

The Crystal Structure of the Misfit Layer Compound $(\text{YS})_{1.23}\text{NbS}_2$

P. RABU, A. MEERSCHAUT,¹ AND J. ROUXEL

I.P.C.M., Laboratoire de Chimie des Solides UMR 110, 2, rue de la Houssinière, 44072 Nantes Cedex 03, France

AND G. A. WIEGERS

Laboratory of Inorganic Chemistry, Materials Science Centre of the University, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received December 6, 1989

Single crystal X-ray diffraction has shown that $(\text{YS})_{1.23}\text{NbS}_2$ is a misfit layer compound, built of alternately $\{100\}$ slices of rocksalt-type $|\text{YS}|$ and sandwiches $|\text{NbS}_2|$ with Nb in trigonal prisms of S, like Nb in 2H-NbS_2 . The unit cell dimensions and space groups of the two sublattices $|\text{YS}|$ and $|\text{NbS}_2|$ in the composite crystal are

$$|\text{YS}|: a_1 = 5.393(1) \text{ \AA}, b_1 = 5.658(8) \text{ \AA}, c_1 = 22.284(8) \text{ \AA}, \text{S.G. } Fm2m, Z = 8$$

$|\text{NbS}_2|: a_2 = 3.322(1) \text{ \AA}, b_2 = 5.662(4) \text{ \AA}, c_2 = 11.13(2) \text{ \AA}, \beta_2 = 92.62(6)^\circ, \text{S.G. } C2, Z = 2$. The lattice vectors \vec{a}_1 and \vec{a}_2 , \vec{b}_1 and \vec{b}_2 are parallel, $|\vec{a}_1| = |\vec{a}_2|$, $|\vec{b}_1| = |\vec{b}_2|$, while the stacking vectors \vec{c}_1 and \vec{c}_2 diverge slightly. Refinements converged to $R_F = 0.060$ for the $|\text{YS}|$ part, $R_F = 0.075$ for the $|\text{NbS}_2|$ part, and $R_F = 0.063$ for the common part ($0kl$ reflections). Y is coordinated to S atoms on the vertices of a distorted square pyramid: Y–S = 2.764(4) Å ($1 \times$), 2.763(19) Å ($1 \times$), 2.996(19) Å ($1 \times$), 2.752(1) Å ($2 \times$). The $|\text{NbS}_2|$ lattice shows disorder, the Nb–S distances are 2.473(8) Å. © 1990 Academic Press, Inc.

Introduction

Single crystal X-ray diffraction of a number of compounds $(\text{MS})_n\text{TS}_2$ ($M = \text{Sn, Pb, Bi, rare earth metals}; T = \text{Nb, Ta}; n = 1.08\text{--}1.17$) has shown (1) that these compounds are misfit layer compounds, built of alternately $\{100\}$ slices of rocksalt-type $|\text{MS}|$ and sandwiches $|\text{TS}_2|$ with T in trigonal prisms of S. Misfit layer compounds are a subgroup of the class of composite crystals involving structures composed of subsystems, in our case $|\text{MS}|$ and $|\text{TS}_2|$. Each sub-

system has its own three-dimensional space group symmetry, but being mutually incommensurate. The structure of the composite crystal can be described in higher dimensional space (2, 3). For these compounds mentioned above the two sublattices have centered (F and C) orthorhombic lattices, with corresponding axes a_1 and a_2 , b_1 and b_2 , c_1 and c_2 parallel (the subscripts 1 and 2 refer to the $|\text{MS}|$ and $|\text{TS}_2|$ lattice, respectively). The b axes are equal in length, while the c axes, perpendicular to the layers, are equal or differ by a factor of two. Along the a axes the lattices are incommensurate, the ratio a_1/a_2 is around $\sqrt{3}$; a_1 and b_1 are approximately equal to the cell edge of NaCl-

¹ To whom correspondence should be addressed.

