

Table 5. Comparison of the Lorentz factors L_ψ defined in (23a) and (23b) for the Umweganregung events of the 'almost forbidden' 222 reflection of diamond, marked in Figs. 9 and 10, calculated for Cu $K\alpha_1$ with $\Delta\lambda/\lambda(\alpha_1) = 0.000301$

Cell constant: $a = 3.5667 \text{ \AA}$, $\theta_{\text{prim}} = 48.43^\circ$.

$L_\psi(P)$: $\delta_p = \delta_s = 0.01^\circ$, $r = 100 \text{ \mu m}$, $\eta = 0.001^\circ$, corresponding to Fig. 10(b).

$L_\psi(R)$: $\delta_p = \delta_s = 1^\circ$, $r = 5 \text{ \mu m}$, $\eta = 0.18^\circ$ corresponding to Fig. 9(b).

| No. | $h_{\text{op}}/h_{\text{coop}}$ | $h_{n,\psi}$ (\AA^{-1}) | β ($^\circ$) | L_ψ (19c) | $L_\psi(P)$ (19a) | $L_\psi(R)$ (19a) |
|-----|---|---------------------------------------|-------------------------|-------------------|----------------------|----------------------|
| 1 | 313/ $\bar{1}\bar{1}\bar{1}$ | 0.458 | 4.78 | 25.65 | 25.74 | 28.61 |
| 2 | 113/ $\bar{1}\bar{1}\bar{1}$ | 0.458 | 78.50 | 2.18 | 2.18 | 2.18 |
| 3 | $\bar{1}\bar{1}\bar{3}$ / $\bar{1}\bar{3}\bar{1}$ | 0.793 | 54.88 | 1.51 | 1.51 | 1.51 |
| 4 | $\bar{3}\bar{1}\bar{3}$ / $\bar{1}\bar{3}\bar{1}$ | 0.916 | 26.25 | 2.42 | 2.42 | 2.42 |

depend on the four parameters $\Delta\lambda$, δ , ε and η in a distinct manner, *UMWEG90* is an efficient tool for the determination of the divergence and wavelength spread of the incident beam as well as of the mosaic spread and block size in the sample.

Furthermore, Figs. 1(b), (c), 9(a), (b) and 10(a), (b) demonstrate the ability of *UMWEG90* to predict the *Umweganregung* patterns for measurements carried out under very different experimental conditions.

Acta Cryst. (1992). **A48**, 610-618

Refinement of Incommensurate Structures against Diffraction Data from a Twinned Crystal

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(Received 19 December 1991; accepted 6 February 1992)

Abstract

Twinning can lead to a diffraction pattern with additional reflections that are incommensurate with the reflections of a crystal with only one orientation of the structure. The integer indexing of such a diffraction pattern involves more than three reciprocal-basis vectors. Analogously, for incommensurate crystals, the original number of $(3+d)$ reciprocal vectors should be extended to a larger set for a twinned incommensurate crystal. In this paper, it is shown

0108-7673/92/040610-09\$06.00

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that the diffraction symmetry for a twinned crystal can be analyzed in a way analogous to the treatment of the symmetry of an incommensurate structure. The theory is implemented in a refinement program for X-ray and neutron diffraction data and allows all intensity data from isolated and overlapping reflections to be taken into account. The method can also be applied to the refinement of ordinary crystal structures. The program has been used to determine the modulated structure of the inorganic misfit layer compound $(\text{HoS})_{1.23}\text{NbS}_2$.

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Introduction

The problem of structural analysis from diffraction data of a twinned crystal is well known. Surprisingly, the incorporation of the appropriate procedures in refinement programs is not a standard option. For example, the widely used crystallographic program packages *XTAL* (Hall & Stewart, 1990) and *SHELX* (Sheldrick, 1976) are not able to account for the effects of twinning.

Twinning is defined as the occurrence of several orientations of a structure in a single block of material. Quite often, microcrystals of each of the different orientations are dispersed throughout the complete crystal with approximately constant densities. It is then not possible to separate the different twin individuals physically and the diffraction pattern will have contributions from all domains.

There are several different ways in which twinning can affect the diffraction pattern. For example, for an orthorhombic structure with two lattice constants equal, two orientations of the orthorhombic structure can occur, which are related by a fourfold axis. All reflections will have contributions from both twin domains, which in principle are different in magnitude. An already more complicated situation is illustrated by an orthorhombic structure with $a = 2b$. If such a crystal occurs as a twin, with both domains related by a fourfold c axis, reflections with h even will have contributions from both domains, while reflections with h odd are due to the first domain only. A further complicating factor is that there are also reflections entirely due to the second domain, which cannot be indexed on the unit cell of the first domain, *i.e.* they would have half-integer k indices.

Generally, a diffraction pattern will have joined spots where reflections of different twin domains overlap and it will have isolated diffraction spots where only single domains contribute. To be able to take into account all diffraction spots simultaneously, a refinement program should generate a sum of intensities for the former positions, while it should calculate the structure factor of a single domain for the latter.

