It is seen that a first-order description of the structure includes an $F2mm$ displacement of the TiO_6 octahedra relative to the remaining atoms rather than a movement of Ti atoms relative to their surrounding O atoms. This produces a larger dipole moment than is the case for many other Aurivillius phases and is probably induced by the lone pair of electrons on each Bi^{3+} ion. The structure shows a substantial spread in Bi—O distances that would have been equal for zero displacements from the $Fmmm$ parent structure. Distances are given in Table 10. The Ti—O distances are more equal but the Ti atoms do not lie at the centres of mass of their surrounding O octahedra. Deviations of O—Ti—O angles from 180° for opposed O atoms are included in Table 10. The large z displacement components of Ti(2) and Ti(2)' are such as to increase their distance from Ti(1).

In the parent structure each Bi atom is at $0, \frac{1}{2}, z$ and is surrounded by O atoms at about the same z height at (vii) $0,0,z$; (viii) $0,1,z$; (ix) $\frac{1}{2},\frac{1}{2},z$; (x) $-\frac{1}{2},\frac{1}{2},z$ at distances of about 2·7 Å. It is seen that the $Fmm2$ mode (Fig. 3) reduces the Bi—O^x distances at the expense of Bi—O^{ix} distances and that the $Bmab$ mode (Fig. 2) shortens one and lengthens the other of the pairs of Bi—O^{vii} and Bi—O^{viii} distances in an alternating pattern for the sequence Bi(2)', Bi(1)', Bi(1), Bi(2). The Bi(2) and Bi(2)' atoms have a 0·106 Å $Bmab$ displacement that assists the bond-length reduction of the shorter bond. The $Bbam$ rotations of the Ti(1)O_6 octahedron cause the Bi(1) and Bi(1)' environments to be quite different. This is highlighted in the first four distances tabulated for each atom. All Bi environments are highly asymmetric as is expected since each Bi^{3+} ion has a lone pair of electrons.

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Structure of the Incommensurate Composite Crystal $(PbS)_{1\cdot12}VS_2$

BY MITSUKO ONODA AND KATSUO KATO

National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan

AND YOSHITO GOTOH AND YOSHINAO OOSAWA

National Chemical Laboratory for Industry, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Abstract

The structure of the incommensurate composite crystal of the monoclinic layered sulfide $(PbS)_{1\cdot12}VS_2$, $M_r = 384\cdot20$, has been analyzed on the basis of a four-dimensional superspace group. The crystal is composed of alternately stacked two-atom-thick PbS layers with a distorted NaCl-type structure, and VS_2 sandwiches with a distorted CdI_2-type structure. For 1780 unique reflections measured by single-crystal

X-ray diffraction using Mo $K\alpha_1$ radiation ($\lambda = 0\cdot70930$ Å), R_F was $0\cdot083$ on a model without modulation with 30 structure parameters, and $0\cdot059$ on a modulated structure model with 156 parameters. The unit cell, the symmetry operations of the superspace group employed and other crystal data are $a_1 = 5\cdot7279$ (3), $a_2 = 5\cdot7886$ (7), $a_3 = 23\cdot939$ (2) Å, $\beta = 98\cdot947$ (3)°, $\sigma = (0\ 1\cdot778\ 0)$, $(0,0,0,0; \frac{1}{2},\frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2},0; \frac{1}{2},0,\frac{1}{2},\frac{1}{2}) + x_1,x_2,x_3,x_4; -x_1,x_2,-x_3,x_4$, $V = 784\cdot14$ Å^3, $Z = 4 \times 1\cdot778$, $D_x = 5\cdot788$ Mg m^{-3}, $\mu = 46\cdot45$ mm^{-1}. The superspace group can be transformed into $P^{C\bar{2}}_{\bar{1}}$ with a basis transformation.

Introduction

Recently, layered ternary chalcogenides with composite crystal structures have attracted much interest (Kato, Kawada & Takahashi, 1977; Otero-Diaz, Fitzgerald, Williams & Hyde, 1985; Guemas, Rabu, Meerschaut & Rouxel, 1988; Wiegers, Meetsma, Haange & de Boer, 1988, 1989; Williams & Hyde, 1988; Meerschaut, Rabu & Rouxel, 1989; Oosawa, Gotoh & Onoda, 1989a,b; Meetsma, Wiegers, Haange & de Boer, 1989; Kuypers, van Tendeloo, van Landuyt & Amelinckx, 1989; van Smaalen, 1989; Wiegers, Meetsma, van Smaalen, Haange, Wulff, Zeinstra, de Boer, Kuypers, van Tendeloo, van Landuyt, Amelinckx, Meerschaut, Rabu & Rouxel, 1989; Gotoh, Onoda, Goto & Oosawa, 1989; Gotoh, Onoda, Uchida, Tanaka, Iida, Hayakawa & Oosawa, 1989; Kato, 1990; Gotoh, Goto, Kawaguchi, Oosawa & Onoda, 1990). In general, the structures of these crystals can be described as an interpenetration of two layered structures, whose layers, inspite of the misfit between their two-dimensional lattices, alternate regularly throughout the whole crystal (Kato, Kawada & Takahashi, 1977; Makovicky & Hyde, 1981; Meerschaut, Rabu & Rouxel, 1989; Meetsma, Wiegers, Haange & de Boer, 1989). The two-layered structures are mutually incommensurate, and such a total structure does not have a three-dimensional lattice periodicity. Recent progress in superspace-group theory has enabled advanced descriptions of the composite crystal structures (Janner & Janssen, 1980a,b). A composite crystal has a basic structure composed of subsystems, and each subsystem has in turn a basic structure with three-dimensional space-group symmetry. Atomic displacive modulation often occurs through mutual interactions between the subsystems (Janner & Janssen, 1980b). A superspace-group characterization of symmetry properties is applicable to both the basic structure and the actual structure with modulation of the composite crystal.

In this study the symmetry properties of a layered composite crystal, $(PbS)_{1\cdot12}VS_2$, are analyzed in four-dimensional formalism with the aid of a least-squares technique using the computer program *FMLSM* (Kato, 1990) based on the superspace-group approach for composite crystals (Janner & Janssen, 1980b).

Experimental

The sample was synthesized in an evacuated silica tube from the elements at 1073 K (Gotoh, Onoda, Goto & Oosawa, 1989). The Pb/V ratio in the crystal was estimated to be 1:1 from an ICP–AES (inductively coupled plasma–atomic emission spectroscopy) analysis.

Weissenberg photographs (Gotoh, Goto, Kawaguchi, Oosawa & Onoda, 1990) revealed that the reflections can be indexed using two monoclinic unit cells with common a, c and β: for the PbS part, $a = 5\cdot728$, $b = 5\cdot789$, $c = 23\cdot939$ Å and $\beta = 98\cdot95°$ with the conditions $h + k = 2n$, $k + l = 2n$ and $l + h = 2n$ (F lattice); for the VS$_2$ part, $a = 5\cdot728$, $b' = 3\cdot256$, $c = 23\cdot939$ Å and $\beta = 98\cdot95°$ with the conditions $h + k' = 2n$ and $l = 2n$ (double C lattice with twofold c dimension). In the b direction these unit cells are mutually incommensurate. No satellites are observed in X-ray photographs, although they appear in electron diffraction patterns as shown in Fig. 1. As some satellites, for example $120\bar{1}$ in Fig. 1, did not vanish by tilting the crystal in the electron microscope, their existence was considered to be confirmed, although their intensities might have been enhanced by multiple reflection in the symmetric orientation. The intensity data were collected on an Enraf–Nonius CAD-4 diffractometer using monochromatized Mo $K\alpha_1$ radiation based on the two sets of cell dimensions given above. The lattice parameters, determined using 23 strong reflections from the PbS part with $27\cdot42 < \theta < 31\cdot44°$, were $a = 5\cdot7279$ (3), $b = 5\cdot7886$ (7), $c = 23\cdot939$ (2) Å and $\beta = 98\cdot947$ (3)°, while $b' = 3\cdot2560$ (7) Å was obtained by using 16 reflections from the VS$_2$ part. Up to $(\sin\theta)/\lambda = 0\cdot964$ Å^{-1}, 4832 reflections with $-11 \le h \le 11$, $0 \le k \le 11$, $0 \le k' \le 6$ and $-45 \le l \le 45$ were measured by the θ–2θ scan technique; no satellite reflections were measured. The number of unobserved reflections was 1707. After averaging equivalent reflections, 1780 reflections with $I > 3\sigma(I)$ (1098 for the PbS part, 499 for the VS$_2$ part and 183 for $h0l$ reflections for the common projection) remained. R_{int} $(\Sigma|F - \langle F\rangle|/\Sigma F)$ was $0\cdot022$ for the PbS and the projection parts, and $0\cdot029$ for the VS$_2$ part. Lorentz, polarization and absorption corrections were applied ($\mu = 46\cdot45$ mm^{-1}). The shape of the crystal, $0\cdot043 \times 0\cdot132 \times 0\cdot016$ mm, was approximated by seven planes, and the transmission factor varied between $0\cdot038$ and $0\cdot257$.