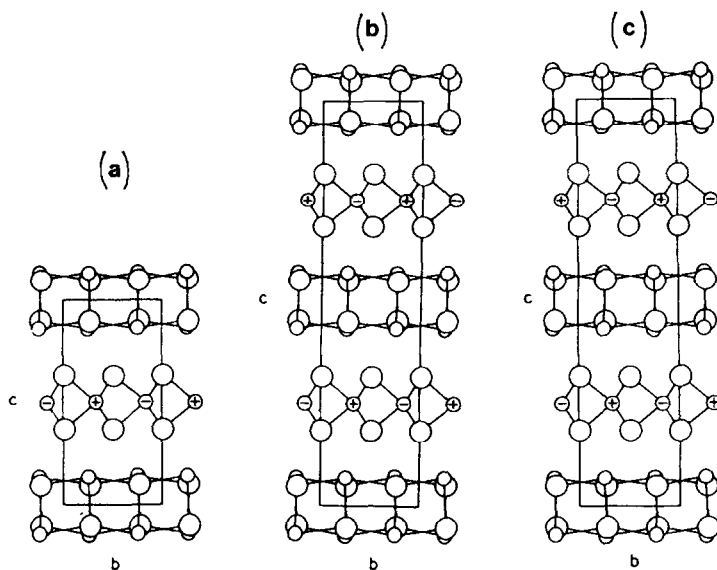


FIG. 1. The structures of three types of misfit layer compounds with centered orthorhombic lattices projected along the misfit axes; (a) The CC type, e.g., $(\text{SnS})_{1.17}\text{NbS}_2$; (b) the CF type e.g., $(\text{LaS})_{1.14}\text{NbS}_2$; (c) the FF type, e.g., $(\text{PbS})_{1.13}\text{TaS}_2$. Large circles represent sulfur atoms. In order to demonstrate the centering, T atoms (at $z = 1/2$ for CC and at $z = 1/4$ and $z = 3/4$ for CF and FF) in the same plane parallel to (100) have the same symbol (+ or -); atoms $(1/2)a_1$ apart have different symbols.

type MS ; a_2 and b_2 ($b_1 = b_2$) correspond to a and $a\sqrt{3}$, respectively, of 2H-TS_2 (hexagonal, $a \approx 3.3 \text{ \AA}$). Three structure types, differing in the way the layers of the same type are stacked, were found, viz., the CC type with both sublattices C-centered orthorhombic, $c_1 = c_2 \approx 11\text{--}12 \text{ \AA}$; the CF type with the $[MS]$ lattice C-centered, $c_1 \approx 11\text{--}12 \text{ \AA}$, the $[TS_2]$ lattice F-centered, $c_2 = 2c_1 \approx 22\text{--}24 \text{ \AA}$, and the FF type with both sublattices F centered, $c_1 = c_2 \approx 22\text{--}24 \text{ \AA}$. The composition (viz., the value of n) is determined by the ratio a_1/a_2 taking into account the number of formula units per unit cell of the two sublattices and the difference in lengths of the c axes. Projections along $[100]$ are given in Fig. 1. In this paper the structure determination of $(\text{YS})_{1.23}\text{NbS}_2$ is described. The compound constitutes a new structure type among misfit layer compounds.

Experimental

$(\text{YS})_{1.23}\text{NbS}_2$ was prepared by heating a mixture of Y_2S_3 and NbS_2 in a 0.6 : 1 ratio at a temperature of 1000°C in a silica tube; the mixture was compacted before heating. Silica tube was protected by a thin carbon film deposited by cracking acetone. Niobium and yttrium sulfides were handled in a glove box under nitrogen. After 10 days at 1000°C , products are intermediately crushed and reheated for 1 week. Single crystals in platelet shape are obtained using iodine as transport agent ($<5 \text{ mg. cm}^{-3}$).

Weissenberg photographs ($h0l$, $h1l \dots$ planes) gave evidence of two different symmetries, i.e., orthorhombic for $[\text{YS}]$ and monoclinic for $[\text{NbS}_2]$ parts. Lattice parameters were refined by least-square methods for separate parts (see Table I). The powder data were recorded on a cylindrical position-

TABLE I
INEL POWDER PATTERN (THE 27
FIRST INDEXED LINES)