The most difficult problem in the analysis of twin data is the possibility of partially overlapping reflections. This can, for example, occur in monoclinic compounds. For a structure characterized by $\gamma^* \neq 90^\circ$ and with a common $\mathbf{b}^*\mathbf{c}^*$ reciprocal-lattice plane between the two twin domains, the second domain can be defined by $\gamma^*(\text{II}) = (180 - \gamma^*)$. Depending on the exact magnitudes of the lattice parameters, there will be diffraction positions where reflections of both twins can be closer to each other than the experimental resolution. In this case, it should be ensured during data collection that separate intensities are measured for each diffraction position, or that all intensity is measured in a single scan. For the

refinement program, one should then be able to indicate which domains contribute to each individual diffraction position. In practice, the solution to this problem will often be to exclude the lines or layers in reciprocal space for which there is partial overlap of reflections.

Inorganic misfit layer compounds are a simple example of the more general class of incommensurate intergrowth crystals (Makovicky & Hyde, 1981; Wieggers *et al.*, 1989; Janner & Janssen, 1980; van Smaalen, 1991*a, b*). Their structures can be characterized as an alternate stacking of two chemically different layers (Fig. 1). One fraction of the atoms (*e.g.* the NbS_2 layers) have an ordered structure according to one unit cell, while the remaining fraction (*e.g.* the HoS layers) are ordered according to a second unit cell. Both lattices are incommensurate with respect to each other. This means that an integer indexing of the diffraction pattern of a single-domain crystal will require four or more basis vectors.

In this paper we will show that the indexing problem related to twinning can be solved by using four or more basis vectors, in a way much resembling the higher-dimensional analysis of incommensurate crystals. For a twinned incommensurate crystal, both the incommensurateness inherent to the structure and the incommensurateness due to the twinning may give rise to additional basis vectors for indexing the

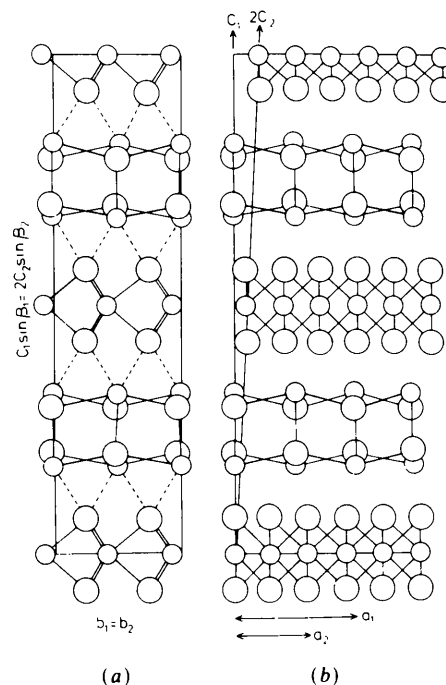


Fig. 1. The structure of the inorganic misfit layer compound $(\text{HoS})_{1.23}\text{NbS}_2$. (a) Projection along the incommensurate a axis; (b) projection along the common b axes. Large circles denote sulfur atoms, small circles correspond to the metal atoms in their respective subsystems.

diffraction spots. The multiple-indexing approach is shown to provide an efficient algorithm for deciding which of the domains contributes to the intensity at each diffraction position. In this way, the present approach is more general than several others [*REMOS85* by Yamamoto (1985) and *PROM-ETHEUS* by Zucker, Perenthaler, Kuhs, Bachmann & Schulz (1983)], where it is assumed that all diffraction positions have contributions from all domains (twinning by merohedry). With this method, the inorganic misfit layer structure of $(\text{HoS})_{1.23}\text{NbS}_2$ is solved.

Theory

The crystallography of incommensurate crystals is now well established (Janner, Janssen & de Wolff, 1983; Cummins, 1990; van Smaalen, 1991*a*, 1992; Steurer, 1990). All different kinds of incommensurate phases, modulated crystals, intergrowth compounds and quasicrystals have in common that an integer indexing of their diffraction patterns requires $(3+d)$ reciprocal-basis vectors, with d a positive integer. A common property with ordinary three-dimensional translationally symmetric crystals is that the intensity in each diffraction spot is proportional to the absolute square of the Fourier transform of the electron density, *i.e.* to the absolute value of the square of the structure factor.

A basic assumption of the present approach is that all individual twin domains have an identical structure, each of which gives rise to diffraction spots at positions expressed as integral combinations of $(3+d)$ reciprocal vectors. The relation between these domains can be described by a set of orthogonal twinning operators that forms a group G_T of order n .

Let $M_1 = \{\mathbf{a}_1^*, \dots, \mathbf{a}_{3+d}^*\}$ be the set of $(3+d)$ reciprocal-basis vectors describing the first twin part. The twinning operators $T_k \in G_T$ will transform this set into

$$M_k = \{T_k \mathbf{a}_1^*, \dots, T_k \mathbf{a}_{3+d}^*\} \quad (1)$$

for $k=1, \dots, n$, where T_1 is chosen as the unit operator. This generates a total of $n(3+d)$ vectors, for which a new basis $M_i = \{\mathbf{b}_1^*, \dots, \mathbf{b}_m^*\}$ of m rationally independent reciprocal vectors can be selected such that any diffraction spot has an integer indexing with respect to M_i . As few vectors \mathbf{b}_j^* as possible are chosen, which leads to $(3+d) \leq m \leq n(3+d)$. The lower limit represents a similar situation to the twinning by merohedry or by pseudomerohedry with obliquity equal to zero of regular crystals (Catti & Ferraris, 1976). The higher limit represents twinning without overlapping of the diffractions spots of individual twin parts.

Without loss of generality, the first $(3+d)$ vectors of M_i can be chosen as the vectors comprising M_1 . The remaining $m - (3+d)$ vectors play a similar role

to the modulation vectors for modulated and intergrowth structures. The main difference is that there are no satellites in addition to the sets of main reflections, as the assumption was made that the diffraction pattern can be created as a pure summation of the diffraction patterns of the n individual domains. This method is similar to the one for composite crystals, but without the interaction between the different twin parts.

From the selection of the basis M_i , it is clear that the vectors $T_k \mathbf{b}_i^*$ ($i=1, \dots, m$) can again be expressed as an integral combination of the basis M_i :

$$T_k \mathbf{b}_i^* = \sum_{j=1}^m \mathbf{b}_j^* T_{ji}(k). \quad (2)$$

This provides an m -dimensional matrix representation for the operators T_k of the twinning group.

Let v_k ($k=1, \dots, n$) be the volume fraction of the k th individual twin domain, constrained by the normalization condition

$$\sum_{k=1}^n v_k = 1. \quad (3)$$

Then, the corrected intensity for the diffraction position, defined by the m integer indices $\mathbf{H} = (H_1, \dots, H_m)$, can be expressed in terms of structure factors of individual twin parts,

$$I_r(\mathbf{H}) = \sum_{k=1}^n v_k F^2(T_k \mathbf{H}) \prod_{j=4+d}^m \delta[(T_k \mathbf{H})_j, 0], \quad (4)$$

where $F(\mathbf{H})$ is equal to the structure factor $F(H_1, \dots, H_{3+d})$ of a single domain, taken as a function of the first $3+d$ elements of its argument. The function δ represents the Kronecker delta; it is one if the arguments are equal and is otherwise zero. In this way, overlap of reflections of the individual domains is easily detected.

A procedure based on (5) has been incorporated in the program *COMPREF* (Petříček, Maly, Coppens *et al.*, 1991) of the program system *JANA* (Petříček, Maly & Cisarova, 1991). It has been used to determine the structure of the inorganic misfit layer compound $(\text{HoS})_{1.23}\text{NbS}_2$, as reported in the remainder of this paper.

Experimental

The synthesis of the compound and the details of the X-ray diffraction have been described by Wieggers, Meetsma, Haange & de Boer (1992). The present analysis started from the basic structure they determined and the original measured intensities.

All reflections could be indexed on three monoclinic unit cells, chosen with unique \mathbf{b} axes. Two of them, corresponding to $\text{NbS}_2(\text{I})$ and $\text{NbS}_2(\text{II})$, were connected by a twofold axis along the a direction. The fact that the ratio of integrated intensities of two

corresponding diffraction spots was, within the accuracy of measurement, constant led to the conclusion that the studied compound was a twin. The twinning operator can be taken as the twofold axis along **a**. The HoS subsystem has a pseudo-orthorhombic lattice, which means that the lattices of the expected twin individuals coincide.

Lattice parameters and their standard deviations for these three lattices were determined from the setting angles of 23 reflections in four alternate settings (Wiegers, Meetsma, Haange & de Boer, 1992). For the NbS₂(I) subsystem, we have $a_{11}^I = 3.312$ (1), $a_{12}^I = 5.661$ (1), $a_{13}^I = 22.250$ (14) Å and $\beta_1^I = 93.01$ (3)°. The lattice parameters for the HoS subsystem are: $a_{21} = 5.396$ (1), $a_{22} = 5.661$ (1), $a_{23} = 22.195$ (8) Å and $\beta_2 = 90.19$ (3)°. The lattice parameters determined for the second twin individual of NbS₂ are equal to the first within standard deviations: $a_{11}^{II} = 3.313$ (1), $a_{12}^{II} = 5.662$ (1), $a_{13}^{II} = 22.246$ (16) Å, $\beta_1^{II} = 93.01$ (3)°. The lattice parameters of I have been used in the present analysis.

To facilitate the superspace description as well as the comparison with other misfit compounds, the *c* axis of the NbS₂ lattice has been doubled. In addition to the *C* centering, this introduces the centering translation $(0, 0, \frac{1}{2})$. The HoS lattice is *F* centered.

The twinning matrix defining the relation between unit-cell vectors of two NbS₂ lattices was calculated from the experimentally determined orientation matrices according to

$$T = (O^{II})^{-1} O^I, \quad (5)$$

where O^I and O^{II} are the orientation matrices for NbS₂(I) and NbS₂(II) domains, respectively. The twinning matrix is

$$T = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.716 & 0 & -1 \end{pmatrix}. \quad (6)$$

From (6) it follows that reflections $3n, k, l$ of the NbS₂(I) domain are very close to reflections $3n, -k, l - n$ of the NbS₂(II) domain. The overlap is not exact (except for $n = 0$). The corresponding splitting of several $3, k, l$ spots was observed on the diffractometer. As it is very difficult to correct for such partial overlapping, we did not use the $h = 3$ ($n = 1$) reflections in our analysis (the maximum value of h in the experiment was 5). From the lattice parameters, one can calculate that the 31 component of the matrix describing a twofold axis along **a** is equal to -0.706 , to be compared with the experimental value of -0.716 . It thus follows that the 2_x axis can be taken as the twinning operator.

For the HoS subsystem, no splitting of diffraction spots could be observed. This can be attributed to the monoclinic angle β being close to 90°. The expected 31 component of the twinning matrix for the 2_x

axis in this subsystem is -0.03 , apparently too small to be observed. It is therefore assumed that the measured intensities of the pseudo-overlapping reflections are always the sum of intensities of the individual domains.

The twinning operator is of order two and only two domains were found. The structure factors for the overlapping spots are thus a sum of two independent contributions,

$$F^2(hkl) = (1 - v)F^2(hkl) + vF^2(h\bar{k}\bar{l}), \quad (7)$$

where v is the volume fraction of the second domain.

Space-group symmetry

Each twin domain in the crystal of (HoS)_{1.23}NbS₂ is composed of the two subsystems NbS₂ ($\nu = 1$) and HoS ($\nu = 2$). All reflections will have contributions from both subsystems, for which structure factors rather than intensities should be combined (van Smaalen, 1991c, 1992). The analysis of the structure and diffraction of misfit layer compounds makes use of the so-called superspace description (Janner & Janssen, 1980; de Wolff, Janssen & Janner, 1981; van Smaalen, 1991a, b, 1992). It has been described previously for (SnS)_{1.17}NbS₂ (van Smaalen, 1989), (LaS)_{1.14}NbS₂ (van Smaalen, 1991c), (PbS)_{1.18}TiS₂ (van Smaalen, Meetsma, Wiegers & de Boer, 1991), (LaS)_{1.20}CrS₂ (Kato, 1990) and (PbS)_{1.12}VS₂ (Onoda, Kato, Gotoh & Oosawa, 1990).

For a single domain, the reciprocal lattices describing the basic structures of the subsystems can be expressed as $\Lambda_\nu = \{\mathbf{a}_{\nu 1}^*, \mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*\}$. As for all misfit layer compounds, the $(\mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*)$ plane is common to the primitive reciprocal lattices of the two subsystems NbS₂ and HoS. An integer indexing of the complete diffraction pattern of a single domain can then be obtained with four reciprocal vectors. This set $M = \{\mathbf{a}_1^*, \dots, \mathbf{a}_4^*\}$ was chosen as $\mathbf{a}_1^* = \mathbf{a}_{11}^*$, $\mathbf{a}_2^* = \mathbf{a}_{12}^*$, $\mathbf{a}_3^* = \mathbf{a}_{13}^*$, $\mathbf{a}_4^* = \mathbf{a}_{21}^*$. The superspace is obtained by considering the elements of M as the projections of the reciprocal-basis vectors in four-dimensional space.

The basis vectors of the subsystem reciprocal lattice, Λ_ν^* , are a linear combination of the set M ,

$$\mathbf{a}_{\nu i}^* = \sum_{k=1}^4 Z_{ik}^\nu \mathbf{a}_k^*. \quad (8)$$

The fourth vector in M can be expressed as a linear combination of the first three vectors, thus defining the σ matrix,

$$\sigma = (\alpha_0 \ 0 \ \gamma) = (0.614 \ 0 \ -0.203). \quad (9)$$

The interaction between the two subsystems makes each subsystem a modulated structure, with a modulation wave vector determined by the basic structure periodicities of the other subsystem. The modulation vectors can also be expressed as a linear combination

of vectors of the set M ,

$$\mathbf{q}^\nu = \sum_{k=1}^4 V_{1k}^\nu \mathbf{a}_k^* \quad (10)$$

The $3 \times (3+1)$ matrix Z^ν and the $1 \times (3+1)$ matrix V^ν can be combined into a square nonsingular $(3+1) \times (3+1)$ matrix W^ν as (van Smaalen, 1989, 1991*b*, 1992)

$$W^\nu = \begin{pmatrix} Z^\nu \\ V^\nu \end{pmatrix}. \quad (11)$$

This matrix gives Λ_ν and \mathbf{q}^ν in terms of M . For the present definition of M , the matrices

$$W^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad W^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad (12)$$

are obtained.

W^ν can also be considered as a coordinate transformation in superspace. In particular, it gives the relation between the subsystem indexing of the reflections and the indexing with respect to M ,

$$(HKL M) = (h_\nu k_\nu l_\nu m_\nu) W^\nu, \quad (13)$$

where $m_\nu \neq 0$ characterizes satellite reflections of subsystem ν . The main reflections of the first subsystem give rise to $HKL0$ reflections and of the second one to $0KLM$. As no satellite reflections were measured, reflections $HKLM$ with both H and M not equal to zero were not available for the present analysis.

After the transformation to the superspace indexing (13), the symmetry and extinction condition of the diffraction pattern can be analyzed in the usual way. As for the individual subsystems, the diffraction pattern of the complete domain has monoclinic symmetry, generated by $(2, \bar{1})$ and $(m_y, 1)$. Systematic extinctions for the $HKLM$ reflections were found to be $H+K+M=2n+1$, $L+M=2n+1$ and $H+K+L=2n+1$ (n is an integer). This corresponds to a superspace centering given by the centering vectors

$$\begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}; \quad (14)$$

The Bravais class is thus $P: F2/m(\alpha_0 0 \gamma) \bar{1}1$, where F is not the usual F centering but denotes the translations in (14). Using the transformation $\sigma' = (1 0 1) - \sigma$ and multiplying \mathbf{a}_3^* by two shows that the Bravais class is equivalent to $P: C2/m(1 - \alpha_0 0 \frac{1}{2} - \gamma/2) \bar{1}1$, no. 4 in Table 1 of de Wolff, Janssen & Janner (1981). It is also part of the more general Bravais class $B+1_{ab}$, as derived by Mermin & Lifshitz (1992). Reflection indices for the standard setting can be obtained as $H+M, K, (L+M)/2, -M$ (Petříček, 1989).

Table 1. Symmetry operators of the superspace groups and subsystem superspace groups

Note: n_i , $i=1, \dots, 4$ assume all integer values. All elements may be combined with the centering translations and/or any lattice translation. The position of the origin relative to the symmetry elements is given by the values of τ_i , $i=1, 3, 4$. In this paper we use $\tau_i=0$.

| $G_s = G_s^1$ | G_s^2 |
|--|--|
| $(E 1 n_1, n_2, n_3, n_4)$ | $(E 1 n_4, n_2, n_3, n_1)$ |
| $(E 1 \frac{1}{2}, 0, \frac{1}{2})$ | $(E 1 \frac{1}{2}, 0, \frac{1}{2})$ |
| $(E 1 0, 0, \frac{1}{2}, \frac{1}{2})$ | $(E 1 \frac{1}{2}, 0, \frac{1}{2}, 0)$ |
| $(E 1 \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$ | $(E 1 \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$ |
| $(2, \bar{1} \tau_1, 0, \tau_3, \tau_4)$ | $(2, \bar{1} \tau_4, 0, \tau_3, \tau_1)$ |

To test for possible translation parts of the operators, extinctions rules for the $0K00$ and the $H0LM$ reflections have been checked. None were found. However, the extinction conditions describing the centering reduce to $H+M=2n+1$, $H+L=2n+1$ and $L+M=2n+1$ for the $H0LM$ reflections (n is an integer). As no reflections have been measured with both H and M nonzero, the first condition leads to $H=2n+1$ and $M=2n+1$ for all reflections included in the experiment (n is an integer). Only measurement of satellite reflections would make it possible to distinguish between $H+M=2n+1$ and the case $H=2n+1$ and $M=2n+1$. The former corresponds to the mirror plane $(m_y, 1 | 0, 0, 0, 0)$. The latter corresponds to a glide plane $(m_y, 1 | 0.5, 0, 0, 0)$. This leads to five possible superspace groups: $P: F2_y/m_y(\alpha_0 0 \gamma) \bar{1}1$, $P: F2_y/m_y(\alpha_0 0 \gamma) \bar{1}s$, $P: Fm_y(\alpha_0 0 \gamma) 1$, $P: Fm_y(\alpha_0 0 \gamma) s$, and $P: F2_y(\alpha_0 0 \gamma) \bar{1}$.

Analysis of the satellite intensities would make it possible to distinguish between the two centrosymmetric superspace groups or between the two Fm acentric groups. Based on an analysis of related structures and in particular on the knowledge of the structure of the individual layers, it can be inferred that the correct superspace group is non-centrosymmetric, $G_s = P: F2_y(\alpha_0 0 \gamma) \bar{1}$.

With the W^ν matrices, the subsystem superspace groups and the subsystem space groups corresponding to G_s can be derived (van Smaalen, 1989, 1991*a*). The subsystem superspace groups are $G_s^1 = G_s$ and $G_s^2 = P: F'2_y(\alpha_0^{-1} 0 - \gamma/\alpha_0) \bar{1}$, where the F' -centering translation is obtained from (14) by interchanging the first and the last components. The subsystem space groups are the restriction of the corresponding superspace groups to the first three coordinates: $G_1 = C2$ and $G_2 = F2$. The elements of G_s for both G_s^ν 's are given in Table 1.

Symmetry of the diffraction pattern

As shown in the experimental section, the crystal is twinned by a twofold axis along the collinear a axes. For the pseudo-orthorhombic HoS subsystem, the

twofold twinning operator belongs to the lattice symmetry and complete overlapping of the (reciprocal) lattices of both twin domains is assumed. Then no additional vectors are required for an integer indexing of the diffraction pattern. For the NbS₂ subsystem the monoclinic angle is considerably different from 90°. Within experimental error, it was found that the twin domains share the (\mathbf{a}_{12}^* , \mathbf{a}_{13}^*) reciprocal-lattice plane. To describe the diffraction pattern of the twinned NbS₂ subsystem, one reciprocal vector is needed in addition to $\Lambda_1(\text{I})$, for example $\mathbf{a}_{11}^*(\text{II})$.

The diffraction pattern of a single domain of (HoS)_{1,23}NbS₂ can be described by the set M of four reciprocal vectors. For the twinned crystal, one additional vector is needed, leading to a set of five vectors, $M_t = \{\mathbf{b}_1^*, \dots, \mathbf{b}_5^*\}$, defined by $\mathbf{b}_1^* = \mathbf{a}_{11}^*(\text{I})$, $\mathbf{b}_2^* = \mathbf{a}_{12}^*$, $\mathbf{b}_3^* = \mathbf{a}_{13}^*$, $\mathbf{b}_4^* = \mathbf{a}_{21}^*$ and $\mathbf{b}_5^* = \mathbf{a}_{11}^*(\text{II})$. The first four vectors are identical to M as defined for domain I. With respect to M_t , the matrix representation of the twinning operator 2_x is

$$T(2_x) = \begin{pmatrix} 0 & 0 & 0 & 0 & 1 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 0 \end{pmatrix}. \quad (15)$$

Equations (2) and (4) assume that the indexing for a single domain is known. When only the indexings of the subsystem reflections in one domain are known, the indexing with respect to M_t can be derived directly by application of matrices W_t^v , defined analogously to the W^v matrices of intergrowth compounds. The matrices W_t^v give the reciprocal lattices Λ_v and modulation wave vectors \mathbf{q}_j^v in terms of the set M_t . As M_t was chosen to equal M plus one additional vector, W_t^v can be obtained by juxtaposition of W^v and the $(3+d) \times (m-3-d)$ matrix with only zeros. As the modulation of one domain by periodicities of the other domain does not exist, it is not useful to define additional modulation vectors here. W_t^v therefore remains a matrix of rank $(3+d)$.