Symmetry

In order to index all reflections, four integers H, K, L and M are used as shown in Fig. 1. The vector $\mathbf{q}$ corresponding to each reflection is expressed by

$$\mathbf{q} = H\mathbf{a}^* + K\mathbf{b}_1^* + L\mathbf{c}^* + M\mathbf{b}_2^*$$

where $\mathbf{a}^*$ and $\mathbf{c}^*$ are the reciprocal bases corresponding to $\mathbf{a}$ and $\mathbf{c}$. $\mathbf{b}_1^*$ and $\mathbf{b}_2^*$ are reciprocal to $\mathbf{b}$ of the PbS part and the VS$_2$ part, respectively, and are incommensurate to each other ($b_1^*/b_2^* = 1/1 \cdot 778$). The reciprocal base vectors of the PbS part ($\mathbf{a}^*$, $\mathbf{b}_1^*$, $\mathbf{c}^*$) and those of the VS$_2$ part ($\mathbf{a}^*$, $\mathbf{b}_2^*$, $\mathbf{c}^*$) are related to the minimal vector set in reciprocal space $\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*\} = \{\mathbf{a}^*, \mathbf{b}_1^*, \mathbf{c}^*, \mathbf{b}_2^*\}$ through the following Z matrices (Janner & Janssen, 1980b)

$$\text{Subsystem 1 (PbS)} \quad Z^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix},$$

$$\text{Subsystem 2 (VS}_2) \quad Z^2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$

The vectors in the minimal set are considered to be the projections of the base vectors of a four-dimensional reciprocal lattice. The PbS and VS$_2$ parts are thus embedded in a four-dimensional structure and form two subsystems of the latter. The cell constants are $a_1 = 5 \cdot 728$, $a_2 = 5 \cdot 789$, $a_3 = 23 \cdot 939$ Å and $\beta = 98 \cdot 95°$, and the σ matrix defined by

$$\mathbf{a}_4^* = \sigma \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \end{pmatrix}$$

is expressed as $(0 \ 1 \cdot 778 \ 0)$ because $\mathbf{a}_4^* = 1 \cdot 778 \mathbf{a}_2^*$. The relations mentioned above give $(HKLM) = (hkl0)$ for the PbS part and $(HKLM) = (h0lk')$ for the VS$_2$ part, and the systematic conditions for observed reflections are as follows: for $HKL0$, $H + K = 2n$, $K + L = 2n$ and $L + H = 2n$; and for $H0LM$, $H + M = 2n$ and $L = 2n$. The conditions can be joined into $H + K + M = 2n$, $K + L = 2n$ and $H + L + M = 2n$. From these conditions and the symmetry of the diffraction pattern, the translation parts of the four-dimensional symmetry operations can be expressed as $(0,0,0,0; \frac{1}{2},\frac{1}{2},0,\frac{1}{2}; 0,\frac{1}{2},\frac{1}{2},0; \frac{1}{2},0,\frac{1}{2},\frac{1}{2})$ and the possible rotation parts are

$$+x_1,x_2,x_3,x_4; \ -x_1,x_2,-x_3,x_4; \ -x_1,-x_2,-x_3,-x_4;$$

$$x_1,-x_2,x_3,-x_4$$

or

$$+x_1,x_2,x_3,x_4; \ -x_1,x_2,-x_3,x_4$$

or

$$+x_1,x_2,x_3,x_4; \ x_1,-x_2,x_3,-x_4.$$

The extra extinction rules observed for the monoclinic cell suggest that the symmetry operations described above are expressed in terms of a nonstandard setting. If we choose another basis $\mathbf{a}_1'^* = \mathbf{a}_1^*$, $\mathbf{a}_2'^* = \mathbf{a}_4^*$, $\mathbf{a}_3'^* = \mathbf{a}_2^* + \mathbf{a}_3^* - \mathbf{a}_4^*$ and $\mathbf{a}_4'^* = -2\mathbf{a}_2^* + 2\mathbf{a}_4^*$, the relations between the indices are expressed as $H = H'$, $K = L' - 2M'$, $L = L'$ and $M = K' - L' + 2M'$. For the new indices the systematic reflection conditions are reduced only to $H' + K' = 2n$, which is the rule for a C-centered monoclinic lattice with the holohedral point group, $2/m$. In this basis $\mathbf{a}_4'^* = 2(1 \cdot 778 - 1)\mathbf{a}_2'^*/1 \cdot 778 = 0 \cdot 876\mathbf{a}_2'^*$. Hence the Bravais lattice is $P_{1\bar{1}}^{C2/m}$ with lattice constants $a_1' = 5 \cdot 728$, $a_2' =$
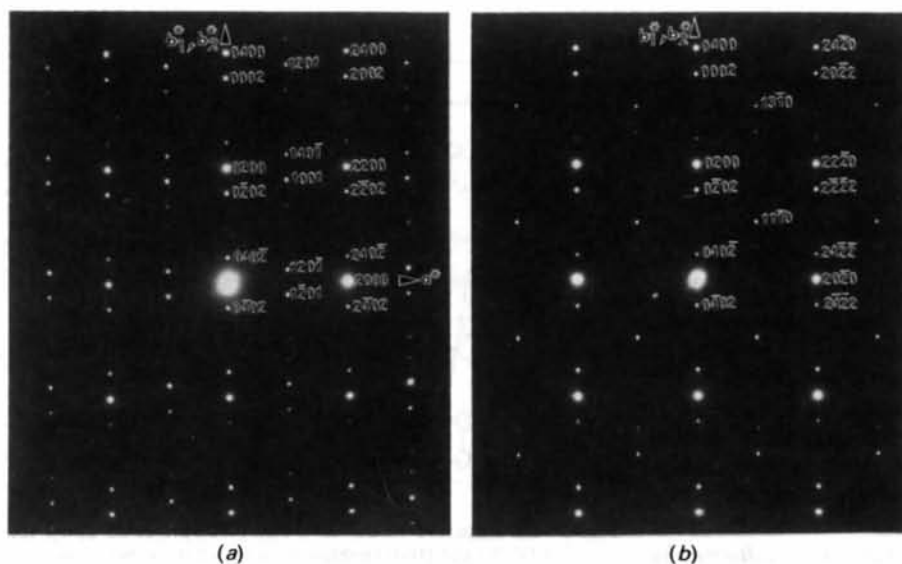

(a)

(b)

Fig. 1. Electron diffraction patterns of (PbS)$_{1 \cdot 12}$VS$_2$ with incident beams parallel to (a) [001] and (b) [101] directions of the subsystems. The spots are assigned by four integers H, K, L and M.

3·256, $a_3' = 23\cdot939$ Å and $\beta' = 98\cdot95°$ and $\sigma' =$ (0 0·876 0). Then the possible superspace groups of the standard cell are $P^{C2/m}_{1\ \bar{1}}$, $P^{C2}_{\bar{1}}$ or $P^{Cm}_{\bar{1}}$ and they are equivalent to $P^{B2/m}_{\bar{1}\ \bar{1}}$, $P^{B2}_{\bar{1}}$ or $P^{Bm}_{\bar{1}}$ of the literature (de Wolff, Janssen & Janner, 1981).

In this study, structure analysis was performed by using the former setting based on the nonstandard cell to facilitate intuitive understanding of the subsystem relations.

Structure refinement

Refinement was performed on the basis of $|F|$ through the full-matrix least-squares refinement program *FMLSM* (Kato, 1990). Only one scaling factor common to the subsystems is refined and site occupancies are normalized by taking into account the volume ratio of the subsystems. The Fourier amplitudes of the modulation functions were considered as structural parameters. If the atoms are located on special positions related by $\{R|v\}$ in the basic structure, where R and v are rotational and translational parts of a symmetry operation in the superspace, the complex Fourier amplitudes $f(\mathbf{k})$ (scalar, vector or tensor in the superspace) of the modulation function for a modulation vector $\mathbf{k}$ satisfy the following relations. For occupancy or isotropic temperature factors, $f(\mathbf{k}) = f(\mathbf{k}R)\exp(-i\mathbf{k}v)$; for displacement, $f_i(\mathbf{k}) = \sum_j R_{ij} f_j(\mathbf{k}R)\exp(-i\mathbf{k}v)$; for anisotropic temperature factors, $f_{ij}(\mathbf{k}) = \sum_{lm} R_{il} \times f_{lm}(\mathbf{k}R)R_{jm}\exp(-i\mathbf{k}v)$. In the four-dimensional lattice, $\mathbf{k}R$ is $\mathbf{k}$ or $-\mathbf{k}$ and $f(-\mathbf{k})$ is the conjugate complex of $f(\mathbf{k})$. These relations involve restrictions in the modulation-function shapes of atoms localized in special positions.

The structure model without modulation

After some trials, a starting model with the projections along the [010] and [100] directions of the subsystems shown in Fig. 2 is assumed to have the symmetry operations

$$(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},0,\tfrac{1}{2};\ 0,\tfrac{1}{2},\tfrac{1}{2},0;\ \tfrac{1}{2},0,\tfrac{1}{2},\tfrac{1}{2})$$

$$+\ x_1,x_2,x_3,x_4;\ -x_1,x_2,-x_3,x_4.$$

The superspace group employed is equivalent to $P^{C2}_{\bar{1}}$ [$P^{B2}_{\bar{1}}$ in the table of de Wolff, Janssen & Janner (1981)]. The model is composed of two-atom-thick layers of PbS with a distorted NaCl-type structure, and VS$_2$ sandwiches with a distorted CdI$_2$-type structure. The space groups of the basic structures of the two subsystems, the PbS and VS$_2$ parts, are both *C*2. Least-squares refinement of the structure model without modulation was tried with a secondary-extinction correction. Scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography*

(1974), and unit weights were assigned to all reflections. The agreement was fairly good with anisotropic temperature factors, but not fully satisfactory;* $R_F = 0\cdot083$ and $wR_F = 0\cdot093$. R_F values for *HKL*0 ($K \neq 0$), *H0LM* ($M \neq 0$) and *H0L*0 are 0·072, 0·106 and 0·098 respectively. The final structure parameters are listed in Table 1. The occupancy of each atom was assumed to be 1·0, and the composition of the specimen was estimated to be (PbS)$_{1\cdot12}$VS$_2$ from the cell-volume ratio of the subsystems.

Modulated structure model

The structure was then assumed to be modulated displacively through mutual interactions between the subsystems (Janner & Janssen, 1980*b*). Although the intensities of satellite reflections with both K and M not equal to zero are too weak to be observed in X-ray diffraction, the intensities of main reflections of each subsystem are considered to be affected by the modulation. So refinement of the modulated structure was attempted on the basis of the measured intensities of the *HKL*0, *H0LM* and *H0L*0 reflections. The modulated structure may be described by the same superspace group as derived before, because the satellites do not add any restrictions to the extinction rules.

In the present case, modulation functions up to the second order are considered. The first and second harmonics are described by their cosine ($A_\mathbf{k}$) and sine ($B_\mathbf{k}$) parts. The restrictions for $A_\mathbf{k}$ and $B_\mathbf{k}$ were
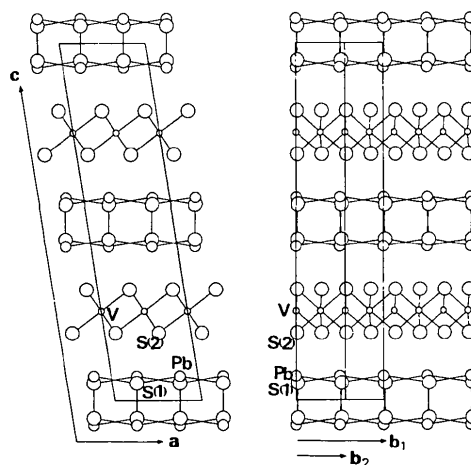

Fig. 2. The structure model of (PbS)$_{1\cdot12}$VS$_2$ projected along the [010] (left) and [100] (right) directions of the subsystems.

Table 1. *Atomic parameters of* $(PbS)_{1.12}VS_2$ *with estimated standard deviations in parentheses*

(a) Structure model without modulation

Subsystem 1	$x\ (=x_1)$	$y\ (=x_2)$	$z\ (=x_3)$	$B_{eq}(Å^2)$†
Pb	0·79399 (12)	0·0*	0·06793 (3)	2·13 (2)
S(1)	0·2811 (9)	−0·0203 (10)	0·0485 (2)	1·40 (13)

Subsystem 2	$x\ (=x_1)$	$y\ (=x_4)$	$z\ (=x_3)$	$B_{eq}(Å^2)$‡
V	0·0	0·0*	0·25	1·18 (8)
S(2)	0·6284 (4)	−0·023 (2)	0·18926 (10)	0·71 (6)

(b) Modulated structure model

A_k and B_k are the cosine and sine amplitudes of the Fourier series of the modulation function, where k is the modulation vector.

Subsystem 1	$x\ (=x_1)$	$y\ (=x_2)$	$z\ (=x_3)$	$B_{eq}(Å^2)$†
Pb				
Average	0·7946 (2)	0·0*	0·06890 (5)	2·61 (4)
A_{0001}	0·0062 (7)	−0·0097 (12)	−0·0015 (2)	0·06 (15)
B_{0001}	0·0067 (7)	−0·0032 (12)	0·0009 (2)	−0·39 (14)
A_{0002}	−0·0065 (9)	0·0045 (16)	−0·0011 (2)	0·20 (13)
B_{0002}	0·0082 (8)	−0·0011 (11)	0·0034 (2)	1·03 (14)
S(1)				
Average	0·2822 (12)	−0·0100 (14)	0·0482 (3)	1·7 (2)
A_{0001}	−0·007 (3)	−0·019 (3)	0·0033 (6)	0·5 (3)
B_{0001}	−0·021 (3)	−0·016 (3)	0·0037 (8)	−1·2 (4)
A_{0002}	0·001 (2)	0·011 (3)	−0·0027 (6)	−0·8 (3)
B_{0002}	−0·012 (3)	0·022 (2)	−0·0017 (6)	1·8 (3)

Subsystem 2	$x\ (=x_1)$	$y\ (=x_4)$	$z\ (=x_3)$	$B_{eq}(Å^2)$‡
V				
Average	0·0	0·0*	0·25	1·19 (10)
A_{0100}	−0·005 (2)	0·0	0·0008 (3)	0·0
B_{0100}	−0·007 (3)	0·0	0·0002 (8)	0·0
A_{0200}	0·0	−0·044 (4)	0·0	0·5 (2)
B_{0200}	0·0	−0·025 (4)	0·0	−0·2 (4)
S(2)				
Average	0·6284 (5)	0·002 (3)	0·18943 (12)	0·45 (9)§
A_{0100}	−0·0024 (14)	0·050 (2)	−0·0000 (3)	0·2 (2)
B_{0100}	−0·005 (3)	0·005 (6)	−0·0025 (6)	−0·1 (3)
A_{0200}	0·001 (3)	−0·001 (7)	0·0003 (7)	−0·1 (2)
B_{0200}	−0·002 (3)	−0·003 (5)	0·0011 (8)	−0·1 (4)

* Not refined to fix the phase origin.

† $B_{eq} = (4/3)(\beta_{11}a_1^2 + \beta_{22}a_2^2 + \beta_{33}a_3^2 + \beta_{13}a_1a_3\cos\beta)$.

‡ $B_{eq} = (4/3)[\beta_{11}a_1^2 + \beta_{22}(a_2/1·778)^2 + \beta_{33}a_3^2 + \beta_{13}a_1a_3\cos\beta]$.

§ Negative refined β_{22} value for S(2).

Table 2. *Selected interatomic distances* (Å)

	Minimum	Average	Maximum
(a) Structure model without modulation			
Pb—S(1)		2·904 (5)	
—S(1')		2·901 (5)	
—S(1''')		2·757 (5)	
—S(1'''')		2·815 (5)	
—S(1ᵛ)		3·046 (5)	
—S(2)	3·193 (2)	3·329 (3)	3·584 (3)
—S(2'')	3·221 (2)	3·356 (3)	3·609 (3)
V—S(2'')		2·385 (2)	
—S(2'')		2·324 (4)	
—S(2''')		2·427 (4)	
—S(2''''')		2·385 (2)	
—S(2ⁱˣ)		2·324 (4)	
—S(2ˣ)		2·427 (4)	
(b) Modulated structure model			
Pb—S(1)	2·72 (2)	2·91 (2)	3·20 (2)
—S(1')	2·61 (2)	2·92 (2)	3·08 (2)
—S(1''')	2·650 (15)	2·77 (2)	2·98 (2)
—S(1'''')	2·66 (2)	2·88 (2)	3·26 (2)
—S(1ᵛ)	2·71 (2)	3·00 (2)	3·17 (2)
—S(2)	3·162 (15)	3·31 (2)	3·55 (2)
—S(2'')	3·162 (15)	3·340 (15)	3·55 (2)
V—S(2'')	2·37 (2)	2·39 (2)	2·41 (2)
—S(2'')	2·12 (2)	2·38 (2)	2·57 (2)
—S(2''')	2·20 (2)	2·37 (2)	2·62 (2)
—S(2''''')	2·37 (2)	2·39 (2)	2·41 (2)
—S(2ⁱˣ)	2·12 (2)	2·38 (2)	2·57 (2)
—S(2ˣ)	2·20 (2)	2·37 (2)	2·62 (2)

Symmetry operations: (i) $1 + x_1,\ x_2,\ x_3,\ x_4$; (ii) $-1 + x_1,\ x_2,\ x_3,\ x_4$; (iii) $1 - x_1,\ x_2,\ -x_3,\ x_4$; (iv) $\frac{1}{2} + x_1,\ \frac{1}{2} + x_2,\ x_3,\ \frac{1}{2} + x_4$; (v) $\frac{1}{2} + x_1,\ -\frac{1}{2} + x_2,\ x_3,\ \frac{1}{2} + x_4$; (vi) $-\frac{1}{2} + x_1,\ \frac{1}{2} + x_2,\ x_3,\ \frac{1}{2} + x_4$; (vii) $-\frac{1}{2} + x_1,\ \frac{1}{2} + x_2,\ x_3,\ -\frac{1}{2} + x_4$; (viii) $1 - x_1,\ \frac{1}{2} + x_2,\ \frac{1}{2} - x_3,\ x_4$; (ix) $\frac{1}{2} - x_1,\ x_2,\ \frac{1}{2} - x_3,\ \frac{1}{2} + x_4$; (x) $\frac{1}{2} - x_1,\ x_2,\ \frac{1}{2} - x_3,\ -\frac{1}{2} + x_4$.

applied to V atoms located on the twofold axis. At first, refinement based only on the displacive modulation was attempted. The decrease of R_F to 0·080 was slight. Then the model with modulation in both atomic coordinates and anisotropic temperature factors was adopted. A total of 156 parameters were used to describe the modulated structure model. The final R_F and wR_F were 0·059 and 0·069 for all reflections. The R_F values for the HKL0 $(K \neq 0)$, H0LM $(M \neq 0)$ and H0L0 reflections were 0·051, 0·079 and 0·071 respectively. The fitted parameters are shown in Table 1 together with those for the model without modulation.

Discussion

The modulation amplitudes in the PbS part are larger than those in the VS_2 part. This may indicate that the PbS part is more susceptible to modulation by VS_2 than is the VS_2 part by PbS.

Interatomic distances calculated using the fitted parameters of Table 1 are listed in Table 2. The calculation procedure for distances is the same as that used in Kato (1990). The maximum distance between two atoms A and B each belonging to different subsystems can be defined as $d_{max} = \max_t\{\min_j[d(t,j)]\}$, where $d(t,j)$ represents the interatomic distance $A^j—B^j$ as a function of an auxiliary coordinate t in the four-dimensional description and the symmetry code j in the superspace. Any section of the four-dimensional model at a hyperplane $-1·778x_2 + x_4 = t$ with an arbitrary value of t represents the real structure of the composite crystal. Sections with different t correspond to different phases of the modulation wave in the modulated structure model. $\min_j$ represents the partial minimum with respect to j covering all the symmetry operations of the superspace group, $\max_t$ the maximum concerning t. This is illustrated in Fig. 3 by plots of distances between Pb as atom A and S(2), as well as S(2ⁱᵛ) as atom B, for the model without modulation as a function of the fourth coordinate t. Although Pb atoms protrude toward VS_2 layers, the distances between Pb and S(2) are larger than those between Pb and S(1) as shown in Table 2.

The probable effect of modulation on the diffraction intensities has been suggested for the layered composite crystal $(SnS)_{1.17}NbS_2$ by van Smaalen (1989) and Meetsma, Wiegers, Haange & de Boer (1989). As in the present case the displacive modulation alone did not satisfactorily improve the agreement between observed and calculated inten-

sities, modulation also had to be introduced in the thermal parameters, although the physical meaning of the latter was unknown. The improvement of R_F thus achieved may be partly due to the larger number of adjustable parameters. In the least-squares refinement of a modulated structure, it is considered difficult to achieve convergence of thermal parameters and amplitudes of displacive modulations because of their strong correlations. Although in the present case no such difficulties arose, the intensities of satellite reflections (*HKLM* with both K and M nonzero) should be measured and used to analyze the displacive modulations more precisely. The intensities of satellite reflections calculated for the modulated model in Table 1(*b*) were very small and of the same order of magnitude as those of the group of main reflections which were too weak to be recorded in the Weissenberg photographs. The results seem to indicate that weak modulations in coordinates and perhaps in the thermal parameters cause some detectable changes in the intensities of the main reflections, but that their intensity contribution to the satellite reflections is not large enough for the satellites to be observed in X-ray diffraction. This phenomenon, although curious, will be proved to be true if one compares the F_c values for the modulated model and for the modulation-free model with the average structural parameters of Table 1(*b*). Another possible explanation for the low intensity of the satellite reflections may be related to a phase fluctuation of the modulation wave (Yamamoto, Nakazawa, Kitamura & Morimoto, 1984). Although its detailed mechanism is still not known exactly, its effect would be roughly

simulated by introducing an extra thermal parameter for the fourth dimension. The result of a trial refinement with these extra parameters was not satisfactory.

The structural properties of layered composite crystals have not yet been completely understood because of their complexity, and they would be worth studying in further detail based on a larger number of experimental results.

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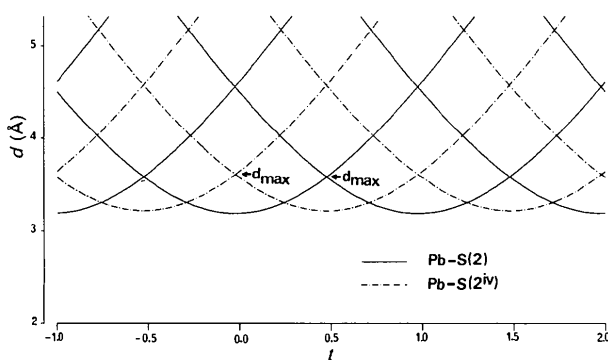YAMAMOTO, A., NAKAZAWA, H., KITAMURA, M. & MORIMOTO, N. (1984). *Acta Cryst.* B**40**, 228–237.

Fig. 3. The interatomic distance $d(t,j)$ between Pb (in subsystem 1) and S(2) (in subsystem 2) calculated by using the parameters in Table 1(*a*) as a function of the fourth coordinate t common to both subsystems. Different branches of the curves represent $d(t,j)$ with different symmetry operations j of the superspace group. Symmetry code (iv) is $\frac{1}{2} + x_1, \frac{1}{2} + x_2, x_3, \frac{1}{2} + x_4$.