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The Incommensurate Misfit Layer Structure of $(PbS)_{1\cdot14}NbS_2$, '$PbNbS_3$' and $(LaS)_{1\cdot14}NbS_2$, '$LaNbS_3$': an X-ray Diffraction Study

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Abstract

Single-crystal X-ray data of the mixed layer compound $La_{32}Nb_{28}S_{88}$ reported by Meerschaut, Rabu & Rouxel [*J. Solid State Chem.* (1989), **78**, 35–45] in an orthorhombic supercell, $a = 23{\cdot}216$, $b = 5{\cdot}806$, $c = 23{\cdot}031$ Å, space group *Bbcb*, were analyzed in terms of a composite crystal $(LaS)_{1\cdot14}NbS_2$, consisting of an LaS part with $a = 5{\cdot}828\,(1)$ $(\simeq 23{\cdot}216/4)$, $b = 5{\cdot}799\,(1)$, $c = 11{\cdot}512\,(2)$ $(\simeq 23{\cdot}031/2)$ Å, $Z = 4$, and an NbS_2 part with $a' = 3{\cdot}310\,(1)$ $(\simeq 23{\cdot}216/7)$, $b' = 5{\cdot}793\,(2)$, $c' = 23{\cdot}043\,(9)$ Å, $Z = 4$. Refinements, performed in space group *Cm2a* for the LaS part, and in *Fm2m* for the NbS_2 part, converged to $R_F = 0{\cdot}048$ and $0{\cdot}087$, respectively. The relative origin of the two structural units was found from the common reflections *0kl*. Reflections not belonging to the LaS or NbS_2 part are weak; they are satellites due to the mutual modulation of the sublattices. Single-crystal X-ray diffraction of $(PbS)_{1\cdot14}NbS_2$ showed the compound to be isostructural with $(LaS)_{1\cdot14}NbS_2$ disregarding the disorder of the NbS_2 sublattice in $(PbS)_{1\cdot14}NbS_2$. The two misfit layer compounds are built of alternate double layers of LaS (PbS) with La and Pb in distorted square-pyramidal coordination by sulfur (as La and Pb in a slab of half the cell edge of NaCl-type LaS and PbS) and sandwiches of NbS_2

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with Nb in trigonal prisms of S atoms (as in 2*H*-NbS_2). NbS_2 sandwiches $\frac{1}{2}c$ apart are displaced with respect to each other by over $\frac{1}{2}b$. The composition of the compounds is determined by the ratio a/a' and the number of formula units per unit cell of the two sublattices. The symmetry of the complete structure, including the effect of the mutual modulation, is analyzed in terms of a four-dimensional superspace group.

Introduction

Guemas, Rabu, Meerschaut & Rouxel (1988), Meerschaut, Rabu & Rouxel (1989), Meetsma, Wiegers, Haange & de Boer (1989), Kuypers, Van Tendeloo, Van Landuyt & Amelinckx (1989), and Wiegers, Meetsma, Haange & de Boer (1988, 1989) found recently that compounds with the assumed composition MTS_3 (M = Sn, Pb, La; T = Nb, Ta) are mixed layer compounds with real composition $(MS)_nTS_2$ (n = 1·13–1·19), built of alternate double layers of MS with M in distorted square-pyramidal coordination by sulfur and sandwiches of TS_2 as also occur in 2*H*-TS_2.

Meetsma *et al.* (1989) described the diffraction pattern of $(SnS)_{1\cdot17}NbS_2$ [designated as '$SnNbS_3$' in the literature (van Maaren, 1972)] by two unit cells and two space groups which were assigned to an SnS and an NbS_2 part of the structure. Both unit cells are *C*-centered orthorhombic with the unit-cell dimensions given in Table 1. The corresponding b and c axes are parallel and the parameters equal in length for the b and c axes, the c axes being perpendicular to the layers. The corresponding a axes are parallel, but the ratio of the lengths a/a' = 1·708 (a for SnS and a' for NbS_2) is irrational, although close to 12/7 = 1·714. The structure determination of this so-called composite crystal (Mackovicky & Hyde, 1981) consisted of three parts, *viz.* the structures of the two structural units (SnS and NbS_2) separately, using hkl and $h'k'l'$ reflections, excluding in both cases $0kl$ reflections, and their relation using the $0kl$ reflections which are common to the two structural units. Structure refinements were performed resulting in residuals (R_F) of 0·088 for the SnS part (306 unique reflections), 0·031 for the NbS_2 part (329 unique reflections) and 0·072 for 98 reflections $0kl$ (the common reflections). The composition of the compound given by the formula $(SnS)_{1\cdot17}NbS_2$ follows from the number of formula units per cell (Z = 4 for SnS and Z = 2 for NbS_2) and the ratio a/a'. The compound is built of alternate two-atom-thick slabs of SnS with Sn in distorted square-pyramidal coordination by sulfur [as in a slab of thickness half the cell edge of a (hypothetical) NaCl structure of SnS] and sandwiches of NbS_2 as also occur in 2*H*-NbS_2 (Fig. 1). One also expects, besides the reflections of the two structural units, reflections resulting from the mutual modulation of the two structural units. These extra reflections (satellites) were not observed by X-ray diffraction, but electron diffraction revealed the presence of satellites at the expected incommensurate positions (Kuypers, Van Tendeloo, Van Landuyt & Amelinckx, 1989). The incommensurate character of the structure becomes visible in the projection along the common [001] axes (Fig. 2). It seems possible to describe the structure of $(SnS)_{1\cdot17}NbS_2$ in terms of a superstructure with

Table 1. *Unit-cell dimensions* (Å) *and space groups of the sublattices of the composite crystals of* $(SnS)_{1\cdot17}NbS_2$ ('$SnNbS_3$'), $(PbS)_{1\cdot14}NbS_2$ ('$PbNbS_3$') *and* $(LaS)_{1\cdot14}NbS_2$ ('$LaNbS_3$')

		a	*b*	*c*	
'$SnNbS_3$'	SnS	5·673	5·751	11·761	*Cm2a**
	NbS_2	3·321	5·751	11·761	*Cm2m*
'$PbNbS_3$'	PbS	5·834	5·801	11·90	*Cm2a*
	NbS_2	3·313	5·801	23·80	*Cm2m*
'$LaNbS_3$'	LaS	5·828	5·797	11·52	*Cm2a*
	NbS_2	3·310	5·797	23·04	*Fm2m*

* The space group chosen by Meetsma *et al.* (1989) was *C2mb* on the basis of the lowest R_F. We now believe on the basis of superspace-group theory that the space group is *Cm2a*.

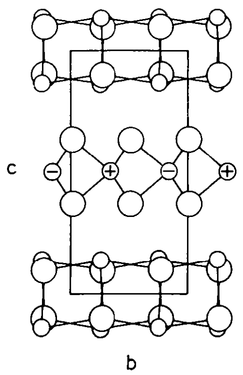

Fig. 1. The composite crystal structure of $(SnS)_{1\cdot17}NbS_2$ projected along the misfit axes; large circles are S atoms; Sn and Nb are small circles. In order to demonstrate the *C* centering of the NbS_2 lattice, Nb atoms $\frac{1}{2}a$ (NbS_2) apart are labelled by + and − symbols.

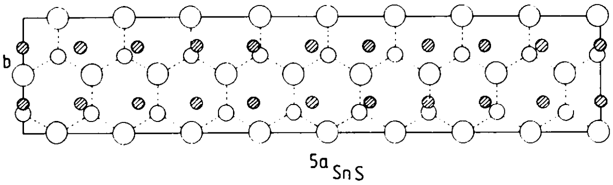

Fig. 2. Projection of the structure of $(SnS)_{1\cdot17}NbS_2$ along the c axes showing the incommensurate character of the structure. Small and large open circles are niobium and sulfur of NbS_2. S atoms of the SnS part are omitted for clarity. Hatched circles are Sn atoms.

$12a(NbS_2) \simeq a \simeq 7a(SnS)$, the satellites mentioned above being considered to be supercell reflections. Such an approach is rather artificial for $(SnS)_{1.17}NbS_2$ because one expects in that description a larger number of superreflections than observed by electron diffraction. Moreover the ratio $12/7 = 1{\cdot}714$ deviates significantly from the measured ratio 1·708 of the two *a* axes.

Meerschaut *et al.* (1989) determined the structure of $(LaS)_{1.14}NbS_2$ (in their paper designated as $La_{32}Nb_{28}S_{88}$) in an orthorhombic cell with $a = 23{\cdot}216$, $b = 5{\cdot}806$, $c = 23{\cdot}031$ Å and with space group *Bbcb* [axes used in their paper are transformed so as to correspond with those of $(SnS)_{1.17}NbS_2$ and $(PbS)_{1.14}NbS_2$]. They noticed that reflections *hkl* ($h = 4n$, $n = 0$, 1, 2, *etc.*) and reflections *hkl* ($h = 7n$, $n = 0$, 1, 2, *etc.*) are much stronger than the remaining reflections.

Single-crystal X-ray diffraction of '$PbNbS_3$' revealed the presence of a diffraction pattern given by two *C*-centered orthohombic unit cells with parallel axes (Table 1); the ratio of the *a* axes, 1·7609 (7), deviates slightly but significantly from the rational ratio $7/4 = 1{\cdot}750$. Taking, however, a supercell with $7a(NbS_2) \simeq a \simeq 4a(PbS)$ one finds a cell which agrees approximately with that of $(LaS)_{1.14}NbS_2$, indicating that the compounds might be isostructural. In this paper the structure determination of $(PbS)_{1.14}NbS_2$ and a refinement of the data of $(LaS)_{1.14}NbS_2$, both in the composite crystal approach, are reported.

Experimental

Crystals of '$PbNbS_3$' and '$LaNbS_3$' suitable for single-crystal X-ray studies could be obtained by vapor transport in a gradient of 1203 to 1073 K for '$PbNbS_3$' and 1383 to 1033 K for '$LaNbS_3$'. To about 200 mg of starting material about 5–10 mg of $(NH_4)_2PbCl_6$ was added. $(NH_4)_2PbCl_6$ decomposes at high temperature into Cl_2, $PbCl_2$ and NH_4Cl; we suppose chlorine to be the transport agent. The crystals grow at the low-temperature side of the quartz tube as thin platelets with a diameter up to 3 mm.

Structure determination of $(PbS)_{1.14}NbS_2$

Single-crystal X-ray diffraction of crystals of '$PbNbS_3$' revealed that the reflections can be indexed using two *C*-centered orthorhombic unit cells, assigned to a PbS and an NbS_2 part, with cell dimensions given in Table 1. Corresponding axes are parallel and the *c* axes are perpendicular to the crystal platelet. The *b* axes of the two units are equal in length while the *c* axis of the NbS_2 part is twice that of the PbS part of the structure. The *a* axes are the misfit axes; the ratio $a/a' = 1{\cdot}7609\,(7)$ (*a* and *a'* being of the PbS and the NbS_2 parts of the structure, respectively), is irrational but close to $7/4 = 1{\cdot}750$. Comparison with the unit-cell dimensions of $(SnS)_{1.17}NbS_2$ (Table 1) shows that the structures must be closely related. The difference concerns the lengths of the *c* axes; for $(SnS)_{1.17}NbS_2$ the lengths of the *c* axes of the NbS_2 and SnS parts are the same while for '$PbNbS_3$' the length of the *c* axis of the NbS_2 part is twice that of the PbS part. Assuming NbS_2 units and PbS units to be present, the difference with $(SnS)_{1.17}NbS_2$ being the stacking of sandwiches of NbS_2, one calculates in a similar way as for $(SnS)_{1.17}NbS_2$ the composition to be $(PbS)_{1.14}NbS_2$.

For the collection of the diffraction data, use was made of a Nonius CAD-4F diffractometer (Mo $K\bar{\alpha}$ radiation). The intensities were corrected for absorption (Spek, 1983) and for polarization and Lorentz effects. From the systematic extinctions it was deduced that the possible space groups for the PbS part are *C*2*mb*, *Cm*2*a*, *Cmmb* or equivalently *Cmma*, similar to the space groups of the SnS structure in $(SnS)_{1.17}NbS_2$. In that case the lowest R_F was obtained in *C*2*mb* with the atoms in 4(*c*): $x,\frac{1}{4},z$; but for *Cm*2*a* with the atoms in 4(*c*): $\frac{1}{4},y,z$ the R_F was only slightly larger, and almost equal to that for *Cmma*. The correct space group is therefore difficult to deduce from refinements. Van Smaalen (1989*a*) deduced from an analysis using superspace-group symmetry that the space group must be *Cm*2*a*. Refinements using the reflections of the PbS part, and excluding reflections common to both structural parts (0*kl* reflections) converged to a residual R_F of 0·062 ($wR = 0{\cdot}066$) for 357 observed reflections. Cell data, data-collection and refinement details are presented in Table 2(*a*). The coordinates and temperature factors are given in Table 3.

Inspection of the structure factors of the NbS_2 part of the structure revealed a pseudo *F* centering (reflections with the indices all odd or all even are much stronger than reflections with mixed even and odd indices), indicating that sandwiches of NbS_2 $\frac{1}{2}c$ apart are approximately related by a displacement of $\frac{1}{2}b$. Refinements performed excluding reflections 0*kl*, showed that in order to explain the occurrence of reflections with mixed indices, disorder in the niobium lattice had to be introduced, *viz.* an occupation of both trigonal prismatic sites in the sulfur lattice, maintaining the *F* centering of the sulfur lattice. This means that without disorder the NbS_2 lattice would be face centered, the space group being *Fm*2*m* with Nb at 4(*a*): $0,y,0$ with *y* chosen equal to zero (the space group lacks a center of symmetry) and S at 8(*a*): $0,y,z$; $0,y,-z$. The structure of the disordered NbS_2 lattice is described in space group *Cm*2*m* with the atoms in two sets of coordinates at special positions as given in Table 3; $R_F = 0{\cdot}085$ ($wR = 0{\cdot}093$)

Table 2. *Crystal data and details of the structure determination of* $(PbS)_{1\cdot14}NbS_2$ *and* $(LaS)_{1\cdot14}NbS_2$

(*a*) LaS, PbS parts

	$(PbS)_{1\cdot14}NbS_2$	$(LaS)_{1\cdot14}NbS_2$
Crystal data		
Crystal system	Orthorhombic	
Space group, No.	*Cm2a*, 39*	
a (Å)	5·834 (2)	5·828 (1)
b (Å)	5·801 (1)	5·799 (1)
c (Å)	11·902 (3)	11·512 (2)
V (Å^3)	402·8(1)	388·2 (4)
Z	4	4
Data collection		
Diffractometer	Enraf–Nonius CAD-4F	
Radiation (Å)	Mo $K\bar{\alpha}$, 0·71073	
Monochromator	Graphite	
Temperature (K)	298	
θ range; min., max. (°)	1·7, 35·0	2·5, 33·0
$\omega/2\theta$ scan (°)	$\Delta\omega = 1\cdot00 + 0\cdot35\tan\theta$	
Data set	h: 0→9; k: 0→9; l: −19→19	h: 0→8; k: 0→8; l: 0→17
Instability constant P	0·013	0·010
Drift correction	1·00–1·00	0·98–1·00
Min. and max. absorption correction factors	1·26–13·82	2·013–4·720
Observed data [$I \geq 2\cdot5\sigma(I)$]	443	305
Refinement		
No. of reflections $h \neq 0$	357	305
No. of refined parameters	12	12
Final agreement factors		
$R_F=\sum(\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0·062	0·048
$wR=\{\sum[w(\lvert F_o\rvert-\lvert F_c\rvert)^2]/\sum w\lvert F_o\rvert^2\}^{1/2}$	0·066	0·053
Weighting scheme	1	1
$S=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(m-n)]^{1/2}$†	5·092	3·067
Min. and max. residual densities in final difference Fourier map (e Å^{-3})	−5·34, 7·37	−2·51, 2·25
Max. (shift/σ) in final cycle	0·066	0·055
Average (shift/σ) in final cycle	0·018	0·0099

(*b*) NbS_2 part

	$(PbS)_{1\cdot14}NbS_2$	$(LaS)_{1\cdot14}NbS_2$
Crystal data		
Crystal system	Orthorhombic	
Space group, No.	*Cm2m*, 38	*Fm2m*, 42*
a (Å)	3·313 (1)	3·310 (1)
b (Å)	5·801 (1)	5·793 (2)
c (Å)	23·807 (1)	23·043 (9)
V (Å^3)	457·7(1)	443·0 (5)
Z	4	4
Data collection		
Diffractometer	Enraf–Nonius CAD-4F	
Radiation (Å)	Mo $K\bar{\alpha}$, 0·71073	
Monochromator	Graphite	
Temperature (K)	298	
θ range; min., max. (°)	0·86, 34·95	2·5, 33
$\omega/2\theta$ scan (°)	$\Delta\omega = 1\cdot20 + 0\cdot35\tan\theta$	
Data set	h: 0→5; k: 0→9; l: −38→38	h: 0→5; k: 0→8; l: 0→33
Instability constant P	0·0097	0·010
Drift correction	1·000–1·000	0·98–1·00
Min. and max. absorption correction factors	1·12–9·27	2·013–4·72
Refinement		
No. of reflections $h \neq 0$	346	161
No. of refined parameters	13	10
Final agreement factors		
$R_F=\sum(\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0·085	0·087
$wR=\{\sum[w(\lvert F_o\rvert-\lvert F_c\rvert)^2]/\sum w\lvert F_o\rvert^2\}^{1/2}$	0·093	0·108
Weighting scheme	1	1
$S=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(m-n)]^{1/2}$†	4·864	7·012
Residual electron density in final difference Fourier map (e Å^{-3})	−9·34, 13·12	−3·07, 5·44
Max. (shift/σ) in final cycle	$0\cdot876 \times 10^{-2}$	$0\cdot040 \times 10^{-2}$
Average (shift/σ) in final cycle	$0\cdot323 \times 10^{-2}$	$0\cdot18 \times 10^{-2}$

(*c*) Projection down [100]

Table 2 (*cont.*)

	$(PbS)_{1\cdot14}NbS_2$	$(LaS)_{1\cdot14}NbS_2$
Crystal data		
Space group, No.	*P*11*m*, 6*	
b (Å)	2·901 (1)	2·899 (1)
c (Å)	23·807 (6)	11·512 (2)
Z	2	1
Refinement		
No. of reflections $h = 0$, $I \geq 2\cdot5\sigma(I)$	115	70
No. of refined parameters	12	11
Final agreement factors		
$R_F=\sum(\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0·138	0·063
$wR=\{\sum[w(\lvert F_o\rvert-\lvert F_c\rvert)^2]/\sum w\lvert F_o\rvert^2\}^{1/2}$	0·142	0·079
Weighting scheme	1	1
$S=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(m-n)]^{1/2}$†	8·134	2·402
Residual electron density in final difference Fourier map (e Å^{-3})	−2·04, 1·96	−0·64, 0·33
Max. (shift/σ) in final cycle	0·0118	0·313
Average (shift/σ) in final cycle	0·0063	0·124

* *International Tables for Crystallography* (1983).

