

Vacancies and Electron Localization in the Incommensurate Intergrowth Compound (La_{0.95}Se)_{1.21}VSe₂

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Abstract

The structure of the inorganic misfit layer compound (La_{0.95}Se)_{1.21}VSe₂ has been determined on the basis of a four-dimensional superspace group. The crystal is composed of an alternate stacking of VSe₂ sandwiches and two-atom-thick LaSe layers. The first subsystem VSe₂ has a distorted CdI₂-type structure with V atoms in trigonal antiprisms of Se atoms. It has space-group symmetry $C\bar{1}$ and its basic structure unit-cell dimensions are $a_{11} = 3.576(3)$, $a_{12} = 6.100(2)$, $a_{13} = 11.690(2)$ Å, $\alpha_1 = 95.12(2)$, $\beta_1 = 85.96(2)$ and $\gamma_1 = 89.91(2)^\circ$. The second subsystem LaSe has a distorted rock-salt structure with space-group symmetry $C\bar{1}$ and a basic structure unit cell given by $a_{21} = 5.911(2)$, $a_{22} = 6.101(2)$, $a_{23} = 11.684(2)$ Å, $\alpha_2 = 95.07(2)$, $\beta_2 = 85.76(2)$, $\gamma_2 = 90.02(2)^\circ$. The two subsystems have the common (\mathbf{a}_{v2}^* , \mathbf{a}_{v3}^*) plane and have a displacive modulation according to the two mutually incommensurate periodicities along the \mathbf{a}_{v1} axes. The symmetry of the complete system is described by the superspace group $G_s = C\bar{1} [0.6050(7), 0.0020(7), -0.007(1)]$ with C -centring $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$. Reciprocal lattice parameters for this superstructure embedding are $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*) = (\mathbf{a}_{11}^*, \mathbf{a}_{12}^*, \mathbf{a}_{13}^*, \mathbf{a}_{21}^*)$. For 2125 unique reflections with $I > 2.5\sigma(I)$, measured using Mo $K\alpha_1$ radiation, refinement smoothly converged to $wR = 0.055$ ($R = 0.045$) on a modulated structure model with 77 parameters including La vacancies. The presence of $\sim 5\%$ of La vacancies in the LaSe subsystem leads to an exact charge balance between La³⁺, V³⁺ and Se²⁻. The largest modulation occurs on the V atoms, which results in strong variation in the V–V distances. Thus, the semiconducting behaviour of this compound is interpreted in terms of La vacancies in LaSe and modulation-induced Mott localization in VSe₂.

1. Introduction

The inorganic rare-earth misfit layer compounds of composition $(MX)_{1+\delta}(TX_2)_n$ (with $M = \text{Sn, Pb, Bi, Sb}$ or rare-earth elements; $T = \text{Nb, Ta, Ti, V, Cr}$; $X = \text{S or Se}$; $0.09 < \delta < 0.25$; $n = 1$ or 2) form one special class of the incommensurate intergrowth compounds (Wiegiers & Meerschaut, 1992). The structure consists of an alternat-

ing stacking sequence of double layers MX with a distorted rock-salt structure and pseudo-hexagonal TX_2 layers with a NbS₂ or TiS₂ type of structure. They can also be regarded as a special class of transition-metal dichalcogenide intercalation compounds, where double layers MX are inserted into the van der Waals gaps of the MX_2 sandwiches. The complete structure can be described by assigning different unit cells to the MX and TX_2 layers. In the plane of the layer each subsystem is characterized by two lattice parameters, \mathbf{a} and \mathbf{b} . Thus far it has always been found that the two subsystems have common reciprocal translation \mathbf{b} and \mathbf{c} and thus the two \mathbf{a} axes are parallel, but the ratio of length is often an irrational number which gives rise to an incommensurate structure for the complete system. In general, the chemical formula $(MX)_{1+\delta}(TX_2)_n$ is determined by the ratio of the lengths of the two \mathbf{a} axes.

The first approach to the structure of the misfit layer compounds with $T = \text{Ti, V or Cr}$ was carried out on 'LaCrS₃', using a supercell description with a large lattice parameter along the incommensurate direction of the two sublattices [so that 72 LaS matches 60 CrS₂ (Kato, Kawada & Takahashi, 1977)]. Their structure model rationally involves considerable disorder on the La sites: 5.5% of the La sites are unoccupied and another 5.5% wrongly occupied by the Cr cations, in order to reach a stoichiometric phase LaCrS₃. However, later this was queried and a structure refinement on the same X-ray data of Kato *et al.* (1977) converged to a significantly lower R value for the model with full occupancy on the La sites (Otero-Diaz, FitzGerald, Williams & Hyde, 1985). The structure of 'LaCrS₃' was re-determined by Kato (1990) using a superspace-group approach. This suggests that gross cation disorder is not present and the phase is close in composition to (LaS)_{1.2}CrS₂. However, there is recently a doubt of the exact stoichiometry of the MX subsystem in the rare-earth misfit layer compounds $(MX)_{1+\delta}CrX_2$ with $M = \text{lanthanides}$ (Rouxel, Moëlo, Lafond, Di Salvo, Meerschaut & Roesky, 1994), because these phases exhibit semiconducting behaviour, instead of a metallic one as expected from a contribution of the MX layers (Kondo, Suzuki & Enoki, 1992; Suzuki, Kondo, Enoki & Bandow, 1993). Investigations on the compounds 'LaCrS₃', 'GdCrS₃' and 'YCrS₃' by Rouxel

et al. (1994) showed that the LnS layers can support a large number of cation vacancies and an exact charge balance exists between trivalent Ln and Cr and divalent S. In this paper we report the structure determination of a misfit layer compound $(\text{LnX})_{1+\delta}\text{VX}_2$, viz. $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$, using a (3+1)-dimensional superspace description.

2. Experimental

A mixture of the elements La, V and Se, in the ratio expected for a misfit layer compound with $\delta = 0.20$, was sealed in an evacuated quartz ampoule and heated in a single-zone furnace at 673 K for 1 d. The reaction temperature was then slowly increased and kept at 1373 K for 2 weeks. The mixture was resealed in a quartz tube with a small amount of iodine for mineralization, heated at 1373 K for 1 week and slowly cooled to room temperature. The product consisted of binary selenides and crystals of the desired phase. Attempts to prepare crystals by vapour transport were not successful.

A single crystal of dimensions ca $0.12 \times 0.15 \times 0.03 \text{ mm}^3$ was selected for X-ray diffraction experiments. Weissenberg photographs of the crystal clearly showed reflections due to two subsystems with common \mathbf{b}^* , \mathbf{c}^* reciprocal lattice vectors. Both subsystems are C-centred triclinic. Single-crystal X-ray diffraction was performed on an Enraf-Nonius CAD-4F diffractometer with monochromatized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Unit-cell dimensions and their standard deviations (Table 1) were determined, independently for each subsystem, from the setting angles in four alternate setting of 23 reflections in the range $26 < \theta < 28^\circ$ for VSe_2 and 25 reflections in the range $14 < \theta < 28^\circ$ for LaSe. The composition of this compound was calculated as $(\text{LaSe})_{1.21}\text{VSe}_2$ from the ratio of $2a_{11}/a_{21}$, equal to the volume ratio $2V_1/V_2$, of the two subsystems.

The intensity data were separately collected by the θ - 2θ scan technique at the nodes of the reciprocal lattices based on the two sets of unit-cell dimensions. All main reflections were measured in one hemisphere up to $\theta = 35^\circ$; no satellite reflections of the mutual modulation were measured. The stability was checked by the standard reflections $(\bar{1}34)$, (134) and (008) for VSe_2 and (240) , $(\bar{2}40)$ and (008) for LaSe measured every 2 h of X-ray exposure time. It showed a long-term variation of less than 2%. The intensities were corrected for scale variation, Lorentz and polarization effects, and for absorption ($\mu = 345 \text{ cm}^{-1}$) using a Gaussian integration method (Spek, 1983). After averaging equivalent reflections using Laue symmetry $\bar{1}$, the two data sets of 1105 reflections for VSe_2 and 1817 reflections for LaSe were brought together to the same scale, using 125 common reflections $(0kl)$ with $l > 2.5\sigma(l)$ which are present in both sets. The internal consistency is $R_I = 0.015$. The result was a single data set for the complete structure

Table 1. Unit-cell dimensions of the VSe_2 and LaSe subsystems

Subcell	ν	a_{v1} (Å)	a_{v2} (Å)	a_{v3} (Å)	α_v (°)	β_v (°)	γ_v (°)
VSe_2	1	3.576 (3)	6.100 (2)	11.690 (2)	95.12 (2)	85.96 (2)	89.91 (2)
LaSe	2	5.911 (2)	6.101 (2)	11.684 (2)	95.07 (2)	85.76 (2)	90.02 (2)

with 2784 unique reflections. Refinements on this data set were carried out with the computer program system JANA93 (Petricek, 1993). Plots of the interatomic distances and bond valences as functions of the external coordinates t have been made with the program MISTEK (van Smaalen, 1991a).

3. Superspace-group symmetry

In order to index the complete diffraction pattern, four integers H, K, L and M are used, based on four reciprocal vectors, $\mathbf{M}^* = (\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*, \mathbf{a}_4^*)$, where \mathbf{a}_2^* and \mathbf{a}_3^* are the common reciprocal lattices \mathbf{b}^* and \mathbf{c}^* , and \mathbf{a}_1^* and \mathbf{a}_4^* are reciprocal to \mathbf{a} of the VSe_2 and LaSe parts, respectively. Superspace is obtained by identification of the four base vectors of \mathbf{M}^* with the perpendicular projection of four independent translation vectors in a (3+1)-dimensional space (Janner & Janssen, 1980). The fourth vector of \mathbf{M}^* can be expressed in terms of the first three by a matrix σ , which defines the incommensurability of the two reciprocal \mathbf{a}^* axes

$$\sigma = (\sigma_1, \sigma_2, \sigma_3) = [0.6050(7), 0.0020(7), -0.007(1)]. \quad (1)$$

The subsystem reciprocal lattices Λ_v^* , together with the subsystem modulation wavevector \mathbf{q}_v for VSe_2 ($\nu = 1$) and LaSe ($\nu = 2$), are related to the four basis vectors of \mathbf{M}^* through the matrices W^ν (van Smaalen, 1991b)

$$\begin{pmatrix} \mathbf{a}_{v1}^* \\ \mathbf{a}_{v2}^* \\ \mathbf{a}_{v3}^* \\ \mathbf{q}_v \end{pmatrix} = W^\nu \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{a}_2^* \\ \mathbf{a}_3^* \\ \mathbf{a}_4^* \end{pmatrix}, \quad (2)$$

with

$$W^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad W^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}. \quad (3)$$

The W^ν matrices define a coordinate transformation between the superspace with respect to \mathbf{M}^* and each subsystem superspace with respect to Λ_v and \mathbf{q}_v . For instance, they give the relation between the reflection indices (H, K, L, M) on \mathbf{M}^* and the subsystem indices $(h_\nu, k_\nu, l_\nu, m_\nu)$ corresponding to Λ_ν and \mathbf{q}_ν

$$(H, K, L, M) = (h_\nu, k_\nu, l_\nu, m_\nu)W^\nu. \quad (4)$$

Table 2. Reliability factors for the refinements REF-a, REF-m, REF-i and REF-f in (3 + 1)-dimensional superspace

The R factors are defined as $R = \Sigma |F_{\text{obs}}| - |F_{\text{calc}}| / \Sigma |F_{\text{obs}}|$ and $wR = [\Sigma w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \Sigma w |F_{\text{obs}}|^2]^{1/2}$, with weights $w = 1/[\sigma^2(F_{\text{obs}} + 0.01|F_{\text{obs}}|)^2]$. Partial R factors are defined with a subset of the reflections.

Reflection subset	Number of reflections	REF-a	REF-m	R/wR	REF-i	REF-f
All	2125	0.0986/0.1400	0.0470/0.0580		0.0465/0.0557	0.0454/0.0547
VSe ₂	684	0.1515/0.1891	0.0480/0.0565		0.0479/0.0565	0.0478/0.0565
LaSe	1316	0.0819/0.1176	0.0480/0.0559		0.0479/0.0555	0.0463/0.0535
Common	125	0.0411/0.0807	0.0363/0.0749		0.0325/0.0547	0.0320/0.0566

a: the average structure; m: the modulated structure; i: the modulated structure, including both La and Se vacancies; f: the modulated structure, including only La vacancies.

For both subsystems, the basic structures have triclinic symmetry. Systematic extinction conditions were found for the (H, K, L, M) reflections as $H + K + M = \text{odd}$ are absent. It implies a C -centring translation

$$\left(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}\right). \quad (5)$$

For a centrosymmetric triclinic structure, there is one possible superspace group

$$G_s = C\bar{1}(\sigma_1, \sigma_2, \sigma_3), \quad (6)$$

with the symbol C representing the centring translation as given by (5). With the coordinate transformations given by W^v , each subsystem superspace group can be derived as (van Smaalen, 1991b)

$$G_s^1 = G_s \text{ and } F_s^2 = C\bar{1}(\sigma_1^{-1}, -\sigma_1^{-1}\sigma_2, -\sigma_1^{-1}\sigma_3) \\ = C\bar{1}[1.653(2), -0.003(1), 0.011(2)]. \quad (7)$$

The space group describing the symmetry of the basic structure of each subsystem can be obtained as the restriction of G_s^v to three-dimensional physical space: $G_1 = G_2 = C\bar{1}$, with C representing the normal C -centring translation $(\frac{1}{2}, \frac{1}{2}, 0)$.

4. Structure refinement

A starting model for the refinement was the structure of 'LaCrS₃' given by Kato (1990). Least-squares refinement was first performed on a structure model without modulation. Scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). The structure is composed of VSe₂ sandwiches with V in distorted octahedra of Se and double layers of LaSe with a distorted rock-salt-type structure. In the basic structure V is located at the special position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$. The coordinates of the other atoms together with anisotropic temperature factors for all atoms were refined; smooth convergence resulted in a fit with a large R factor: $R = 0.1432$ ($wR = 0.2191$), although the partial R factors for the common reflections OKLO were acceptable: $R(\text{common}) = 0.0409$ [$wR(\text{common}) = 0.0809$]. Inspection of the reflection list showed that the largest ΔF values occurred for the reflections (h_1, k_1, l_1) of VSe₂, with $h_1 = 3n$, and (h_2, k_2, l_2)

of LaSe, with $h_2 = 5n$ ($n = \text{integers}$), and that the measured intensities are larger than those calculated. It reminded us that the reflections $(3n, K, L, 0)$ and $(0, K, L, 5n)$ probably overlap, because of the almost commensurate value of $a_{11}^*/a_{21}^* \approx 5/3$. Therefore, further refinement was performed excluding these overlapping reflections and the R factors were easily lowered to $R = 0.0986$ and $wR = 0.1400$; the partial R factors for each subset of reflections are given in column REF-a in Table 2. However, the agreement was still not fully satisfactory.

The large R factors for the average structure can be understood, because in the rare-earth misfit layer compounds the mutual modulation is much stronger than that in the Sn, Pb, Sb and Bi misfit layer compounds. Thus, in the next stage of the refinement each subsystem is considered to be displacively modulated with the mutual modulation wavevector given by the periodicity along the \mathbf{a}^* axis of the other subsystem. Although the satellite reflections with both H and M non-zero were not measured, the intensities of the main reflections of both subsystems can be used to determine the modulation parameters.

In the modulated structure model the coordinates of atom μ of subsystem v in the superspace section t can be expressed with respect to its own subsystem lattice Λ_v (van Smaalen, 1991a,b)

$$x_{vi}^\mu = \bar{x}_{vi}^\mu + u_{vi}^\mu(\bar{x}_{v34}), \quad (8)$$

for $v = 1, 2$ and $i = 1, 2, 3$, and with the basic structure coordinates \bar{x}_{vi} given by

$$\begin{aligned} \bar{x}_{1i}^\mu &= n_{1i} + x_{1i}^0(\mu) & i = 1, 2, 3; \\ \bar{x}_{21}^\mu &= n_{21} + x_{21}^0(\mu) - t, \\ \bar{x}_{2i}^\mu &= n_{2i} + x_{2i}^0(\mu) & i = 2, 3, \end{aligned} \quad (9)$$

where n_{vi} are integers and $x_{vi}^0(\mu)$ the coordinates of atom μ with respect to the subsystem unit cell. The modulation functions with periodicity *one* in their arguments \bar{x}_{v34} can be expressed as Fourier series

$$u_{vi}^\mu(\bar{x}_{v34}) = \sum_{n=1}^{\infty} [A_{ni}^\mu \sin(2\pi n \bar{x}_{v34}) + B_{ni}^\mu \cos(2\pi n \bar{x}_{v34})]. \quad (10)$$

The Fourier amplitudes A_{ni}^{μ} and B_{ni}^{μ} , up to second order, were used in the refinement as structural parameters. Symmetry restrictions on the modulation functions of V at the special position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ were obtained as: $A_{ni} = 0$ for $n = \text{odd}$ and $B_{ni} = 0$ for $n = \text{even}$. Refinement of the modulated structure, based on the main reflections excluding those overlapped, showed a dramatic improvement of the overall R value from 0.0986 to 0.0470. The largest improvement occurs for VSe_2 from $R = 0.1515$ to 0.048. The partial R factors are listed in column REF-m of Table 2.

In the last stage of the structure refinement possible vacancies in the LaSe layers were dealt with, since the LaSe part might support a large number of defects as was found in the compound 'GdCrS₃' (Rouxel *et al.*, 1994). A vacancy model concerning both La(2) and Se(2) vacancies with the same ratio gave a slightly lower R value of 0.0465 compared with 0.0470 (the partial R factors are listed in column REF-i of Table 2) and resulted in a composition of $(\text{LaSe})_{1.16}\text{VSe}_2$. However, refinement of a vacancy model with only La vacancies offered a better fit with the lowest R factor of 0.0454; standard deviations for all refined parameters are better than those obtained from other refinements. The partial R factors are summarized in column REF-f of Table 2. This final structural model consists of ca 5% La vacancies in the LaSe subsystem [occupancy of La being 0.951 (3)], indicative of a true composition of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$. The basic coordinates, temperature factors and modulation parameters are listed in Tables 3–5.*

5. Discussion

The complete structure of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ is projected along the [100] direction in Fig. 1, which shows the characteristic arrangement of the two subsystems for the misfit layer compounds. The rows of La, parallel to the incommensurate \mathbf{a}_{v1} axes, just fall in the middle of the valleys of the Se(1) rows of the VSe_2 part. In this way the two \mathbf{b} axes match each other and the La atoms can reach the maximal possible coordination by Se, depending on the actual position along the mismatched direction. Selected interatomic distances for the modulated structure, calculated using the fitted parameters of Table 3 and 5, are summarized in Table 6.

In the LaSe subsystem each La atom is coordinated by five Se(2) atoms. The La atoms protrude towards VSe_2 from the Se(2) planes on both sides of the LaSe double layers, due to the inter-subsystem interaction. The out-of-plane distortion of LaSe along the \mathbf{c} direction in the basic

Table 3. Basic atomic coordinates and site occupancy factor (s.o.f.) as obtained from the final refinement REF-f in $(3+1)$ -dimensional superspace of the modulated structure

Coordinates refer to the subsystem lattice bases.

Atom	ν	x_{v1}^0	x_{v2}^0	x_{v3}^0	s.o.f.
V(1)	1	0.25	0.25	0.5	1
Se(1)	1	0.2809 (2)	0.56279 (8)	0.37186 (5)	1
La(2)	2	-0.02388 (8)	0.27649 (7)	0.16373 (4)	0.951 (3)
Se(2)	2	-0.0147 (1)	0.7666 (1)	0.10087 (6)	1

structure can be quantified by the following dimensionless parameter ϵ_o , similar to a spontaneous strain scale

$$\epsilon_o = 2 \frac{\Delta^+ - \Delta^-}{\Delta^+ + \Delta^-}, \quad (11)$$

where Δ^+ and Δ^- are, respectively, the average distance from La and Se(2) perpendicular to the midplane of the LaSe double layers. It is found that the distortion parameter ϵ_o is much larger for the rare-earth misfit layer compounds than for the Sb and Bi compounds, *e.g.* $\epsilon_o = 0.4751$ (8) and 0.447 (2) for $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ and $(\text{LaS})_{1.19}\text{CrS}_2$ (Kato, 1990), respectively, in comparison to $\epsilon_o = 0.221$ (7) and 0.210 (2) for $(\text{SbS})_{1.15}\text{TiS}_2$ (Ren, Meetsma, Petricek, van Smaalen & Wiegiers, 1995) and $(\text{BiSe})_{1.09}\text{TaSe}_2$ (Petricek, Cisarova, de Boer, Zhou, Meetsma, Wiegiers & van Smaalen, 1993), respectively. The out-of-plane distortion of Sn and Pb compounds is intermediate, *e.g.* with $\epsilon_o = 0.333$ (9) for $(\text{SnS})_{1.17}\text{NbS}_2$ (Meetsma, Wiegiers, Haange & de Boer, 1989) and $\epsilon_o = 0.320$ (9) for $\text{O}(\text{PbS})_{1.18}\text{TiS}_2$ (van Smaalen, Meetsma Wiegiers & de Boer, 1991). This quantity ϵ_o ,

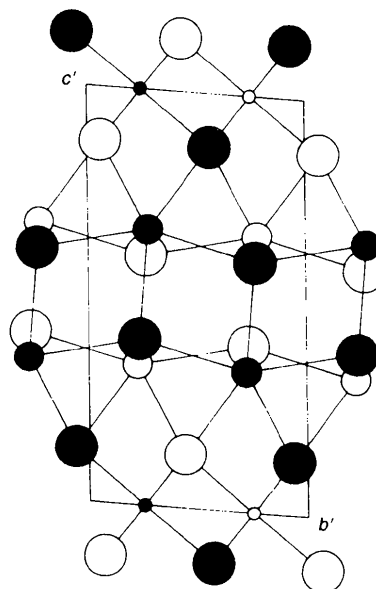


Fig. 1. Orthogonal projection of the structure of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ along the common [100] direction. $b' = a_{v2} \sin \gamma_v$ and $c' = a_{v3} \sin \beta_v$ for $\nu = 1, 2$. Large open and filled circles denote Se atoms, small open and filled circles denote V atoms and medium ones denote La atoms.

*Lists of structure factors, anisotropic displacement parameters, unit-cell dimensions, atomic coordinates and site occupancy factor, and displacive modulation parameters have been deposited with the IUCr (Reference: JS0018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Final values for the temperature factors (\AA^2) as obtained from the final refinement REF-f in (3 + 1)-dimensional superspace of the modulated structure

The temperature factor appearing in the expression of the structure factor is defined by $T = \exp[-\beta_{11}h_i^2 + \beta_{22}k_i^2 + \beta_{33}l_i^2 + \beta_{12}h_i k_i + \beta_{13}h_i l_i + \beta_{23}k_i l_i]$ and $\beta_{ij} = 2\pi^2 U_{ij} a_{vi}^* a_{vj}^*$.

Atom	ν	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
V(1)	1	0.0345 (11)	0.0180 (9)	0.0088 (6)	0.0032 (8)	-0.0008 (7)	0.0010 (6)
S(1)	1	0.0149 (3)	0.0073 (2)	0.0145 (3)	-0.0008 (2)	-0.0008 (2)	0.0009 (2)
La(2)	2	0.0135 (2)	0.0091 (2)	0.0109 (2)	-0.0005 (2)	-0.0006 (2)	0.0005 (2)
Se(2)	2	0.0134 (3)	0.0102 (3)	0.0110 (3)	-0.0003 (3)	-0.0006 (2)	-0.0005 (2)

Table 5. Displacive modulation parameters, $A_{i,n}^{\mu} a_{vi}$ (\AA) and $B_{i,n}^{\mu} a_{vi}$ (\AA), as obtained from the final refinement REF-f of the modulated structure

Atom (μ)	n	$A_{i,n}^{\mu} a_{vi}$	$A_{i,n}^{\mu} a_{vi}$	$A_{i,n}^{\mu} a_{vi}$	$B_{i,n}^{\mu} a_{vi}$	$B_{i,n}^{\mu} a_{vi}$	$B_{i,n}^{\mu} a_{vi}$
V(1)	1	0	0	0	0.029 (11)	-0.012 (4)	-0.002 (5)
	2	-0.062 (7)	0.142 (5)	-0.028 (4)	0	0	0
Se(1)	1	-0.032 (5)	-0.013 (1)	-0.009 (2)	0.003 (5)	0.012 (1)	0.002 (2)
	2	0.053 (3)	0.016 (2)	-0.077 (2)	0.012 (3)	-0.004 (2)	0.063 (2)
La(2)	1	0.003 (3)	-0.089 (1)	0.004 (2)	0.005 (3)	0.036 (1)	0.010 (2)
	2	0.031 (2)	-0.001 (2)	-0.050 (2)	-0.049 (2)	0.011 (2)	-0.020 (2)
Se(2)	1	0.004 (5)	-0.044 (2)	0.009 (3)	0.007 (5)	0.013 (2)	-0.013 (3)
	2	-0.003 (3)	0.002 (3)	-0.026 (4)	0.013 (3)	0.004 (3)	-0.012 (4)

Table 6. Selected interatomic distances (\AA)

The basic structure positions of the atoms are: V(1) = $(x_{11}^0, x_{12}^0, x_{13}^0)$, V(1) $^{\nu\pm}$ = $(E1 \pm 1, 0, 0)V(1)$, V(1) $^{\mu\pm}$ = $(E1 \pm \frac{1}{2}, \pm \frac{1}{2}, 0, \pm \frac{1}{2})V(1)$, V(1) $^{\nu\pm}$ = $(E1 \pm \frac{1}{2}, \pm \frac{1}{2}, 0, \pm \frac{1}{2})V(1)$; Se(1) = $(x_{21}^0, x_{22}^0, x_{23}^0)$, Se(1) $^{\nu}$ = Se(1), S(1) $^{\nu}$ = $(i\bar{1}|\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})Se(1)$, Se(1) $^{\nu}$ = $(E1|\frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2})Se(1)$, Se(1) $^{\nu}$ = $(i\bar{1}|0, 1, 0, 0)Se(1)$, Se(1) $^{\mu}$ = $(E1|-\frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2})Se(1)$, Se(1) $^{\nu}$ = $(i\bar{1}|1, 0, 0)Se(1)$; Se(2) = $(x_{21}^0, x_{22}^0, x_{23}^0)$, Se(2) $^{\nu\pm}$ = $(E1 \pm \frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2})Se(2)$, Se(2) $^{\nu\pm}$ = Se(2), Se(2) $^{\nu}$ = $(E1|0, -1, 0, 0)Se(2)$, Se(2) $^{\nu}$ = $(i\bar{1}|0, 1, 0, 0)Se(2)$; and the basic coordinates x_{ij}^0 , corresponding to each atom, refer to Table 3.

Atom pair	Basic structure		Modulated structure
	Average	Average	Minimum–maximum
V(1)–V(1) $^{\nu\pm}$	3.576	3.578	3.449–3.663
V(1)–V(1) $^{\mu\pm}$	3.538	3.542	3.362–3.720
V(1)–V(1) $^{\nu\pm}$	3.533	3.533	3.237–3.868
V(1)–Se(1) $^{\nu}$	2.527	2.530	2.456–2.612
V(1)–Se(1) $^{\nu}$	2.527	2.530	2.461–2.601
V(1)–Se(1) $^{\nu}$	2.538	2.542	2.455–2.597
V(1)–Se(1) $^{\nu}$	2.538	2.542	2.478–2.603
V(1)–Se(1) $^{\mu}$	2.533	2.537	2.478–2.596
V(1)–Se(1) $^{\nu}$	2.533	2.537	2.478–2.623
La(2)–Se(2) $^{\nu+}$	3.047	3.048	2.997–3.094
La(2)–Se(2) $^{\nu-}$	3.042	3.043	3.002–3.089
La(2)–Se(2) $^{\nu+}$	3.141	3.142	3.097–3.206
La(2)–Se(2) $^{\nu-}$	3.131	3.131	3.069–3.198
La(2)–Se(2) $^{\nu}$	3.073	3.074	3.044–3.103

reflects the relative strength of the inter-subsystem interaction. The large distortion ϵ_o in $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ indicates a strong interaction between the two subsystems, which is further reflected by the inter- and intra-subsystem La–Se distances. The La–Se(2) distances within the same subsystem LaSe are plotted against the superspace phase parameter t in Fig. 2, which shows highly correlated variations. The two Se(2) atoms on opposite sides of La along \mathbf{a} as well as along \mathbf{b} vary regularly against the centre La atom, namely, when one Se(2) approaches La the other on the opposite side will depart from La, such that the lengths of each LaSe unit cell along these two in-plane directions does not change much. The smallest variation in distance occurs for the La–Se(2) pair along the \mathbf{c} direction; it reaches its

maximum when one of the two La–Se(2) distances along the \mathbf{b} direction is at its maximum. The shortest La–Se(2) distance of a La–Se(2) pair along the \mathbf{c} axis occurs when the two La–Se(2) distances along the \mathbf{b} direction are equal and when the distances of the La–Se(2) distances along the \mathbf{a} axis are also the same. The variation of the La–Se(2) distances has the periodicity $T = 0.605$ in t , while the La–Se(2) distances along the \mathbf{a} axis show a quasi-period with a periodicity $\frac{1}{2}T$. The shortest distances from a La atom to a Se(1) atom of the VSe_2 subsystem have the same magnitude as the intra-subsystem La–Se(2) distances.

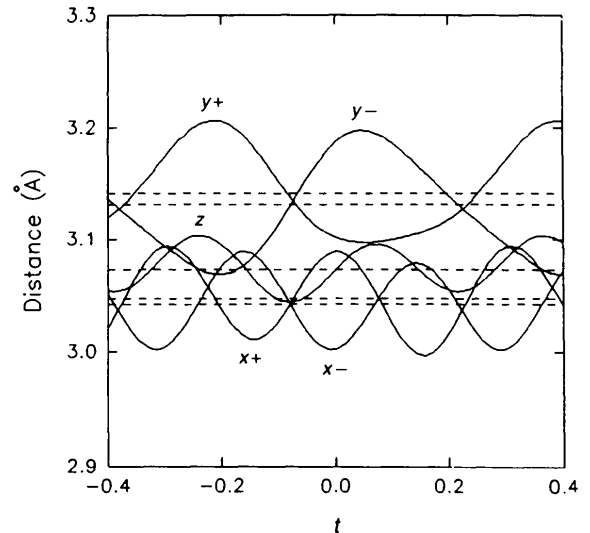


Fig. 2. Coordination of La ($\nu = 2$) by Se(2) of the same subsystem as a function of t . The distances (see Table 6) for the basic structure are the dashed horizontal lines and the wavy curves marked by $x+$, $x-$, $y+$, $y-$ and z show the distances for the modulated structure of the La–Se(2) pairs with the same mark in Table 6.

The mutual modulation enlarges the shortest inter-subsystem La—Se(1) distance with *ca* 0.1 Å in the average structure (see Fig. 3 and Table 6).

In $(\text{LaS})_{1.19}\text{CrS}_2$ the intra-layer La—S distances point to trivalent La (Kato, 1990). This compound is a semiconductor; magnetic properties indicate localized $\text{Cr}^{3+} 3d^3$ electrons (Murugesan, Ramesh, Gopalakrishnan & Rao, 1981). With a donation of one electron per Cr, excess electrons remain on the LaS part, assuming La^{3+} and a composition $(\text{LaS})_{1.19}\text{CrS}_2$. Semiconducting behaviour is explained when vacancies are present in the LaS subsystem, such that charge balance exists between La^{3+} , Cr^{3+} and S^{2-} . Rouxel *et al.* (1994) put forward experimental evidence for *Ln* vacancies in 'LaCrS₃', 'YCrS₃' and 'GdCrS₃', with concentrations in agreement with charge balance. It may be noted that VS_2 , CrS_2 and CrSe_2 do not exist in a stable state. Sandwiches CrX_2 are present in intercalates $M\text{CrX}_2$ (*M*: alkali metals, *Ib* metals); they are semiconductors, with $\text{Cr}^{3+} 3d^3$ ions (Bongers, van Bruggen, Koopstra, Omlou, Wiegiers & Jellinek, 1968). In the structural refinement of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ the final model shows *ca* 5% of La vacancies to be present, corresponding to a charge balance between $1.15 \times \text{La}^{3+}$, V^{3+} and $3.21 \times \text{Se}^{2-}$. Both La and V are trivalent and no excess electrons remain in the LaSe subsystem, leading to non-metallic LaSe layers. The valence of La in this compound was calculated [using the parameter $R_{ij}^0(\text{La—Se}) = 2.74 \text{ \AA}$ (Brese & O'Keeffe, 1991)] as a function of *t* (Fig. 4). It can be seen that the modulation tends to reduce the valence of La.

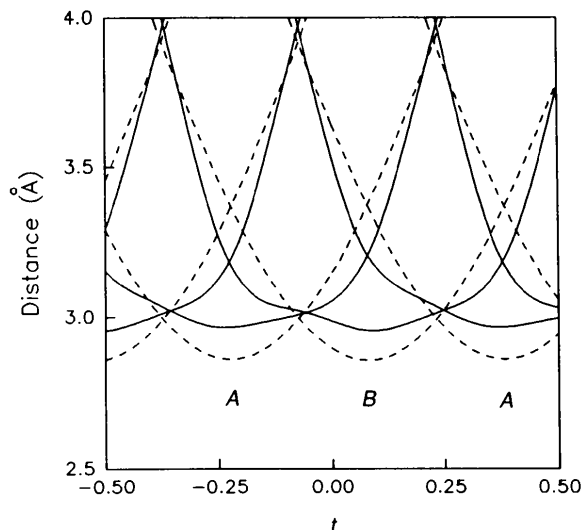


Fig. 3. Coordination of La ($\nu = 2$) by Se(1) ($\nu = 1$) as a function of the subsystem superspace coordinate *t*. Distances are given for the basic structure (broken curves) and for the modulated structure (solid lines). The curves show the distances from La at $(x_{21}^0, x_{22}^0, x_{23}^0)$ to Se(1) at $(n_{11} + x_{11}^0, x_{12}^0, x_{13}^0)$ for the lines marked A and to Se(1) at $(n_{11} - \frac{1}{2} + x_{11}^0, -\frac{1}{2} + x_{12}^0, x_{13}^0)$ for those marked B (n_{11} is an integer and x_{ij} refers to Table 3). The curves with the same mark correspond to different values for N_{11} , but translationally equivalent Se(1) atoms.

Including a contribution of 1.1 from the inter-subsystem, the average valence of La amounts to 3.05.

A resistivity measurement of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ showed semiconducting behaviour (Wiegiers & Baas, 1994), which suggests that carriers on the VSe_2 layers are also localized. The parent compound VSe_2 has a V—V distance in the VSe_2 sandwiches of 3.356 Å (Rigault, Guidi-Morosini, Tomas & Molinie, 1982). The compound is a metal and shows a CDW-type distortion at $\sim 100 \text{ K}$ (van Bruggen & Haas, 1976). LiVSe_2 , with Li^+ cations in octahedral holes between VSe_2 sandwiches, shows a V—V distance of 3.58 Å. The conduction is metallic, but the magnetic susceptibility is a quarter of that expected for localized V^{3+} , with $S = 1$ and $g = 2$ (Murphy, Di Salvo, Hull & Waszczak, 1976). The sodium intercalates Na_xVSe_2 are metallic for $0 < x < 1$, the V—V distances being 3.482 Å for $x = 0.6$, and semiconducting for $x = 1$ with V—V distances of 3.735 Å (Bloembergen, Haange & