x^0_{\nu s4} = \sigma_\nu \cdot \begin{pmatrix} n_{\nu 1} + x^0_{\nu 1} \\ n_{\nu 2} + x^0_{\nu 2} \\ n_{\nu 3} + x^0_{\nu 3} \end{pmatrix} + t_\nu. \tag{15}$$

The first three coordinates of the subsystem superspace description are obtained trivially as $x_{\nu si} = x_{\nu i}$. The fourth coordinate is obtained as the sum of $x^0_{\nu s4}$ and the inner product of σ_ν and $u_{\nu i}(x^0_{\nu s4})$. Note that the $(3 + 1)$-dimensional equivalent of a point atom in physical space is thus obtained as the 1D point set defined by t_ν assuming all real values, which is on average parallel to $x^0_{\nu s4}$ (equation (15)).

Now, consider the complete structure to be described in superspace with respect to Σ. Then, the basic structure coordinates of subsystem ν, with respect to Λ_ν, are given by [14]

$$\bar{x}_{\nu i} = n_{\nu i} + x^0_{\nu i}(j) - (Z^\nu_d t)_i. \tag{16}$$

The t-dependent part reflects a shift of the origin with respect to the one obtained with the standard superspace description. The atomic positions in the modulated structure are the sum of $\bar{x}_{\nu i}$ and the modulation function,

$$x_{\nu i} = \bar{x}_{\nu i} + u^j_{\nu i}(\bar{x}_{\nu s4}) \tag{17}$$

where $\bar{x}_{\nu s4}$ is the fourth superspace coordinate for the basic structure (equation (13b)) given by

$$\bar{x}_{\nu s4} = \sigma_\nu \cdot \bar{x}_\nu + V^\nu_d t. \tag{18}$$

From equations (14) to (18) the relation between t and the t_ν is obtained as [14]:

$$t_\nu = (V^\nu_d - \sigma_\nu Z^\nu_d)t. \tag{19}$$

Furthermore, it is found that the section $\mathbb{E}^3(t)$ may change the origin in subsystem ν by $Z^\nu_d t$.

The 1D point set comprising the atom in superspace is now obtained as

$$\begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} = \begin{pmatrix} \bar{x}_{s1} \\ \bar{x}_{s2} \\ \bar{x}_{s3} \\ \bar{x}_{s4} \end{pmatrix} + Y^\nu \begin{pmatrix} u_{\nu 1}(\bar{x}_{\nu s4}) \\ u_{\nu 2}(\bar{x}_{\nu s4}) \\ u_{\nu 3}(\bar{x}_{\nu s4}) \end{pmatrix} \tag{20}$$

where the superspace coordinates refer to Σ. The corresponding basic structure position is

$$\begin{pmatrix} \bar{x}_{s1} \\ \bar{x}_{s2} \\ \bar{x}_{s3} \\ \bar{x}_{s4} \end{pmatrix} = Y^\nu \begin{pmatrix} \bar{x}_{\nu 1} \\ \bar{x}_{\nu 2} \\ \bar{x}_{\nu 3} \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \\ t \end{pmatrix} \tag{21}$$

where $\bar{x}_{\nu i}$ and $\bar{x}_{\nu s4}$ are defined by equations (16) and (18). Y^ν is the pseudo-inverse of Z^ν, suitable for the embedding defined by equations (1) and (2) [6, 12]:

$$Y^\nu = \begin{pmatrix} (Z_3^\nu + Z_d^\nu \sigma)^{-1} \\ \sigma(Z_3^\nu + Z_d^\nu \sigma)^{-1} \end{pmatrix}. \tag{22}$$

4. Symmetry restrictions

The elements of the superspace group are generally given as their matrix representation with respect to the superspace lattice basis Σ. The effect of the symmetry operators is then obtained by application of these matrix representations on the coordinates, equations (20) and (21), in the usual way. The problem is that in that case the coordinate $\bar{x}_{\nu s4}$ must be written as a function of the coordinates $\bar{x}_{s1}, \ldots, \bar{x}_{s4}$.

As discussed in the previous section, we will work with the coordinates of the atoms with respect to the subsystem superspace lattice basis Σ_ν, and the subsystem lattice Λ_ν (equations (14) and (15)). To be able to evaluate the effect of the symmetry operators on these coordinates, their matrix representation is needed with respect to both subsystem superspace lattices Σ_ν. With W^ν the coordinate transformation between Σ and Σ_ν, the subsystem superspace group operators are $(R_s^\nu | \tau_s^\nu)$, with [14]

$$R_s^\nu = W^\nu R_s (W^\nu)^{-1} \tag{23a}$$

$$\tau_s^\nu = W^\nu \tau_s. \tag{23b}$$

The effect on the coordinates (equations (14) and (15)) is then obtained in the usual way [13]. Application of equation (23) leads to the subsystem superspace group $G_s^1 = P\colon Fm2m\colon \overline{1}1s(\alpha, 0, 0)$ for the first subsystem [12]. For the second subsystem a unit cell is obtained with a halved c axis and with $G_s^2 = P\colon Cm2a\colon \overline{1}11(\alpha^{-1}, 0, \frac{1}{2})$.

Assume here that σ has no symmetry-determined commensurate components, a situation that can always be accomplished by a suitable transformation of the basic structure unit cells. Then the 4×4 matrix R_s^ν is the direct sum of a 3D part R_3^ν and a 1D part R_d^ν, and the effect on the coordinates is

$$\begin{pmatrix} x_{\nu 1}' \\ x_{\nu 2}' \\ x_{\nu 3}' \end{pmatrix} = R_3^\nu \begin{pmatrix} \bar{x}_{\nu 1} \\ \bar{x}_{\nu 2} \\ \bar{x}_{\nu 3} \end{pmatrix} + \begin{pmatrix} \tau_1^\nu \\ \tau_2^\nu \\ \tau_3^\nu \end{pmatrix} + (R_3^\nu Z_d^\nu - Z_d^\nu)t + R_3^\nu \begin{pmatrix} u_{\nu 1}((R_d^\nu)^{-1}(\bar{x}_{\nu s4}' - \tau_4^\nu)) \\ u_{\nu 2}((R_d^\nu)^{-1}(\bar{x}_{\nu s4}' - \tau_4^\nu)) \\ u_{\nu 3}((R_d^\nu)^{-1}(\bar{x}_{\nu s4}' - \tau_4^\nu)) \end{pmatrix}. \tag{24}$$

The term $(R_d^\nu Z_d^\nu - Z_d^\nu)t$ reflects the effect of the origin shift $Z_d^\nu t$ on the translational part of the symmetry operator, when the latter is applied to the coordinates given in equations (16) and (17).

Symmetry restrictions on the basic structure coordinates and the modulation functions can be obtained when the symmetry operator maps the point set representing one atom onto itself:

$$\begin{pmatrix} x_{\nu 1}'(t) \\ x_{\nu 2}'(t) \\ x_{\nu 3}'(t) \end{pmatrix} = \begin{pmatrix} x_{\nu 1}(t') \\ x_{\nu 2}(t') \\ x_{\nu 3}(t') \end{pmatrix}. \tag{25}$$

Note that t and t' need not be the same. It can be derived that for the symmetry operator $(R_s | \tau_s)$ the change in t value is [13, 14]

$$t = R_d t' + \tau_4 - \sigma \begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix}. \tag{26}$$

Substitution of equation (17) into (25) and use of equation (24) gives for the basic structure coordinates,

$$\begin{pmatrix} n_{\nu 1} + x_{\nu 1}^0 \\ n_{\nu 2} + x_{\nu 2}^0 \\ n_{\nu 3} + x_{\nu 3}^0 \end{pmatrix} = R_3^\nu \begin{pmatrix} n_{\nu 1} + x_{\nu 1}^0 \\ n_{\nu 2} + x_{\nu 2}^0 \\ n_{\nu 3} + x_{\nu 3}^0 \end{pmatrix} + \begin{pmatrix} \tau_1^\nu \\ \tau_2^\nu \\ \tau_3^\nu \end{pmatrix}. \tag{27}$$

Restrictions on the modulation functions can be obtained from

$$\begin{pmatrix} u_{\nu 1}(\bar{x}_{\nu s4}) \\ u_{\nu 2}(\bar{x}_{\nu s4}) \\ u_{\nu 3}(\bar{x}_{\nu s4}) \end{pmatrix} = R_3^\nu \begin{pmatrix} u_{\nu 1}((R_d^\nu)^{-1}(\bar{x}_{\nu s4} - \tau_4^\nu)) \\ u_{\nu 2}((R_d^\nu)^{-1}(\bar{x}_{\nu s4} - \tau_4^\nu)) \\ u_{\nu 3}((R_d^\nu)^{-1}(\bar{x}_{\nu s4} - \tau_4^\nu)) \end{pmatrix}. \tag{28}$$

For NbS_2 ($\nu = 1$) previous structure refinements have shown that Nb is on a $(0, y, 0)$ and S on a $(0, y, z)$ special position of the basic structure [4]. For the LaS ($\nu = 2$) subsystem, the same paper gives special positions $(\frac{1}{4}, y, z)$ for both atoms La and S. Presently, we employ a setting with the position of the origin defined by the operator $(2^\nu\bar{1}|\tau_1, 0, \tau_3, \tau_4)$, with $\tau_1 = \tau_3 = 0$ and $\tau_4 = -\frac{1}{2}$. Then, the corresponding special positions of the basic structure coordinates can be obtained by application of equation (27) with the appropriate symmetry operators. The special position for Nb is $(0, \bar{x}_{12}, 0)$. For S ($\nu = 1$), $(0, \bar{x}_{12}, \bar{x}_{13})$ is obtained. For the second subsystem, both La and S have the same special position, defined by $(0, \bar{x}_{22}, \bar{x}_{23})$.

The modulation functions are written as a Fourier series:

$$u_{\nu i}^j(\bar{x}_{\nu s4}) = \sum_{n=1}^{\infty} A_{ni}^j \sin(2\pi n \bar{x}_{\nu s4}) + B_{ni}^j \cos(2\pi n \bar{x}_{\nu s4}) \tag{29}$$

for $j = $ Nb1, S1, La1 and S2, respectively. $\bar{x}_{\nu s4}$ is given by equation (18), which results in different expressions for the two subsystems:

$$\bar{x}_{1s4} = \alpha(n_{11} + x_{11}(j)) + t \tag{30a}$$

$$\bar{x}_{2s4} = \alpha^{-1}(n_{21} + x_{21}(j) - t). \tag{30b}$$

Non-zero $x_{\nu 1}^0$ can be obtained for atoms shifted by a centring translation. The restrictions on the Fourier components are obtained from equation (28), and are given in table 1. They apply to the atoms with basic structure coordinates as given in table 2.

5. Structure refinement

Coordinates for the basic structure were obtained by transformation of the coordinates given by Wiegers *et al* [4]. Refinements of these coordinates were performed on the set of main reflections, i.e. on $(H, K, L, 0)$ and $(0, K, L, M)$. The coordinates for the final model differ less than their standard deviation from the values obtained in [4]. Also they

Table 1. Symmetry restrictions on the modulation functions (equation (29)) of the four independent atoms. Note that the coordinates are relative to Λ_ν for each subsystem $\nu = 1$, 2. The parameters $\bar{x}_{\nu 4}$ ($\nu = 1, 2$) are defined in equation (30). For each atom it is given whether the function is odd, even or zero.

Atom	Coordinate	Odd harmonics	Even harmonics
Nb1 ($\nu = 1$)	u_{11}	zero	odd
	u_{12}	zero	even
	u_{13}	even	zero
S1 ($\nu = 1$)	u_{11}	odd	odd
	u_{12}	even	even
	u_{13}	even	even
La1 ($\nu = 2$)	u_{21}	odd	odd
	u_{22}	even	even
	u_{23}	even	even
S2 ($\nu = 2$)	u_{21}	odd	odd
	u_{22}	even	even
	u_{23}	even	even

Table 2. Basic structure coordinates of the independent atoms. For each atom, the coordinates are relative to its own subsystem unit cell and refer to the standard subsystem origin. For the second subsystem they refer to $a_{23} = 23.043$ Å. The position of the origin was fixed by choosing $\bar{x}_{22} = 0$ for La1. The t dependence of the position of the origin can be obtained from equation (16). The superspace positions then follow from equation (21). The values given correspond to the result of the refinement of the modulated structure, and differ only marginally from the values obtained for refining only the basic structure coordinates themselves. Standard deviations in the last digits are given in parentheses.

Atom	$x^0_{\nu 1}$	$x^0_{\nu 2}$	$x^0_{\nu 3}$
Nb1 ($\nu = 1$)	0	$-0.0751(6)$	0
S1 ($\nu = 1$)	0	0.2583(8)	0.0678(2)
La1 ($\nu = 2$)	0	0.0(*)	0.32633(5)
S2 ($\nu = 2$)	0	0.5086(22)	0.3003(2)

are equal within standard deviations to the basic structure coordinates as obtained from the refinement including the modulation; the latter are given in table 2. The R-factors are given in table 3.

To determine the modulation, the first harmonics for La1 (three parameters) were allowed to vary in a refinement against the main reflections and the first-order satellites. This resulted in an improvement of the R_{F^2} value for the main reflections from 0.092 to 0.082. The partial R-factor obtained for the first-order satellites was 0.23. Subsequently, first and second harmonics of the modulation functions for all four independent atoms were added, which are compatible with the symmetry restrictions as given in table 1. Refinement against the complete data set (satellites up to second order) gave a smooth convergence to the final structure model, as is summarized in table 2 (basic structure coordinates), table 4 (modulation function amplitudes) and table 5 (temperature parameters). The R-factors for the final structure model are given in table 3.

Table 3. Crystallographic R-factors for the final fits, for various reflection subsets. The NbS part, LaS part and common reflections only include main reflections. The R-factors are defined as $R_F = (\Sigma||F_{obs}| - |F_{calc}||)/(\Sigma|F_{obs}|)$ and $R_{F^2} = [\Sigma(|F_{obs}| - |F_{calc}|)^2/\Sigma|F_{obs}|^2]^{1/2}$.

Reflection subset	Basic structure		Modulated structure	
	R_F	R_{F^2}	R_F	R_{F^2}
All			0.064	0.077
Main	0.071	0.092	0.057	0.075
NbS$_2$ part	0.097	0.120	0.064	0.074
LaS part	0.051	0.054	0.046	0.049
Common main	0.075	0.102	0.074	0.102
First-order satellites			0.112	0.132
Second-order satellites			0.177	0.179

Table 4. Values of the modulation parameters for the independent atoms given in table 2. The parameters A_m and B_m are the Fourier amplitudes as defined in equation (29). For each atom, the coordinates are relative to its own subsystem unit cell. For the second subsystem they refer to $a_{23} = 23.043$ Å. Standard deviations in the last digits are given in parentheses.

Atom	A_{11}	B_{12}	B_{13}	A_{21}	B_{22}	B_{23}
Nb1 ($\nu = 1$)	0	0	−0.0006(2)	−0.0078(17)	−0.0014(7)	0
S1 ($\nu = 1$)	0.0134(85)	−0.0022(12)	0.0014(14)	0.0129(27)	−0.0073(27)	−0.0012(3)
La1 ($\nu = 2$)	0.0010(22)	0.0171(4)	−0.0005(3)	−0.0144(7)	0.0001(14)	0.0008(3)
S2 ($\nu = 2$)	−0.0059(70)	0.0081(16)	0.0009(12)	0.0030(30)	−0.0002(56)	0.0007(10)

Table 5. Values of the temperature parameters for the independent atoms given in table 2. The temperature factor as occurs in the expression for the structure factor is defined as

$$T = \exp[-(\beta_{11}H^2 + \beta_{22}K^2 + \beta_{33}L^2 + 2\beta_{23}HL)].$$

β_{12} and β_{13} are zero because of the symmetry. For each atom, the parameters refer to its own subsystem unit cell. For the second subsystem they refer to $a_{23} = 23.043$ Å. Standard deviations in the last digits are given in parentheses.

Atom	β_{11}	β_{22}	β_{33}	β_{23}
Nb1 ($\nu = 1$)	0.0305(13)	0.0009(3)	0.00035(2)	0
S1 ($\nu = 1$)	0.0302(41)	0.0023(8)	0.00040(6)	0.0001(2)
La1 ($\nu = 2$)	0.0211(4)	0.0082(3)	0.00063(2)	0.0004(1)
S2 ($\nu = 2$)	0.0173(17)	0.0073(13)	0.00060(7)	0.0011(6)

The R-factor values for the best structure model (table 3) show that a reasonably good fit is obtained. The higher values of the R-factor for the first-order and second-order satellites can be explained in part by the fact that these reflections are on average

much weaker than the main reflections. Especially, most of the second-order satellites are just above the $2.5\sigma(I)$ threshold of observability.

6. Discussion

The parameters describing the basic structure as obtained here compare well with the results given by Wiegers et al [4] and given by Meerschaut et al [5]. Compared with the basic structure refinement presented here, Wiegers et al [4] obtained lower R-factors. This can be explained by the fact that in the latter set of refinements three independent scale factors were used, for the NbS part, LaS part and the common main reflections, respectively.

An analysis of the structure can be made by considering interatomic distances as a function of the physical space section; that is, as a function of the coordinates, $t_1, \ldots, t_d$, along the additional axes. For $(LaS)_{1.14}NbS_2$ there is only one variable t.

With $d = 1$, and the W^ν matrices given in equation (7), the basic structure coordinates for $(LaS)_{1.14}NbS_2$ follow from equation (16):

$$\bar{x}_{1i} = n_{1i} + x^0_{1i}(j) \qquad i = 1, 2, 3 \tag{31a}$$

$$\bar{x}_{21} = n_{21} + x^0_{21}(j) - t \tag{31b}$$

$$\bar{x}_{2i} = n_{2i} + x^0_{2i}(j) \qquad i = 2, 3. \tag{31c}$$

The values for $x^0_{\nu i}$ are given in table 2. The arguments of the modulation functions are given in equation (30). Their harmonic decomposition is given in equation (29), with parameters from table 3. In each case these coordinates refer to the subsystem lattice basis Λ_ν. To be able to calculate atomic distances between atoms belonging to different subsystems, their coordinates need to be transformed to a single basis. Suitable transformation matrices are

$$(Z^\nu_3 + Z^\nu_d \sigma)^{-1} \tag{32}$$

for $\nu = 1, 2$, respectively. Then, the transformed coordinates are with respect to the direct lattice basis belonging to the first three vectors of the set M (equation (1)). The effect of the symmetry operators is given in equation (24). It is now easy to use equations (29) to (31) to calculate interatomic distances.

In figure 1 a projection of a part of the structure of $(LaS)_{1.14}NbS_2$ is shown. It follows that the shortest distances between the two subsystems are between La atoms and sulphur atoms of the NbS$_2$ subsystem. In figure 3, the distance between such a pair is shown. From equation (31) it follows that for one pair of atoms the distance increases indefinitely and linearly in t, when t approaches plus or minus infinity. Therefore this function is not periodic (one of the curves in figure 3). However, as given in figure 3, the distances can be considered between one La atom and all sulphur atoms translationally equivalent along the incommensurate a axis (n_{11} in equation (31) assumes all integer values). The resulting plot (figure 3) is periodic, with the periodicity of the LaS subsystem. From equation (30) as well as figure 3 it follows that the periodicity in t is given by $\alpha = 0.57$ (equation (2)). This means that figure 3 together with a plot of the LaS distances within subsystem 2 can be used to study the La coordination as a function of t.

The true La coordination is obtained when distances are considered from La to all possible sulphur atoms. From figure 2 it follows that sulphur atoms of the first subsystem in the planes at $y = \pm 0.25$ are a possible candidate. Figure 4 gives the basic structure
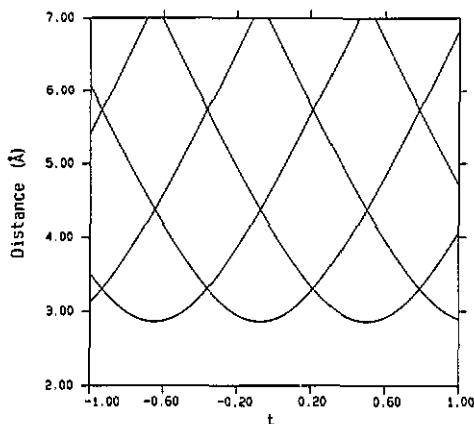
Figure 3. Basic structure distance between La1 ($\nu = 2$) and S1 ($\nu = 1$) as a function of the phase parameter t. The distance is between $(m_z\,1\,|\,0.5, 0, 0.5, 0.5)$ La1 and $(E\,1\,|\,n_{11}, 0, 0, 0)$ S1, with the coordinates taken from table 2. Each curve corresponds to a different integer value for n_{11}, i.e. to a different but translationally equivalent sulphur atom. Note that the symmetry operators refer to the standard superspace basis.
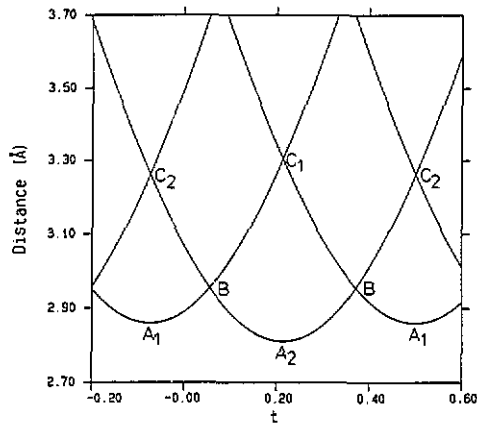
Figure 4. Coordination of La1 ($\nu = 2$) by S1 ($\nu = 1$) as a function of the phase parameter t, in the basic structure. The curves with a minimum marked A$_1$ correspond to the distance between $(m_z\,1\,|\,0.5, 0, 0.5, 0.5)$ La1 and $(E\,1\,|\,n_{11}, 0, 0, 0)$ S1, but with different n_{11}. The curve with a minimum marked A$_2$ correspond to the distance between $(m_z\,1\,|\,0.5, 0, 0.5, 0.5)$ La1 and $(E\,1\,|\,0.5, -0.5, 0, 0.5)$ S1. Values of the distances at the minima and cross-over points are $d(\mathrm{A}_1) = 2.86$ Å, $d(\mathrm{A}_2) = 2.81$ Å, $d(\mathrm{B}) = 2.96$ Å, $d(\mathrm{C}_1) = 3.30$ Å and $d(\mathrm{C}_2) = 3.26$ Å.

distances of La to sulphur of the NbS_2 subsystem†. Again, the periodicity of $\alpha = 0.57$ in t is observed. The minimum distance (2.81 Å) is smaller than the average La–S distances within the LaS subsystem, showing the strong bonding between the layers in this misfit compound, as compared to the van der Waals gap in NbS_2. The minimum distance between La and any sulphur atom of the first subsystem is obtained by following a curve from a point A to a point B, and then switching to the other curve with a minimum distance. Noteworthy is that the variation in the shortest distance is only 0.15 Å, a value that is of the same order as is found for the modulation in modulated compounds. These two effects might be an explanation for the relative stability of the misfit layer compounds. Further analysis of figure 4 shows that the coordination of La varies between $5 + 1$ and $5 + 2$, rather than $5 + 3$.

Alternatively, the coordination of sulphur of the first subsystem can be studied by allowing n_{21} to assume all integer values for La atoms in both the $y \approx 0$ and $y \approx 0.5$ layers. The distances as a function of t between S1 and all possible La atoms are given in figure 5. It follows that the resulting function is periodic with periodicity 1.0 in t. As viewed from the sulphur atoms, the variation in the interatomic distance with La is larger than the other way around: 0.37 Å instead of 0.15 Å. This is easily understood from figures 1 and 2, where it is seen that there is a sulphur atom every $a_{11} = 3.310$ Å, whereas the La atoms are interspaced by $a_{21} = 5.828$ Å. Sulphur atoms of the first subsystem are coordinated by three Nb atoms and between one and two La atoms.

† For $(PbS)_{1.12}VS_2$, a plot similar to figure 4 was given in [9]. However, the effect of the modulation is not included there.
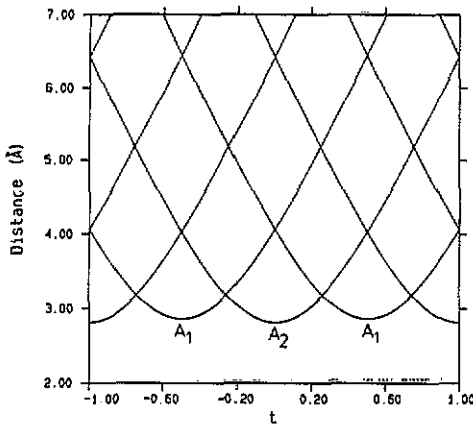
Figure 5. Coordination of S1 ($\nu = 1$) by La1 ($\nu = 2$) as a function of the phase parameter t in basic structure. The curves with a minimum marked A_1 correspond to the distance between (E 1|0, 0, 0, 0) S1 and (m_z 1|0.5, 0, 0.5, n_{21} + 0.5) La1. The curves marked A_2 define the distance between (E 1|0, 0, 0, 0) S1 and (m_z 1|0, 0.5, 0.5, n_{21}) La1.
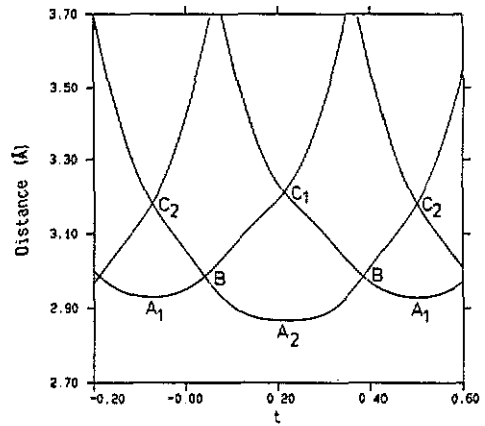
Figure 6. Coordination of La1 ($\nu = 2$) by S1 ($\nu = 1$) as given in figure 4, but now including the modulation. Distances at the minima and cross-over points are $d(A_1) = 2.93$ Å, $d(A_2) = 2.87$ Å, $d(B) = 2.99$ Å, $d(C_1) = 3.21$ Å and $d(C_2) = 3.18$ Å.

Atomic distances in the modulated structure can be obtained as a function of the phase parameter t, when the modulation functions are also taken into account (equations (29) and (30) and table 3). For the La coordination, a plot similar to figure 4 is given in figure 6. Comparison of these figures shows that the effect of the modulation is to increase the shortest distance. However, the range of the shortest distance is decreased, from 0.15 Å for the basic structure to 0.12 Å for the modulated structure. This flattening of the shortest La to S1 distance seems to be the driving force for the modulation. From figure 4 or figure 6, it is then easily understood that an important part of the modulation function must be a second harmonic on La (table 4). Only then can an increase of the distances at both A_1 and A_2 can be obtained.

Because La coordination with the sulphur atoms of the first subsystem has the periodicity of the LaS subsystem, the correlation between the distances as given in figure 6 and the distances within the second subsystem can be analysed. The distances between La and the five closest S atoms in its own subsystem are given in figure 7. First, it is observed that the variation in distance from La to S2 at positions $\pm \frac{1}{2}a$ and along c has a pseudo-period that is twice that of the variation in the distance to S2 at $\pm \frac{1}{2}b$. This is explained by the fact that the principal components of the modulation on La comprise a first harmonic along b and a second harmonic along a (table 4).

Comparison of figure 6 and figure 7 shows that, for t values around the minimum A_1 (figure 6), the La to S distances within subsystem 2 all have approximately their average value. However, around A_2 the range of distances in figure 7 is maximal. Thus, a definite correlation is not observed between the distances 1 to 4 and the occurrence of the minima in figure 6. Further analysis of figure 7 does show that, when La is linearly coordinated by S1 and one of the S2 (curve 5), both La to sulphur distances are increased by the modulation.

Figure 8 shows the distances from S1 to La, including the effect of the modulation (compare with figure 5). The correlation with the S1 to niobium distances can be obtained
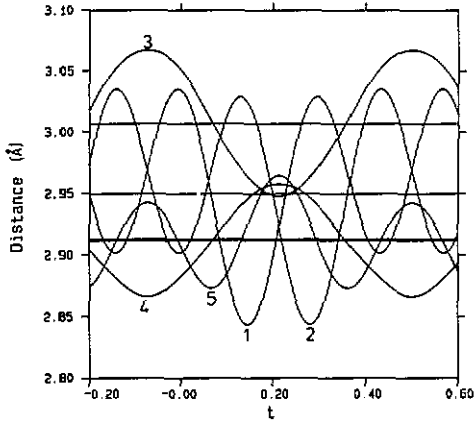
Figure 7. Coordination of La1 ($\nu = 2$) by S of the same subsystem. Shown are the basic structure distances (horizontal lines) and the distances including the modulation, as a function of t. The curves correspond to the distance between $(m_z\,1|0.5,\,0,\,0.5,\,0.5)$ La1 and the following five symmetry equivalents of S2: no. 1, $(m_z\,1|0,\,-0.5,\,0.5,\,0)$ S2; no. 2, $(m_z\,1|0,\,-0.5,\,0.5,\,1.0)$ S2; no. 3, $(m_z\,1|0.5,0,0.5,0.5)$ S2; no. 4, $(m_z\,1|0.5,-1.0,\,0.5,\,0.5)$ S2; and no. 5, $(E\,1|0.5,\,-0.5,\,0,\,0.5)$ S2.
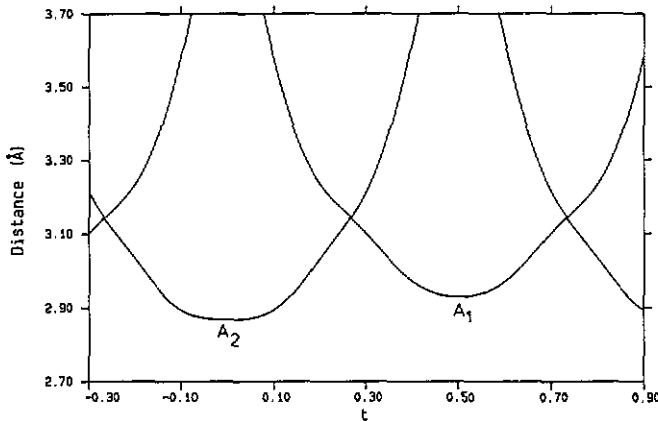

Figure 8. Coordination of S1 ($\nu = 1$) by La1 ($\nu = 2$) as given in figure 5, but now including the effect of the modulation. The curves marked A_1 and A_2 are between the same atoms as given in figure 5. Note that they are equivalent to the correspondingly marked curves in figure 6.

by comparison with figure 9. One minimum in the S1 to La distance (A_1) corresponds to minima for all three S1 to Nb distances, whereas the other minimum in figure 8 (A_2) corresponds to two larger and one smaller S1 to Nb distances. Again, it is found that the modulation, now on S1, is determined by the correlation with the La to S1 basic structure distance rather than by what happens with the other S1 distances. This is further exemplified by considering the relative position of La and Nb along b. From the information given in the figure captions, it follows that curve A_1 in figure 8 and curve 1 in figure 9 correspond to Nb and La atoms at the same side of S1 ($y \approx 0$). The other curves correspond to metal atoms at the other side of S1 ($y \approx 0.5$). It is then seen that, for La with $y = 0$ closest to S1 ($t = 0.50$), the S1 to Nb1 distances with $y \approx 0.5$ are shortest. At $t = 0$ the other La atom ($y \approx 0$) has a relative minimum for its distance to S1, whereas the distances of S1 to Nb with $y \approx \frac{1}{2}$ (curves 2 and 3 in figure 9) are larger than average.

Meerschaut *et al* [5] have refined the modulated structure in the supercell approach. Comparison of the interatomic distances as reported in [5] and the values given here in
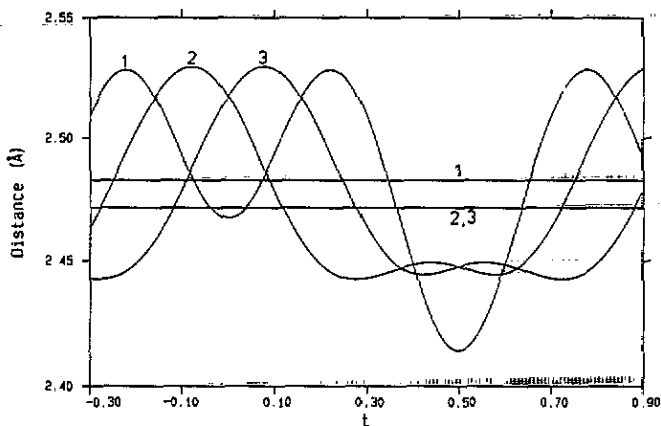
Figure 9. Coordination of S1 ($\nu = 1$) by Nb atoms of the same subsystem. Shown are the basic structure distances (horizontal lines) and the distances including the modulation, as a function of t. The curves correspond to the distance between S1 and the following Nb atoms: no. 1, Nb1; no. 2, $(E\ 1|0.5, 0.5, 0, 0.5)$ Nb1; and no. 3, $(E\ 1|-0.5, 0.5, 0, 0.5)$ Nb1.

figures 1 to 9 show rather large differences. For the shortest inter-subsystem distance between La and S1, Meerschaut *et al* [5] find a range of 0.21 Å, significantly larger than the 0.12Å found here. For the next shortest distance they find a range of 0.11 Å, smaller than found in this work. A more serious discrepancy is the completely different correlation between the interatomic distances. Here, it is found that the shortest distance (2.87 Å, figure 6) is accompanied by a maximum in the next shortest distance. In [5] both the minimum and the maximum in the shortest distance correspond to a maximum in the next shortest one. One explanation could be that the atomic parameters given by Meerschaut *et al* [5] show a large variation in temperature factors for different atoms in the supercell, which in the present approach are treated as equivalent atoms. Apparently, the model by Meerschaut *et al* [5] accounts for the supercell reflections both by a modulation of the temperature factors and by atomic displacements, rather than using a pure displacive modulation, as is found in the present approach. Furthermore it is noted that the R-factor for the model proposed in this paper is slightly lower than the one obtained by Meerschaut *et al* [5], while the present model involves fewer positional parameters as well as fewer temperature parameters.

7. Conclusions

In this paper we report on the determination of the modulated structure of $(LaS)_{1.14}NbS_2$, including harmonics for the displacement modulation function up to second order. It is found that the modulation mainly affects La and the sulphur atoms of the NbS_2 subsystem. That is, the atoms responsible for the contact between the subsystems have the largest modulation amplitudes. The largest displacements appear to be parallel to the layers, i.e. in the xy plane (table 4).

The coordination of the La1 ($\nu = 2$) and S1 ($\nu = 1$) atoms was studied by considering interatomic distances as a function of the fourth coordinate in superspace. In particular, the shortest distances from one atom to atoms of the other subsystem were calculated.

It was found that the variation of this distance is relatively small (figure 4), and of the same order as the variation in distances in ordinary modulated compounds. This gives a possible explanation for the relative stability of the inorganic misfit layer compounds. The principal effect of the modulation is found to be a decrease of the range of the shortest inter-subsystem distance. It was shown that the distance functions have the periodicity of the subsystem to which the central atom belongs. A study of the correlation between the coordination of one atom by atoms of the other subsystem and by atoms of its own subsystem was made. Comparison of the results of the distance calculation for the basic structure and the modulated structure allowed for an analysis of the effect of the modulation.

Acknowledgments

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