With this definition of W_t^v , the relation between the subsystem reflection indices and the superspace indexing is obtained as

$$(HKL M_1 M_2) = (h^k k^k l^k m^k) W_t^v T_k^t, \quad (16)$$

where $k = \text{I, II}$ denotes the twin domains and t defines transpose. The twin operator T_1 is the unit matrix; the operator T_{11} is given by (15). For subsystems defined by (12) and twin domains defined by (15), explicit forms for (16) are:

$$\begin{aligned} (HKL M_1 M_2) &= (h_1 k_1 l_1 m_1 0)_i; \\ (HKL M_1 M_2) &= (m_2 k_2 l_2 h_2 0)_i; \\ (HKL M_1 M_2) &= (0 -k_1 -l_1 m_1 h_1)_{ii}; \\ (HKL M_1 M_2) &= (0 -k_2 -l_2 h_2 m_2)_{ii}. \end{aligned} \quad (17)$$

Table 2. Crystallographic R factors for the final fits

Partial R factors are defined using a subset of the reflections. The NbS₂ and HoS parts comprise the main reflections of the corresponding subsystem, excluding the common reflection 0KL0. The NbS₂ subset of reflections includes 189 reflections measured on the second twin individual. The R factors are defined as $R_F = (\sum |F_{\text{obs}}| - |F_{\text{calc}}|) / (\sum |F_{\text{obs}}|)$ and $R_F^2 = [\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum w |F_{\text{obs}}|^2]^{1/2}$.

| Reflection subset | Number of reflections | Basic structure | | Modulated structure | |
|-----------------------|-----------------------|-----------------|---------|---------------------|---------|
| | | R_F | R_F^2 | R_F | R_F^2 |
| All | 1250 | 0.084 | 0.117 | 0.061 | 0.076 |
| NbS ₂ part | 508 | 0.120 | 0.160 | 0.063 | 0.073 |
| HoS part | 668 | 0.062 | 0.082 | 0.056 | 0.075 |
| Common | 74 | 0.094 | 0.104 | 0.082 | 0.092 |

Reflections from domain I are characterized by $M_2 = 0$, while those from domain II have $H = 0$.

The structure factor becomes [cf. (4)]

$$\begin{aligned} F_{\text{tw}}^2(HKL M_1 M_2) &= (1-v)F^2(HKL M_1)\delta(M_2, 0) \\ &+ vF^2(M_2 \bar{K} \bar{L} M_1)\delta(H, 0). \end{aligned} \quad (18)$$

It follows that all $H = M_2 = 0$ reflections are common to the twin domains. These precisely form the main reflections of the HoS subsystems in either domain, which are thus completely overlapping. For the NbS₂ subsystem only the plane $(0k_1l_1)$ is common between the twin domains. This happens also to be the common reciprocal-lattice plane between subsystems in a single domain.

It is noted that the twinning operator T_{11} only represents a symmetry of the diffraction pattern if $v = 0.5$. As we have found $v \neq 0.5$, T_{11} merely gives the symmetry of the reciprocal-point set.

Structure refinement

First, a refinement of the basic structure was performed. With the twin volume ratio v included in the refinement, a reasonable agreement between observed and calculated structure factors was obtained (Table 2), essentially confirming the results of Wiegers, Meetsma, Haange & de Boer (1991). The high R factor for the NbS₂ subsystem reflections can be explained by the modulation on the HoS subsystem. The $0k_2l_21_1$ first-order satellites of the latter are at the same time main reflections $1k_1l_10_1$ of the first subsystem (van Smaalen, 1991c, 1992).

In the basic structure only Nb is in a special position, on the twofold axis. For the complete structure, the superspace-group symmetry then leads to restrictions on the modulation functions. For Nb on $(0, y, 0)$ it is found that both u_x and u_z should be an odd function of \bar{x}_{2s4} , while u_y is an even function of the same argument.

Table 3. Basic structure coordinates and temperature parameters (\AA^2) as obtained by refinement of the modulated structure

Coordinates refer to the subsystem lattice basis. Standard deviations in the last digits are given in parentheses. The temperature factor that appears in the expression for the structure factor is defined by $T = \exp[-\sum (2\pi^2 U_{ij} a_{vi}^* a_{vj}^* h_{vi} h_{vj})]$.

| | $x_{\nu 1}^0$ | $x_{\nu 2}^0$ | $x_{\nu 3}^0$ | | | |
|----|---------------|---------------|---------------|-------------|--------------|--------------|
| Nb | 0 | -0.0716 (5) | 0 | | | |
| S1 | 0.0256 (9) | 0.2639 (6) | 0.07109 (12) | | | |
| Ho | -0.0030 (3) | 0 | 0.17521 (3) | | | |
| S2 | 0.4993 (13) | 0.0081 (17) | 0.20114 (14) | | | |
| | U_{11} | U_{22} | U_{33} | U_{12} | U_{13} | U_{23} |
| Nb | 0.0042 (5) | -0.0018 (4) | 0.0038 (5) | 0 | 0.0000 (2) | 0 |
| S1 | -0.0086 (69) | 0.0011 (11) | 0.0046 (18) | 0.0032 (13) | -0.001 (3) | -0.0001 (10) |
| Ho | 0.0227 (4) | 0.0124 (5) | 0.0092 (4) | 0.0084 (7) | -0.0007 (5) | -0.0001 (6) |
| S2 | 0.0171 (24) | 0.0121 (16) | 0.0030 (11) | 0.0005 (33) | -0.0065 (20) | -0.0006 (27) |

Table 4. Modulation parameters obtained after the last refinement

The modulation function is defined in (19). Standard deviations in the last digits are given in parentheses.

| | A_{11} | A_{12} | A_{13} | B_{11} | B_{12} | B_{13} |
|----|--------------|--------------|--------------|-------------|--------------|-------------|
| Nb | -0.001 (5) | 0 | -0.0001 (5) | 0 | -0.0061 (8) | 0 |
| S1 | 0.002 (21) | -0.0025 (25) | 0.0028 (8) | 0.051 (9) | -0.0057 (14) | 0.0009 (11) |
| Ho | -0.0035 (13) | -0.0088 (6) | -0.0006 (2) | 0.0003 (12) | -0.0201 (6) | -0.0013 (2) |
| S2 | 0.009 (6) | 0.0023 (30) | -0.0005 (11) | 0.005 (6) | 0.009 (3) | 0.0006 (9) |
| | A_{21} | A_{22} | A_{23} | B_{21} | B_{22} | B_{23} |
| Nb | -0.0065 (21) | 0 | 0.0001 (4) | 0 | 0.0005 (8) | 0 |
| Ho | -0.0049 (6) | -0.0027 (7) | -0.0018 (2) | 0.0062 (6) | 0.0002 (8) | -0.0014 (2) |

The modulation functions are written as

$$u_i(\bar{x}_{\nu s4}) = \sum_{n=1}^{\infty} A_{ni} \sin(2\pi n \bar{x}_{\nu s4}) + B_{ni} \cos(2\pi n \bar{x}_{\nu s4}) \quad (19)$$

for $i = x, y, z$. The symmetry restrictions for Nb imply that, for that atom, $A_{ny} = B_{nx} = B_{nz} = 0$. It appeared feasible to refine the first harmonics of the modulation functions of both independent sulfur atoms while, for the metal atoms, two harmonics could be determined. A final refinement was performed on the basic structure parameters, scale factor, twin volume ratio and the modulation parameters on the observed reflections. The results are summarized in Tables 3 and 4.

The partial R factors show an improvement of the fit on all reflection groups, as compared to the basic structure. The most dramatic improvement is for the NbS_2 subset, which can mainly be attributed to an improvement of the fit to the $1KL0$ reflections.

Description of the structure

The improvement of the partial R factor for the NbS_2 subsystem on introducing the modulation shows the importance of the modulation for fitting the observed diffraction intensities (Table 2). The effect of the modulation on the structure can be visualized by studying interatomic distances. It has been shown that the structural consequences of the incommensu-

rateness is best studied by calculation of the interatomic distance as a function of the coordinates along the d additional dimensions (van Smaalen, 1991c, 1992).

The positions of the atoms can be written as the sum of a basic structure position and the modulation function (van Smaalen, 1991c, 1992):

$$x_{\nu i}(\mu) = \bar{x}_{\nu i}(\mu) + u_{\nu i}^{\mu}(\bar{x}_{\nu s4}). \quad (20)$$

The modulation function is given by (19). The basic structure position for the subsystems $\nu = 1, 2$ are

$$\bar{x}_{1i} = n_{1i} + x_{1i}^0, \quad i = 1, 2, 3; \quad (21a)$$

$$\bar{x}_{21} = n_{21} + x_{21}^0 - t; \quad (21b)$$

$$\bar{x}_{2i} = n_{2i} + x_{2i}^0, \quad i = 2, 3. \quad (21c)$$

The arguments of the modulation functions can be interpreted as the fourth coordinate in the superspace description of the structure; they are:

$$\bar{x}_{1s4} = \alpha_0(n_{11} + x_{11}^0) + \gamma(n_{13} + x_{13}^0) + t; \quad (22a)$$

$$\bar{x}_{2s4} = \alpha_0^{-1}(n_{21} + x_{21}^0 - t) - \alpha_0^{-1}\gamma(n_{23} + x_{23}^0). \quad (22b)$$

Each value of t specifies a different, but equivalent, description of physical space. It is easily seen that different values of t correspond to a relative shift of both subsystems along the mutual incommensurate direction [(21)]. The incommensurateness ensures that such a shift does not lead to a different structure. The required changes of the phases of the modulation functions are incorporated in (22). The interatomic

distances as a function of t in one period along that axis then summarize all possible distances to be encountered in the physical space (van Smaalen, 1991*b, c*; 1992). The distances at a single value of t from one atom to all others give the local environment of that atom somewhere in the crystal. In this way, a comprehensive plot can be made of all environments present.

Projections of the structure along $\mathbf{a}_{\nu 1}^*$ and $\mathbf{a}_{\nu 2}^*$, respectively, are given in Fig. 1. Fig. 1(*b*) clearly shows the incommensurateness between the two subsystems. From Fig. 1, it follows that the shortest interatomic distances between the subsystems occur between Ho of the second subsystem and S of the first subsystem. In Fig. 2, the distances from a single Ho atom to all sulfur atoms of the other subsystem are given. The sulfur atom closest to Ho is described by tracing the line from A_1 to B , then from B to A_2 , and so on. It is found that the distance between Ho and the nearest sulfur atoms of NbS_2 varies only from 2.72 to 2.85 Å (solid curves) depending on the Ho atom chosen. This variation is less by 0.04 Å than the variation of this distance in the corresponding basic structure.

An important feature is that the modulation produces an elongation of the shortest distance (in A_2) from 2.67 Å in the basic structure to 2.72 Å in the real modulated structure. This shows the strong correlation between the modulation and the intrinsic incommensurateness already present in the basic structure. This effect is similar to that observed in the other misfit layer compounds for which the modulated structure has been determined (van Smaalen, 1992). It signifies the importance of the modulation for a proper interpretation of the structure.

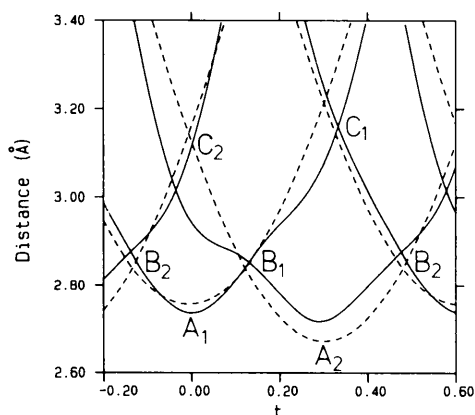


Fig. 2. Coordination of Ho ($\nu=2$) by S1 ($\nu=1$) as a function of t . The curves marked A_1 and A_2 correspond to distances between an Ho atom and S1 atoms differing by 0.5 in their y coordinate. Solid lines and dotted lines denote the modulated structure and the basic structure, respectively.

Concluding remarks

Twinning can be the origin of diffraction spots at positions which do not belong to the reciprocal lattice of the structure of a corresponding non-twinned crystal. In this paper, we have shown that such a diffraction pattern can be described by an integer indexing on four or more reciprocal vectors. This description of the diffraction pattern of a twinned crystal is equivalent to the description of the diffraction pattern of an incommensurate crystal, in particular of an incommensurate intergrowth compound. Of course, the structural effects of twinning are completely different from the special structural characteristics of an intergrowth compound, or any other incommensurate crystal.

A principal difference between the effects of twinning and intergrowth is that the latter type of compounds are composed of interacting modulated subsystems, in principle leading to diffracted intensity at all integer linear combinations of the $(3+d)$ reciprocal vectors ($d \geq 1$). A twinned crystal is composed of individual diffracting microcrystals (domains). There will be intensity only at the nodes of the reciprocal bases of the individual domains; satellite reflections are absent. A twinned incommensurate crystal can also exist. It will lead to a diffraction pattern with an integer indexing on the basis of $m \geq 3+d$ reciprocal vectors.

The domains in a twinned crystal can be characterized by orthogonal transformations that define the orientation of each domain with respect to a fixed set of axes, in particular with respect to the reciprocal basis of the first domain. We have shown that the matrix representations of the twin operators on the set M_i of reciprocal vectors used for the integer indexing [(2)] lead to a comprehensive expression for the diffracted intensity at each possible diffraction point. The use of M_i as a reciprocal basis makes it easy to determine which domains contribute to each spot [(4)]. Therefore, it is possible to include in the refinement many more measured intensities than in an ordinary approach.

The theory [(2)–(4)] has been implemented in the computer program *COMPREF* (Petříček, Maly, Coppens *et al.*, 1991) of the program system *JANA* (Petříček, Maly & Cisarova, 1991) and it has been applied to the refinement of the structure of the inorganic misfit layer compound $(\text{HoS})_{1.23}\text{NbS}_2$. An excellent agreement between observed and calculated intensities was obtained. The main part of the modulation is on Ho and on the sulfur atoms of the NbS_2 subsystem. Its principal effect is to increase the shortest distance between the subsystems, in accordance with the results obtained for other misfit layer compounds (van Smaalen, 1992).

This research was financed in part by the Netherlands Organisation for Scientific Research (NWO).

The research of SvS has been made possible by financial support from the Royal Netherlands Academy of Arts and Sciences (KNAW).

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The Incommensurate Structure of $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$: a Study by Electron Diffraction and High-Resolution Microscopy

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(Received 15 November 1991; accepted 17 February 1992)

Abstract

The modulated structure in $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ has been studied using electron diffraction and high-resolution microscopy. The structure can be considered as consisting of two interpenetrating substructures. The first sheet-like substructure is shown to be hardly modulated while the second substructure, consisting of c-oriented chains, contains most of the modulation. High-resolution electron microscopy allows either separate imaging of the two substructures or identification of the misfit between them.

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1. Introduction

The compound $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ was discovered by Subramanian, Torardi, Calabrese, Gopalakrishnan, Morrissey, Askew, Flippen, Chowdhry & Sleight (1988) as an unwanted by-product of the crystal growth of Bi-based superconducting materials, and by Mehbod, Van Lathem, Deltour, Duvigneaud, Wyder, Verwerft, Van Tendeloo & Van Landuyt (1990) as the secondary phase in iron-doped Bi-Sr-Ca-Cu-O superconducting compounds. Although the present material is semiconducting and not superconducting, it is of interest because of its peculiar structure, which was determined by X-ray diffraction soon after the discovery of this new phase (McCarron,