Type ^a	d_{obsd}	d_{calcd}	(YS) <i>hkl</i>	(NbS ₂) <i>hkl</i>	I_0/I_{obsd}^b
<i>c</i>	11.23	{ 11.15 11.15 }	002	001	66
<i>c</i>	5.568	5.576		002	40
<i>a</i>	3.846	3.853	111		11
<i>c</i>	3.713	3.718	006		89
<i>a</i>	3.458	3.462	113		34
<i>a</i>	2.9309	2.9410	115		41
<i>b</i>	2.8634	2.8646		110	21
<i>c</i>	2.8340	{ 2.8336 2.8341 }	020	020	35
<i>b</i>	2.8009	2.8024		111	14
<i>c</i>	2.7875	2.7882	008		21
<i>c, b</i>	2.7449	{ 2.7463 2.7475 2.7468 }	022	111	52
<i>a</i>	2.6995	2.7024	200		28
<i>a</i>	2.6251	2.6264	202		29
<i>b</i>	2.5886	2.5917		112	13
<i>c</i>	2.5239	2.5265		022	18
<i>a</i>	2.4693	2.4704	117		12
<i>b</i>	2.5041	2.5066		112	23
<i>b</i>	2.3158	2.3155		113	45
<i>c</i>	2.2519	{ 2.2536 2.2538 }	026	023	100
<i>c, b</i>	2.2275	{ 2.2305 2.2254 }		005	41
<i>a</i>	2.1856	2.1859	206		24
<i>a</i>	2.0918	2.0935	119		37
<i>b</i>	2.0384	2.0403		114	20
<i>c</i>	1.9868	{ 1.9874 1.9876 }	028	024	8
<i>a, b</i>	1.9556	{ 1.9556 1.9582 }	220	114	40
<i>a</i>	1.9262	1.9262	222		21
<i>c</i>	1.8586	1.8588		006	39

Note. (INEL $\text{CuK}\alpha_1$ ($\lambda = 1.540598 \text{ \AA}$), [YS] orthorhombic $Fm\bar{2}m$: $a = 5.4048(13)$; $b = 5.6671(12)$; $c = 22.306(5)$; 37 HKL . [NbS₂] monoclinic $C2$: $a = 3.3236(4)$; $b = 5.6682(10)$; $c = 11.1653(15)$; $\beta = 92.727(2)$; 43 HKL .

^a a , b , and c are the reflections of the [YS], [NbS₂], and the common structure, respectively.

^b Intensity normalized at 100.

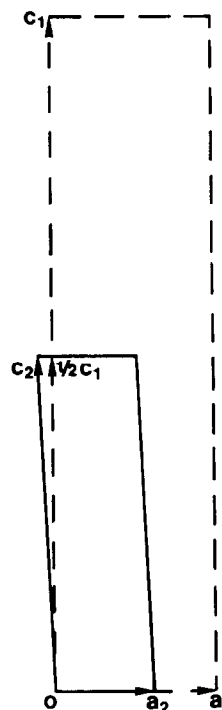


Fig. 2. Relation between the a and c axes of the two sublattices YS (a_1, c_1) and NbS₂ (a_2, c_2).

sensitive detector (INEL apparatus) with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$).

Structure Determination

A crystal of (YS)_{1.23}NbS₂ with dimensions $0.056 \times 0.2 \times 0.26 \text{ mm}^3$ was mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell dimensions, $a_1 = 5.393(1) \text{ \AA}$, $b_1 = 5.658(8) \text{ \AA}$, $c_1 = 22.284(8) \text{ \AA}$, $\alpha_1 = \beta_1 = \gamma_1 = 90^\circ$ and $a_2 = 3.322(1) \text{ \AA}$, $b_2 = 5.662(4) \text{ \AA}$, $c_2 = 11.13(2) \text{ \AA}$, $\alpha_2 = \gamma_2 = 90^\circ$, $\beta_2 = 92.62(6)^\circ$, and preliminary intensity measurements showed that [YS] and [NbS₂] lattices are F-centered orthorhombic and C-centered monoclinic, respectively. The a axes, a_1 and a_2 , and b axes, b_1 and b_2 , are parallel while the c axes diverge slightly, the angle between being 2.62° ; $|\vec{a}_1| = |\vec{a}_2|$, $|\vec{b}_1| = |\vec{b}_2|$, $(1/2)|\vec{c}_1| = |\vec{c}_2| \sin \beta_2$. In recipro-