† m = No. of observations, n = No. of variables.

Table 3. *Atomic positions and temperature factors* (Å^2) *of* $(PbS)_{1.14}NbS_2$

Values are fractional coordinates with respect to the unit cell defined in Table 1. Estimated standard deviations are given in parentheses.

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_ia_j\mathbf{a}_i.\mathbf{a}_j.$$

Thermal vibration amplitudes (Å^2): $F(\mathbf{h}) = F_o(\mathbf{h})\exp[-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2$ or $F(\mathbf{h}) = F_o(\mathbf{h})\exp(-2\pi^2\sum_{i=1}^3\sum_{j=1}^3 h_ih_ja_i^*a_j^*U_{ij})$.

PbS

	x	y	z	s.o.f.*	U_{eq}
Pb(1)	$\frac{1}{4}$	0·0	0·6395 (1)	1·0	0·0302 (3)
S(1)	$\frac{1}{4}$	−0·479	0·5957 (7)	1·0	0·026 (3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}
Pb(1)	0·0475 (7)	0·0226 (6)	0·026 (5)	0·000 (4)	0·0082 (0)
S(1)	0·039 (4)	0·011 (9)	0·027 (3)	−0·005 (6)	0·0058 (0)

NbS_2

	x'	y'†	z'	s.o.f.	U_{iso}
Nb(1)	0·0	−0·0738	0·0	1·0	0·0500 (5)‡
S(3)	0·0	0·260(1)	0·0642 (4)	1·0	0·002 (1)
Nb(2)	0·0	0·423 (3)	0·5	0·691 (2)	0·017 (1)
Nb(3)	0·0	0·085 (2)	0·5	0·309 (2)	0·010 (3)
S(4)	0·0	0·758 (1)	0·5673 (6)	1·0	0·002 (1)

Common part (coordinates given in the unit cell of Table 2*c*)

	x''	y''	z''	s.o.f.	U_{eq}
Pb(1)	—	0·0	0·318 (1)	0·53 (3)	0·023 (4)
Pb(2)	—	0·0	0·179 (1)	0·53 (3)	0·022 (4)
S(1)	—	0·043	0·294 (4)	0·53 (3)	0·01 (1)
S(2)	—	0·043	0·200 (3)	0·53 (3)	0·00 (1)
Nb(1)	—	−0·147 (9)	0·0	1·0	0·003 (4)
Nb(2)	—	−0·14 (1)	0·5	0·69	0·010 (6)
Nb(3)	—	0·19 (3)	0·5	0·31	0·010 (6)
S(3)	—	0·52 (1)	0·064 (2)	1·0	0·050 (7)
S(4)	—	0·53 (2)	0·568 (3)	1·0	0·02 (1)

* Definition of s.o.f. (site-occupancy factor): average population of a site.

† The y' coordinate of Nb(1) has changed from $y' = 0$ to the value deduced from the common projection: $y' = -0\cdot0738 = \frac{1}{2}y''$; the other y' coordinates have been changed accordingly.

‡ Non-positive definite temperature factors.

for 346 observed reflections. The y' coordinates are transformed according to the result of the refinements of the common projection (0*kl* reflections), see below. Cell data, data-collection and refinement details are presented in Table 2(*b*).

The relative origin of the subsystem lattices was found from the 0*kl* reflections, which are common to both substructures. Since reflections 0*kl* occur only for *k* and *l* even (the two sublattices are *C* centered) the *b* axis can be halved. Refinements with isotropic temperature factors were performed in space group $P11m$ with Nb positions at the mirror planes at $z''=0$ and $z''=\frac{1}{2}$ and the midplane of the PbS double layer at $z''=\frac{1}{4}$ and $z''=\frac{3}{4}$. Variables were the coordinates of the atoms, except y'' of Pb and S of the PbS unit, which were kept fixed at their values from the PbS refinement, isotropic temperature factors, the scale factor and the occupancy of PbS. The final R_F was 0·138 for 115 reflections. Cell data, data-collection and refinement details are presented in Table 2(*c*). In this way the relative origin of the two sublattices was obtained. The correct y' values of the NbS_2 units, relative to Pb at $y=0$, can then be inserted in the NbS_2 table. Coordinates and temperature factors are given in Table 3.*

Structure determination of $(LaS)_{1\cdot14}NbS$ *in the composite crystal approach*

For details of the structure determination in a supercell with unit-cell dimensions $a=23{\cdot}216$, $b=5{\cdot}806$, $c=23{\cdot}031$ Å and space group *Bbcb*, we may refer to the paper by Meerschaut *et al.* (1989); the axes given here are transformed from those of Meerschaut *et al.* (1989) so as to correspond with those of $(PbS)_{1\cdot14}NbS_2$.† The data set, Tables 2(*a*–*c*), was split into (*a*) reflections $(h/4,k,l)$ [$(0kl)$ and $(28,k,l)$ excluded], (*b*) reflections $(h/7,k,l)$ [$(0kl)$ and $(28,k,l)$ reflections excluded], (*c*) reflections $(0kl)$, and (*d*) the superreflections (satellites). Accurate unit-cell dimensions (Table 2) were obtained from an indexed powder pattern (Guinier camera, Cu $K\alpha_1$ radiation). Reflections $(h/4,k,l)$ occur only for l is even while reflections $(h/7,k,l)$ show the presence of a face (F) centering (indices all even or all odd). The $(h/4,k,l)$ reflections (the LaS reflections) with the l indices halved were refined in space group $Cm2a$ with the atoms in 4(*c*) as found for the PbS part of $(PbS)_{1\cdot14}NbS_2$. The refinement proceeded smoothly to $R_F=0{\cdot}048$ ($wR=0{\cdot}053$) for 305 reflections. Reflections $(h/7,k,l)$ (the NbS_2 part of the structure), excluding $0kl$ were refined in space group $Fm2m$ with the atoms in 4(*a*) for Nb: $0,y,0$ and 8(*c*) for S: $0,y,z$; $0,y,-z$. The y coordinate of Nb was taken equal to zero to fix the origin in this acentric space group. The refinement proceeded to $R_F=0{\cdot}087$ ($wR=0{\cdot}108$) for 161 reflections.

Table 4. *Atomic positions and temperature factors* (Å^2) *of* $(LaS)_{1\cdot14}NbS_2$

Values are fractional coordinates with respect to the unit cell defined in Table 1. Estimated standard deviations are given in parentheses.

LaS

	x	y	z	s.o.f.	U_{eq}
La(1)	$\frac{1}{4}$	0	0·65268 (9)	1·0	0·0257 (3)
S(1)	$\frac{1}{4}$	0·504 (4)	0·6009 (3)	1·0	0·020 (1)

	U_{11}	U_{22}	U_{33}	U_{23}
La(1)	0·0410 (6)	0·0179 (5)	0·0181 (5)	0·004 (1)
S(1)	0·034 (2)	0·011 (1)	0·017 (1)	0·000 (6)

NbS_2

	x'	y'*	z'	s.o.f.	U_{eq}
Nb(1)	0·0	−0·0750	0·0	1·0	0·0144 (9)
S(2)	0·0	0·258 (1)	0·0679 (4)	1·0	0·018 (3)

	U'_{11}	U'_{22}	U'_{33}	U'_{23}
Nb(1)	0·025 (2)	0·004 (1)	0·015 (1)	0·0000 (< 1)
S(2)	0·025 (5)	0·010 (4)	0·018 (4)	0·001 (2)

Common part (coordinates given in the unit cell of Table 3*c*)

	x''	y''	z''	s.o.f.	U_{eq}
La(1)	—	0·0	0·659 (6)	0·48 (2)	0·014 (2)
S(1)	—	0·009	0·606 (3)	0·48 (2)	0·016 (6)
Nb(1)	—	−0·150 (3)	0·0	1·0	0·005 (2)
S(2)	—	0·517 (5)	0·1353 (9)	1·0	0·009 (3)

* The y' coordinate of Nb(1) has been changed from $y'=0$ to the value deduced from the common projection: $y'=-0{\cdot}075=\frac{1}{2}y''$. The other y' coordinates have been changed accordingly.

Afterwards, the y' coordinates were transformed according to the result of the refinement of the common projection. The common structure was found from the $0kl$ reflections, as discussed for $(PbS)_{1\cdot14}NbS_2$; the final R_F was 0·067 ($wR=0{\cdot}081$) for 70 reflections $0kl$. A peculiar feature is the very low value (0·492) of the occupancy of the LaS unit, compared to the value (0·57) from the ratio of the lengths of the misfit axes; this means an ‘experimental’ chemical formula: $(LaS)_{0\cdot98}NbS_2$. This much-lower LaS ‘content’ than expected is in agreement with the ratio of the experimental scale factors 0·9845:1 for the LaS and NbS_2 refinements respectively. The ‘theoretical’ ratio is 0·8772:1 (from the definition $F_o=K\times F_{\rm rel}$). There are two explanations: (i) there is disorder in the LaS lattice and/or an NbS_2 layer is substituted for an LaS layer, and (ii) the effect of the mutual modulation of the sublattices, which is probably strongest for the LaS lattice, the NbS_2 lattice being rigid. This modulation leads to satellites which ‘borrow’ intensity from the main reflections, the decrease probably being strongest for the LaS lattice. The solution of this problem is *outside the scope of our possibilities using conventional refinement programs* (*XTAL*). Coordinates and temperature factors for the various refinements are given in Table 4. It may be noted that the structure is completely described by tables for PbS (LaS) and NbS_2.

In all our calculations neutral-atom scattering factors (Cromer & Mann, 1968) were used with anomalous-dispersion corrections (Cromer & Liberman, 1970). The calculations were carried out on the CDC-Cyber 170/760 computer of the

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52685 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Transformation matrix:

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\rm new} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{\rm old}$$

University of Groningen with the program packages *XTAL* (Hall & Stewart, 1987) and *EUCLID* (calculation of geometric data; Spek, 1982).

Superspace-group description

Considering only the basic structure *i.e.* the structure without modulation, we have the situation where one of the subsystems (LaS) has a c axis equal to only half of the c axis of the other subsystem. That such a combination is possible is easily seen, when we consider the points common to both lattices. In reciprocal space, these common points are those with $h(\mathrm{LaS}) = h(\mathrm{NbS_2}) = 0$. From Fig. 3 it follows that the primitive lattices of both subsystems coincide in the $(0kl)$ plane. The extension of lattices in the third direction is different for the F centering and the C-centered lattice with the halved c axis. This shows that a combination of these two lattices in one compound is indeed possible.

Alternatively, it is not difficult to show that both subsystem symmetries can be derived as the subsystem space groups from a single (3 + 1)-dimensional superspace group, the latter describing the symmetry of the complete intergrowth system. Following the procedures given elsewhere (Janner & Janssen, 1980; van Smaalen, 1989*a*, 1989*b*), a (3 + 1)-dimensional superspace group for 'LaNbS$_3$' can be derived as $P^{Fm2m}_{\bar{1}\bar{1}s}(\alpha,0,0)$ with the F centering given by

$$\begin{pmatrix} \frac{1}{2}, & \frac{1}{2}, & 0, & \frac{1}{2} \\ \frac{1}{2}, & 0, & \frac{1}{2}, & 0 \end{pmatrix}.$$

The NbS$_2$ ($\nu = 1$) subsystem is obtained from

$$\begin{pmatrix} \mathbf{a}^*_{11} \\ \mathbf{a}^*_{12} \\ \mathbf{a}^*_{13} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{a}^*_1 \\ \vdots \\ \mathbf{a}^*_4 \end{pmatrix}$$

and the LaS ($\nu = 2$) subsystem follows from

$$\begin{pmatrix} \mathbf{a}^*_{21} \\ \mathbf{a}^*_{22} \\ \mathbf{a}^*_{23} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix} \begin{pmatrix} \mathbf{a}^*_1 \\ \vdots \\ \mathbf{a}^*_4 \end{pmatrix}$$

where $\{\mathbf{a}^*_1,\ldots,\mathbf{a}^*_4\}$ corresponds to the reciprocal axes in superspace, with $|\mathbf{a}^*_{21}| = |\mathbf{a}^*_4| = |\alpha\mathbf{a}^*_1| = |\alpha\mathbf{a}^*_{11}|$, and $\alpha \simeq 4/7$ expresses the incommensurability between the two subsystems, Because $\alpha \simeq 4/7$, the structure can approximately be described as periodic, with a supercell which has $7|\mathbf{a}_{11}| = |\mathbf{a}| = 4|\mathbf{a}_{21}|$. An analysis of the structure in this supercell was performed by Meerschaut *et al.* (1989). Using the space group *Bb*2*b*, however, they were not able to obtain a satisfactory agreement between calculated and observed structure factors.

In the present analysis, we have obtained an accurate decription of the basic structure, where a different unit cell is assigned to each subsystem. The supercell approach is easily derived from this description. Its space group is obtained as the maximal common subgroup of the subsystem space groups. Depending on the relative position of the subsystem lattices along **a**, one of the space groups $Bm2_1b$, *Bb*2*b* or *B*11*b* applies to the supercell. For α is commensurate only one of these groups is correct, but the others give a reasonable approximation. For α is incommensurate, the supercell space-group choice depends on which part of the structure is used for the commensurate approximation.

Now, we can understand why the analysis oι Meerschaut *et al.* (1989) gave the correct structure for the LaS part (partial $R_F = 0{\cdot}06$) but failed to describe the NbS$_2$ part ($R_F = 0{\cdot}25$). The latter has an essentially acentric structure, and can thus only be described in an acentric spacegroup, *e.g.* *Bb*2*b*. The LaS part is pseudocentrosymmetric, so that both *Bb*2*b* and *Bbcb* lead to reasonable results.

When the modulation is taken into account the situation is more complicated. Then, the subsystems themselves are modulated, and their symmetry is already given by a superspace group. Depending on α being commensurate or incommensurate, the structure can be described truly or only approximately in the supercell. The space group of the supercell must now be derived directly from the superspace group. Each element $(\mathbf{R} \in | \tau_1\tau_2\tau_3\tau_4)$ of the superspace group defines an element of the space group if $\mathbf{a}^*_4.(\tau_1,\tau_2,\tau_3) = \tau_4 (\mathrm{mod}\ 1)$ (Yamamoto & Nakazawa, 1982).

Depending on the phase of the modulation wave, as expressed by the value of τ_4 in $(2^y\bar{1} \mid 0\ 0\ 0\ \tau_4)$, we obtain for the supercell space group

$$Bm2_1b\ (\tau_4 = n/7,\ n \in \mathbb{Z})$$

$$Bb2b\ (\tau_4 = 1/14 + n/7,\ n \in \mathbb{Z})$$

$$B11b \equiv Bb\ (\tau_4 \neq n/14,\ n \in \mathbb{Z}).$$

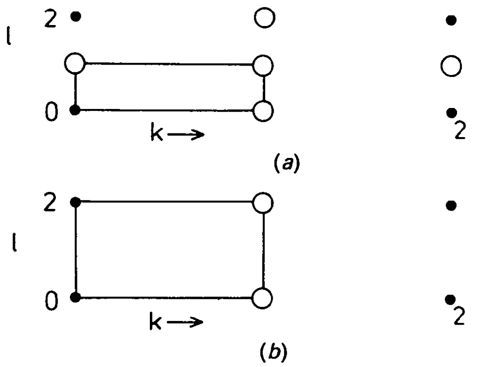

Fig. 3. The $H = 0$ plane of reciprocal space. In (*a*) and (*b*) the same primitive net is drawn, as indicated by the filled circles. Open circles denote the positions of absent reflections, in (*a*) for an F-centered lattice with c = 22 Å, and in (*b*) for a C-centered lattice with c = 11 Å.

Table 5. *Relation between the index H of superreflections HKL of* 'LaNbS$_3$' *and* h_1 *and* h_2

$H = 7h_1 + 4h_2$; values are given for combinations with minimal h_2 and minimal h_1, respectively.

	Minimal $\lvert h_2 \rvert$		Minimal $\lvert h_1 \rvert$	
H	h_1	h_2	h_1	h_2
0	0	0	0	0
1	−1	2	−1	2
2	2	−3	2	−3
3	1	−1	1	−1
4	0	1	0	1
5	−1	3	−1	3
6	2	−2	2	−2
7	1	0	1	0
8	0	2	0	2
9	3	−3	−1	4
10	2	−1	2	−1
11	1	1	1	1
12	0	3	0	3
13	3	2	−1	5
14	2	0	2	0
15	1	2	1	2
16	4	−3	0	4
17	3	−1	−1	6
18	2	1	2	1
19	1	3	1	3
20	4	−2	0	5
21	3	0	−1	7
22	2	2	2	2
23	5	−3	1	4
24	4	−1	0	6
25	3	1	−1	8
26	2	3	2	3
27	5	−2	1	5
28	4	0	0	7

Examples: 'superreflection' $1KL$ is a combination of first- and second-order satellites [first order (−1) satellite of an LaS reflection with $h_2 = 2$ and a second-order satellite of an NbS$_2$ reflection with $h_1 = -1$]. $13KL$ is a superposition of satellites of first, second, third and fifth order. It is also seen that a main reflection of one lattice may overlap with satellites of its own lattice and satellites of the other main lattice; *e.g.* $20KL$ is a main ($h_2 = 5$) reflection of the LaS lattice, a fourth-order satellite of the LaS lattice with $h_2 = -2$ and a second-order satellite of the NbS$_2$ lattice with $h_1 = 4$.

As for the basic structure, when $\alpha = 4/7$ is commensurate, the true three-dimensional structure depends on the value of τ_4 (van Smaalen, 1987). Then, the structure analysis must indicate which value of τ_4 applies to the structure, and which three-dimensional space group gives the symmetry. When α is incommensurate, the structure is independent of τ_4. For each supercell space group a value of τ_4 exists, such that this space group approximately describes the symmetry of the structure around the origin. However, to determine all components of the incommensurate modulation wave, τ_4 must be chosen such that the symmetry is given by *Bb*.

The complete structure can be described as an intergrowth of two incommensurately modulated subsystems. The diffraction pattern, however, cannot be dissected that easily into two parts arising from different subsystems. This problem has already been encountered for the basic structure, for which we have seen that the ($0kl$) reflections are common to both systems. When the modulation is taken into account, this problem is even more profound, as is shown below.

The position of each satellite can be described by four integers ($h_1\ k\ l\ h_2$), where h_1 pertains to $\mathbf{a}^*$ of the NbS$_2$ subsystem, and h_2 corresponds to $\mathbf{a}^*$ of LaS (or PbS). The corresponding indexing with respect to the supercell is obtained as (HKL), with $K = k$, $L = l$, and $H = 7h_1 + 4h_2$. For a given position (HKL), *i.e.* a given H, this latter relation has infinitely many combinations (h_1, h_2) as solutions.

Considering only one such combination, we see that, like the ($0KL$) reflections, each reflection has a contribution from both subsystems. The intensity is given by $I = |F_1 + F_2|^2$, for F_ν the structure factor of subsystem ν. As F_ν ($h_1\ k\ l\ h_2$) decreases rapidly for increasing order of the satellite, $m_1 = h_2$ or $m_2 = h_1$, often one of the contributions can be neglected. Then, the measured intensity can be used to determine the structure of a single subsystem. For example for $H = 8$, (h_1, h_2) = (0, 2), the $h = 2$ main reflection of LaS is also a second-order satellite of the NbS$_2$ subsystem. That contributions of the latter type can be neglected in good approximation is validated by the results obtained in this paper.

For α is commensurate, for each H only one combination of (h_1, h_2) should be used. Then the supercell approach and the modulated structure approach can be used equivalently.

However, for $\alpha = 4/7$ is incommensurate, the different combinations of (h_1, h_2) indicate different reflections (satellites), which have slightly different positions. The measured intensity is now obtained as the sum of intensities of the different (h_1, h_2). Again, when one combination is of higher order than all others, only one reflection will contribute, and can thus be used to represent the experimental intensity. This assumption also underlies the work in this paper, *e.g.* the $h = 6$ main reflection of LaS ($H = 24$) coincides with the $h = 4$, $m = -1$ satellite of NbS$_2$ (Table 5). On the other hand, this may hamper the determination of the modulation. In particular, most of the first-order satellites of NbS$_2$ are either reflections of equal or lower order in LaS too ($H = 3$, 4, 11) or coincide with a reflection of equal or lower order in LaS ($H = 17$, 24, 25). Only the reflections with $H = 10$ and 18 can be approximated as pure NbS$_2$ satellites.

A direct application of the supercell approach is not possible now, because sometimes a sum of structure factors must be used ($H = 0$, 3, 6, 11, 22), but for other reflections the measured intensity is a sum of intensities ($H = 17$, 25, 28) (Table 5).

In the preceding paragraphs we have shown that the structure can be described both in the modulated structure approach (superspace group) and in a supercell. For α is commensurate, both approaches are correct. For α is incommensurate, only the superspace group gives an exact description of the structure. Although the structure can thus always (approximately) be described in a supercell, the superspace-group approach has several advantages.

It allows for a natural division of the structure into a basic structure and a relatively small deviation from it (the modulation). To describe the basic structure only a few parameters are needed (six positional parameters, for LaS and NbS_2 combined). They can be easily determined, as is described in this paper. The determination of the modulation can be deferred to a later stage. A description is possible with as many harmonics (first-order harmonic, second-order harmonic, *etc.*) available as satellite orders (first-order satellites, second-order satellites, *etc.*) of reflection data. In the supercell approach, there is no way to subdivide the structural parameters into a more important set and a less important set. All parameters need to be determined at one time, which can be very difficult for supercells of increasing size. For '$LaNbS_3$', Meerschaut *et al.* (1989) needed 32 positional parameters, with the incorrect supercell space group *Bbcb*. For the correct group, *Bb*2*b*, even more parameters will be needed. Furthermore, the superspace group may give more symmetry than is described by the supercell space group, thus also leading to a reduction of the number of parameters.

When we consider the determination of a structure by means of a diffraction method, the composite crystal approach is even more favored. For α is incommensurate, as we assume here, the intensity at a certain point *HKL* can be either $|F_1|^2 + |F_2|^2$, or $|F_1 + F_2|^2$, or $|F_\nu|^2$, as was explained above. In the superspace-group approach this is described correctly. However, in a straightforward application of the supercell description, the intensity will always be obtained as the square of the sum of structure factors.

Discussion of the structures of $(\mathrm{PbS})_{1\cdot14}\mathrm{NbS}_2$ and $(\mathrm{LaS})_{1\cdot14}\mathrm{NbS}_2$

A projection of the PbS (LaS) structure along the [001] axis is shown in Fig. 4. It is seen that there are two-atom-thick layers of PbS (LaS) with the Pb (La) atoms sticking somewhat out of the planes of sulfur.

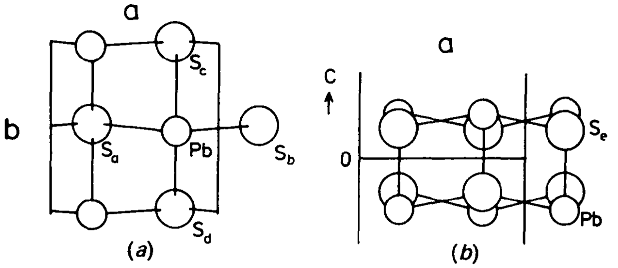

Fig. 4. (*a*) Projection of the LaS (PbS) part of the structure along [001]. Large and small circles are sulfur and lanthanum (lead) respectively; only the upper half of the double layer is indicated for sake of clarity; (*b*) projection along [010].

Table 6. *M—S* (*M* = Pb, La) *and* NbS *distances* (Å)

	$(\mathrm{PbS})_{1\cdot14}\mathrm{NbS}_2$	$(\mathrm{LaS})_{1\cdot14}\mathrm{NbS}_2$
M—S_a	2·966 (2)	2·963 (2)
M—S_b	2·966 (2)	2·963 (2)
M—S_c	3·07 (4)	2·99 (2)
M—S_d	2·82 (4)	2·94 (2)
M—S_e	2·802 (9)	2·921 (5)
Nb_1—S_{1a}	2·470 (8) (× 2)	2·487 (8) (× 2)
Nb_1—S_{1b}	2·450 (7) (× 4)	2·475 (6) (× 2)
Nb_2—S_{2a}	2·52 (2) (× 2)	
Nb_2—S_{2b}	2·49 (1) (× 4)	

Note: (1) The numbering of atoms refers to Figs. 4 and 5. (2) The Nb_2—S_2 distances of $(\mathrm{LaS})_{1\cdot14}\mathrm{NbS}_2$ are equal to the corresponding distances Nb_1—S_1, the lattice being *F* centered.

Each Pb (La) atom is coordinated to five S atoms approximately on the corners of a square pyramid; four Pb—S (La—S) bonds are approximately in the plane parallel to (001); the fifth Pb—S (La—S) bond is approximately parallel to [001]; distances are given in Table 6. Such a double layer can be made from NaCl-type PbS (a = 5·936 Å) and LaS (a = 5·854 Å) by cutting a slice parallel to the cell edge, the thickness of the slice being half the cell edge. A similar arrangement of SnS is present in $(\mathrm{SnS})_{1\cdot17}\mathrm{NbS}_2$.

The NbS_2 structure is for both structures essentially the same as in 2*H*-NbS_2, Nb atoms being in slightly distorted trigonal prisms of sulfur. The *a* and *b* axes of the NbS_2 part agree almost with the orthohexagonal axes of 2*H*-NbS_2, a = 3·324, $b = a\surd3$ = 5·757 Å. Sandwiches of NbS_2, $\frac{1}{2}c$ apart, are displaced over $\frac{1}{2}b$ in $(\mathrm{LaS})_{1\cdot14}\mathrm{NbS}_2$; in $(\mathrm{PbS})_{1\cdot14}\mathrm{NbS}_2$ owing to disorder of only the niobium part of the structure, a strict face centering is not present. The Nb—S distances in both compounds are given in Table 6; they are close to those found in $(\mathrm{SnS})_{1\cdot17}\mathrm{NbS}_2$ (2·473 Å) (Meetsma *et al.*, 1989). As already noted, the Pb and the La atoms are outside the layers of sulfur of PbS and LaS; the shortest interactions between PbS (LaS) and NbS_2 sandwiches are therefore between Pb (La) and S atoms of NbS_2, not between S atoms as occurs in 2*H*-NbS_2. The weak bonding interaction between S atoms of neighboring sandwiches in 2*H*-NbS_2 is therefore replaced by a pseudo van der Waals gap with probable bonding interactions. It is therefore possible to designate these compounds as 'coordination complexes'. Projections of the NbS_2 sandwich are shown in Fig. 5. A projection of the complete structure of $(\mathrm{LaS})_{1\cdot14}\mathrm{NbS}_2$ is shown in Fig. 6.

It may be remarked that the structures found in this way are average structures because the modulation has not been taken into account. The effect of neglecting the modulation is already visible in the exceptionally high values of the temperature factor U_{11} (along the *a* axis) of PbS and LaS. The compound $(\mathrm{LaS})_{1\cdot20}\mathrm{CrS}_2$ was the first compound found with a misfit layer structure containing a transitionmetal dichalcogenide (Kato, Kawada & Takahashi, 1973; Otero-Diaz, FitzGerald, Williams & Hyde, 1985; Williams & Hyde, 1988). $(LaS)_{1\cdot20}CrS_2$ is built of double layers of LaS [as LaS in $(LaS)_{1\cdot14}NbS_2$] and sandwiches of CrS_2 with Cr in distorted octahedral coordination. The *c* axis is not perpendicular to the layers. Compounds Ln*M*S$_3$ (Ln some rare earths, *M* = V, Cr) reported by Murugesan *et al.* (Murugesan, Ramesh, Gopalakrishnan & Rao, 1981) probably have the same or a strongly related structure.

A new type of stacking of alternate layers of PbS and TaS_2 was found for the compound $(PbS)_{1\cdot13}TaS_2$; in this case both lattices PbS and TaS_2 are *F*-centered orthorhombic (Wulff, Haange, van Smaalen, de Boer, Meetsma & Wiegers, 1990). Ta atoms are in distorted trigonal prisms of sulfur with Ta—S distances of 2·524 (4) (×2) and 2·443 (3) (×4) Å.

The electrical transport and magnetic properties of $(SnS)_{1\cdot17}NbS_2$ are those of intercalated 2*H*-NbS$_2$ (Wiegers *et al.*, 1989), indicating that the interaction between the SnS and the NbS_2 part of the structure is of the donor–acceptor type in which the SnS part acts as an electron donor. Similar properties were found for $(PbS)_{1\cdot14}NbS_2$ (Wiegers *et al.*, 1988) and $(PbS)_{1\cdot13}TaS_2$ (Wulff *et al.*, 1990). The electrical transport properties of $(LaS)_{1\cdot14}NbS_2$ show a much larger donation of electrons in agreement with trivalent La (Wiegers & Haange, 1990).

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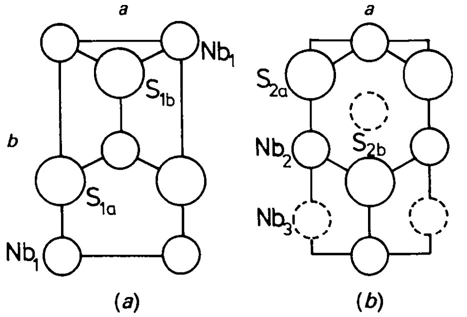

Fig. 5. (*a*) Projection along [001] of the NbS_2 sandwich with *z* of Nb equal to 0; (*b*) the NbS_2 sandwich with *z* of Nb equal to $\frac{1}{2}$. The interstitial Nb sites at $z = \frac{1}{2}$ [found for $(PbS)_{1\cdot14}NbS_2$] are indicated by dotted circles.

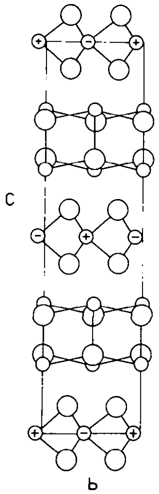

Fig. 6. Projection of the complete structure of $(LaS)_{1\cdot14}NbS_2$ along the misfit [100] axes. In order to demonstrate the *F* centering of the NbS_2 lattice Nb atoms (at $z = 0$ and $z = \frac{1}{2}$) in the same parallel plane (100) have the same symbol (+ or −); atoms $\frac{1}{2}a$ of NbS_2 apart have a different symbol.

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