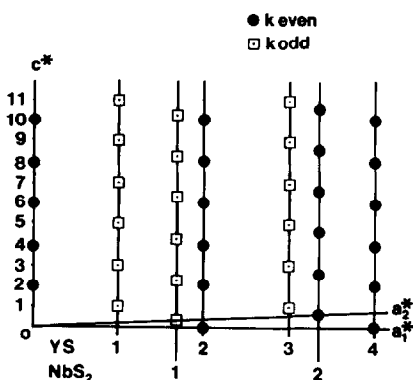


FIG. 3. The reciprocal lattices of YS and NbS_2 sublattices, a_1^* , c_1^* and a_2^* , c_2^* , respectively; $c_2^* = 2c_1^*$; a_1^* and a_2^* make an angle of 2.62° ; c^* based on $c = 22.28 \text{ \AA}$.

cal space, \vec{b}_1^* and \vec{b}_2^* , \vec{c}_1^* and \vec{c}_2^* are parallel while \vec{a}_1^* and \vec{a}_2^* diverge. The relation between the unit cells is shown in Figs. 2 and 3. Measurements of a number of crystals showed identical results.

Data collection is summarized in Table II. An absorption correction was applied using the dimensions of the crystal platelet given above; the crystal was bounded by the (001, 100, and 010) faces, respectively. The linear absorption coefficient is 109 cm^{-1} . Corrections for absorption, Lorentz, and polarization effects were applied using the Enraf-Nonius Structure Determination Package (SDP programs (4)), which was also used for structure refinements. Structure refinements were performed using $h_1k_1l_1$ and $h_2k_2l_2$ reflections for the |YS| and | NbS_2 | parts, respectively, excluding in both cases the $0kl$ reflections which are common for both sublattices; these reflections were used for the determination of the relative origin (y and z) of the two sublattices. Because of the incommensurate character it is not possible to fix common x coordinates. Approximate coordinates of the atoms were obtained by considering the structures of the misfit compounds already known. The

|YS| part refined smoothly to $r_F = 0.060$, $\omega R = 0.065$ for 186 reflections with $I \geq 3 \sigma(I)$, with Y and S on sites (8c) of space group $Fm2m$. The y coordinate of Y was kept fixed at 0 (the space group has no center of symmetry; see Table III). Attempts to refine the | NbS_2 | part in space group $C2$ with Nb at (2a) = 0, 0, 0 (y kept at 0) and S at (4c), $x \approx 0$, $y \approx 1/3$, $z \approx 0.14$, were less successful ($R_F = 0.229$ with an isotropic refinement; if anisotropy was applied, β_{11} for both Nb and S atoms showed large negative values). The difference-Fourier synthesis showed peaks which were assigned to a | NbS_2 | sandwich displaced with respect to the first by $\Delta x \approx .15$, $\Delta y \approx .5$, $\Delta z \approx 0$. Refinements were performed with both sandwiches partially occupied, the total occupancy fixed to 1. The second | NbS_2 | sandwich (Nb2, S2, and

TABLE II

(a) YS part	
Crystal data	
Orthorhombic symmetry S.G. $Fm2m$ (42), $Z = 8$	
$a_1 = 5.393(1) \text{ \AA}$, $b_1 = 5.658(8) \text{ \AA}$, $c_1 = 22.284(8) \text{ \AA}$	
Data collection	
Diffractometer	: Enraf-Nonius CAD4
Radiation	: $\text{MoK}\alpha$ ($\lambda = 0.71703 \text{ \AA}$)
Monochromator	: graphite
θ range	: $1.5\text{--}35^\circ$
scan	: ω mode
$\Delta\omega$: $1.00 + 0.35 \text{ tg } \theta$
(b) NbS_2 part	
Crystal data	
Monoclinic symmetry S.G. $C2$, $Z = 2$	
$a_2 = 3.322(1) \text{ \AA}$, $b_2 = 5.662(4) \text{ \AA}$, $c_2 = 11.13(2) \text{ \AA}$, $\beta_2 = 92.62(6)^\circ$	
Data collection	
Diffractometer	: Enraf-Nonius CAD 4
Radiation	: $\text{MoK}\alpha$ ($\lambda = 0.71703 \text{ \AA}$)
Monochromator	: graphite
θ range	: $1.5\text{--}35^\circ$
Scan	: ω mode
$\Delta\omega$: $1.00 + 0.35 \text{ tg } \theta$
(c) Common part	
S.G. Pm , $b = 2.829 (b_1/2)$, $c = 11.142 (c_1/2)$	
Conditions defined for YS part	

TABLE III

ATOMIC COORDINATES AND THERMAL PARAMETERS (\AA^2) OF THE |YS| PART; $a_1 = 5.393(1) \text{\AA}$, $b_1 = 5.658(8) \text{\AA}$, $c_1 = 22.284(8) \text{\AA}$, SPACE GROUP $Fm2m$

Atom	Site	x	y	z	
Y	(8c)	0	0.	0.3240(1)	
S	(8c)	0	0.021 (2)	0.2001(2)	
Anisotropic thermal parameter (\AA^2)					
		U_{11}	U_{22}	U_{33}	U_{23}
Y		0.0364(8)	0.036(1)	0.0219(7)	-0.007 (3)
S		0.032 (2)	0.019(2)	0.014 (2)	0.002 (5)

S3) was refined in the riding mode with the first sandwich (Nb1 and S1). Variables were x , y , z of Nb2 and S1 and the occupancies (which means that the absolute value of the coordinate differences of Nb2 and S2 and S3 are kept equal to those of Nb1 and S1). Anisotropic temperature factors were refined for Nb1 and Nb2, the S atoms were refined isotropically; see Table IV (where y coordinates of all atoms are shifted by $-0.124/2$ in agreement with the refinement for the common part—Table V), $R_F = 0.075$, $\omega R = 0.091$ for 229 reflections with $I \geq 3 \sigma(I)$.

The relative origin of the two sublattices (common y and z coordinates) was obtained from the $0kl$ reflections of the |YS| part record. Since these reflections occur for $k = 2n$ and $l = 2n$ in the unit mesh $b = 5.658 \text{\AA}$, $c = 22.284 \text{\AA}$, the axes describing the projection along the misfit [100] axes can be halved, viz., $b' = 2.829 \text{\AA}$, $c' = 11.142 \text{\AA}$. The symmetry of this projection is that of the two-dimensional plane group Pm ($m \perp c$), the midplane of type |YS| double layer fixed at $z = 1/2$ and Nb of |NbS₂| at $z = 0$, which gives equal distances between alternate layers |YS| and |NbS₂|. Refinements were performed in the space group Pm with y of Y fixed at 0; we have constrained the y and z coordinates of Y and S (viz. differences 0.042 (2×0.021) and 0.2478 (2×0.1239), respectively, as found from the |YS| refinement (see Table III)); we also constrained the y and z coordinates of Nb1 and S1 (viz. differences 0.6720 (2×0.336) and 0.1422 , respectively, as found from the |NbS₂| refinement (see Table IV)). Variables were the y and z coordinates of one sublattice with respect to the other, and the occupancy of Y and S constraint to be equal. Isotropic temperature factors were taken into account. The refinement proceeded to $R_F = 0.063$ and $\omega R = 0.071$ for 75 reflec-

TABLE IV

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF S ATOMS OF THE |NbS₂| PART: $a_2 = 3.322(1) \text{\AA}$, $b_2 = 5.662(4) \text{\AA}$, $c_2 = 11.13(2) \text{\AA}$, $\beta_2 = 92.62(6)^\circ$, SPACE GROUP $C2$

Atom	Site	x	y	z	Occupancy	B_{eq} , B_{iso}^* (\AA^2)	
Nb1	(2a)	0	-0.062 (-)	0	.65	1.94 (4)	
S1	(4c)	0.022 (1)	0.274(1)	0.1422(6)	.65	2.07 (8)*	
Nb2	(4c)	0.151 (1)	0.459(1)	-0.0010(6)	.175	2.8 (2)	
S2	(4c)	0.173 (1)	0.795(1)	0.1411(6)	.175	2.0 (2)*	
S3	(4c)	0.129 (1)	0.795(1)	-0.1432(6)	.175	2.0 (2)*	
Anisotropic thermal parameters (\AA^2)							
		U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nb1		.0214(9)	.0121(8)	0.039(1)	.0	-.0082(7)	.0
Nb2		.032 (3)	.010 (4)	0.064(6)	.004 (2)	-.019 (3)	.003(3)

TABLE V
 ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF THE COMMON PART,
 $b = 2.829 \text{ \AA}$, $c = 11.142 \text{ \AA}$

Atom	Site	x	y	z	$B(\text{\AA}^2)$	Occupancy
Y	(2c)	—	0	0.6481(5)	2.3 (1)	0.56
S	(2c)	—	0.042	0.4003	1.8 (2)	0.56
Nb1	(1a)	—	-0.124(2)	0.	1.12(4)	1.
S1	(2c)	—	0.548	0.1422	1.5 (1)	1.

tions with $I \geq \sigma(I)$. The occupancy of |YS| (0.56) is however much lower than expected (0.615) (refinements of occupancy were made step by step, 0.56 corresponding to the lowest R_F factor) (see Table V). It is also possible to deduce the occupancy from the experimental scale factors for |YS|, |NbS₂|, and the common reflections, 0.216, 0.126, and 0.124. The ratio $0.126/0.216 = 0.584$ is somewhat larger than the ratio 0.56 from refinement of $0kl$. The discrepancy between the occupancy from the ratio of lengths of misfit axes (0.615) and the experimental ratio (0.56–0.58) is not easily explained. There are several possibilities: the effect of the mutual modulation of the subsystems is a decrease of the intensity of the main reflections and, since it is found that the |MS| lattice is stronger modulated than the |TS₂| lattice, the decrease in intensity is probably strongest for the |YS| lattice. A more sophisticated refinement program which combines data sets of all reflections, including the satellites, is needed to analyze this quantitatively. Another possibility is substitution of some |YS| double layers for |NbS₂| forming |NbS₂| pairs of sandwiches in the structure. It may be remarked that it is possible to prepare compounds $(MS)_n(TS_2)_2$ (5) in which |MS| double layers alternate with two sandwiches |TS₂| in an ordered way. A percentage of about 5% of substitution is sufficient to explain the observed occupancy. It is now possible to introduce the true y coordinates of the |NbS₂| unit with respect to Y of |YS| at $y = 0$. These values are obtained by halv-

ing the y coordinate of Nb1 in Table V; the other y coordinates of Table IV are changed accordingly.

Discussion of the Structure

The structure is built of alternately double layers of |YS| and sandwiches |NbS₂|. The formula $(YS)_{1.23}NbS_2$ is obtained from the ratio a_1/a_2 and the number of formula units per cell in each of the two sublattices, $Z = 8$ for |YS|, space group $Fm2m$, and $Z = 2$ for |NbS₂|, space group $C2$, taking into account the difference in length of the c axes: $1.23 = 2 \times (3.322/5.393)$. The |YS| sublattice consists of double layers |YS| with their midplanes at $z = 1/4$ and $z = 3/4$. Double layers $(1/2)c$ apart are displaced over $(1/2)a$ (or equivalently $(1/2)b$ with respect to each other. Each double layer is a distorted {100} slice of rocksalt type |YS|; the quadratic lattice of |YS| is distorted to rectangular while the Y atoms are protruding the planes of sulfur. The Y–Y (3.908 Å) and Y–S distances (Fig. 4) are close to those observed in the parent substance YS with rocksalt structure, $a = 5.493 \text{ \AA}$ (Y–Y = 3.884 Å, Y–S = 2.747 Å (6)). For compounds $(MS)_nTS_2$ studied so far the smallest value of the cell edge of the parent compound MS is found for |YS|. Concerning the distortion in the ab plane of the |YS| sublattice of $(YS)_{1.23}NbS_2$, the ratio b_1/a_1 is the largest observed for misfit layer compounds considering that $b_1 = b_2$ is approximately equal to $a\sqrt{3}$ of the parent substance 2H-

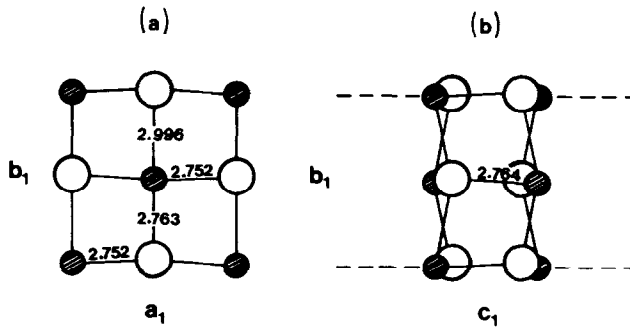


FIG. 4. The YS double layer centered at $y = 1/4$; (a) projected along $[001]$, only upper-half shown; (b) projected along $[100]$. Small hatched circles are Y, large open circles S. (Distances in angstroms.)

NbS_2 ($a\sqrt{3} = 5.757 \text{ \AA}$). So b_1 is elongated from 5.493 for solid YS to 5.658 \AA while b_2 is compressed from 5.757 \AA for 2H- NbS_2 to

5.662 in the misfit layer compound. The a axis (a_2) of the $[\text{NbS}_2]$ lattice in $(YS)_{1.23}\text{NbS}_2$ is almost equal to a of 2H- NbS_2 ($a = 3.324 \text{ \AA}$ (7)).

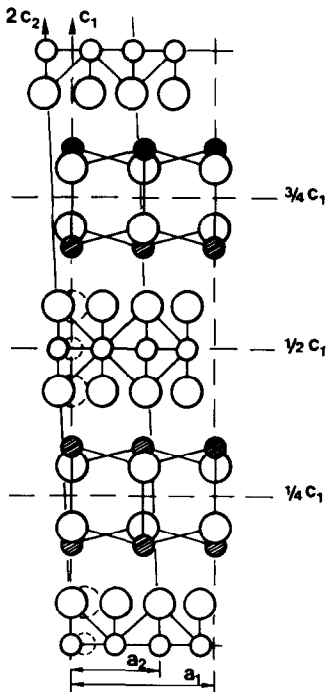


FIG. 5. Structure of $(YS)_{1.23}\text{NbS}_2$ projected along $[010]$. Small hatched circles, small open circles, and large open circles for Y, Nb, and S, respectively. Note: some of the displaced NbS_2 sandwiches are shown (dashed); notice that the line which connects a "normal" NbS_2 with the displaced NbS_2 ($1/2)c_1$ apart is perpendicular to a_2 .

The $[\text{NbS}_2]$ sandwiches in the complete structure are centered at $z = 0$ and $z = 1/2$; both sandwiches are identical since the repeat distance along c is half that of the $[\text{YS}]$ sublattice. Owing to the deviation δ of the x coordinate of S1 from $x = 0$ ($\delta = 0.022$) and the deviation of β_2 from 90° , the $[\text{NbS}_2]$ sandwich is not distorted compared to 2H- NbS_2 (note $0.022 \times 3.322 \text{ \AA} = 0.073 \text{ \AA} \approx 0.1422 \times 11.13 |\cos \beta_2| \text{ \AA} = 0.072 \text{ \AA}$) as indicated in Fig. 5. A projection of the complete structure along the $[100]$ axes of both sublattices is shown in Fig. 6. The Nb-S distances in the trigonal prisms of S are 2.473(8) \AA . It is further seen that the x coordinate of the "displaced" sandwich is such that Nb2-S2 and Nb1-S1 distances ($c_2 = 11.13 \text{ \AA}$) apart are on top of each other which suggests that the disorder of the $[\text{NbS}_2]$ lattice is due to a tendency to form a composite crystal with orthorhombic sublattices; (note 0.151 (the x coordinate of the displaced Nb) $\times 3.322 \text{ \AA} = 0.50 \text{ \AA} \approx |c_2 \cos \beta_2| = 0.509 \text{ \AA}$).

As mentioned in the introduction, the symmetry of the composite crystals $(MS)_n\text{TS}_2$ could be described in $(3 + 1)D$ superspace. It is easily seen that the symme-

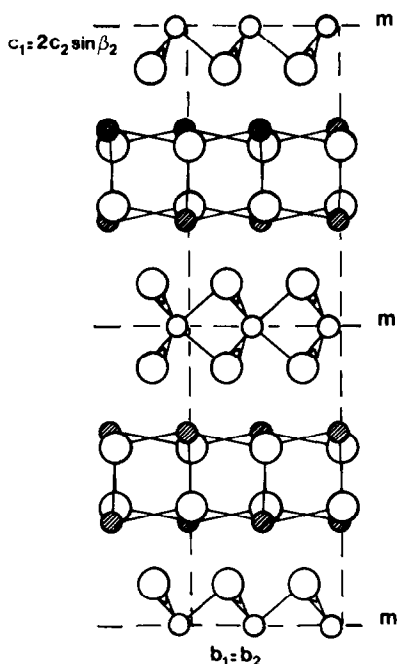


FIG. 6. Projection along [100]. Since the two sublattices have no common x coordinate, the relative position is arbitrary.

try of $(YS)_{1.23}NbS_2$ can also be described in $(3 + 1)D$ space; all reflections, including satellites due to the mutual modulation of the two sublattices, are given by four lattice vectors:

$$S = Ha_1^* + Kb_1^* + Lc_1^* + Ma_2^*$$

($HKLO$ are the $|MS|$ reflections, $OKLM$ the $|NbS_2|$ reflections, while general reflections $HKLM$ are satellites). An extensive discussion of symmetry aspects is outside the scope of this paper.

In our study, satellites due to the mutual modulation were too weak to be observed. By not taking into account the modulation, the structure as determined is in fact an average structure.

Two factors are of importance considering the stability of $(YS)_{1.23}NbS_2$. First the Y atoms at $y = 0$ and $y = 1/2$ (Table III) are

lying in groves formed by rows at $y \approx 0.27$ and $y \approx 0.77$ (Table IV) of sulfur of neighboring $|NbS_2|$ sandwiches. In this way each Y atom is, beside the S atoms of the $|YS|$ double layer, also coordinated to S of $|NbS_2|$, the Y atoms being on the outside the planes of S of $|YS|$. The number of coordinating S atoms of each Y atom is therefore seven or eight; the actual number depending on the position along the misfit axis. The second factor concerns electron transfer from the $|YS|$ to the $|NbS_2|$ part. Such a transfer was deduced from electrical transport and magnetic properties of $(LaS)_{1.14}NbS_2$ and $(CeS)_{1.14}NbS_2$ (8, 9). Since La , Ce , and also Y prefer the trivalent state in MS (note solid YS is represented by $Y^{3+}(e^-)S^{2-}$, one electron in a $3d$ conduction band) it is obvious that electron transfer to the $4d_z^2$ conduction band of the $|NbS_2|$ part may occur in $(YS)_{1.23}NbS_2$.

Acknowledgment

We thank M. Maestro (Rhone-Poulenc Company) for providing us with Y_2S_3 samples.

References

1. G. A. WIEGERS, A. MEETSMA, S. VAN SMAALEN, R. J. HAANGE, J. WULFF, TH. J. ZEINSTR, J. L. DE BOER, S. KUYPERS, G. VAN TENDELOO, J. VAN LANDUYT, S. AMELINCKX, A. MEERSCHAUT, P. RABU, AND J. ROUXEL, *Solid State Commun.* **70**(4), 409–414 (1989).
2. A. JANNER AND T. JANSSEN, *Acta Crystallogr., Sed. A* **36**, 399–415 (1980).
3. S. VAN SMAALEN, *J. Phys. Condens. Matter* **1**(7), 2791–2800 (1989).
4. B. FRENZ, "Enraf-Nonius Structure Determination package," Delft Univ. Press (1982).
5. A. MEERSCHAUT, L. GUERMA, C. AURIEL, AND J. ROUXEL, *Eur. J. Solid State Inorganic Chem.*, to be submitted.
6. H. BERGMANN, "Gmelin Handbook of Inorganic Chemistry," Vol. 39, Part C7, Springer-Verlag, Heidelberg New York (1983).
7. W. G. FISHER AND M. J. SIENKO, *Inorg. Chem.* **19**, 39–43 (1980).
8. A. MEERSCHAUT, P. RABU, AND J. ROUXEL, *J. Solid State Chem.* **78**, 35–45 (1989).
9. G. A. WIEGERS AND R. J. HAANGE, *J. Phys. Condens. Matter* **2**, 455–463 (1990).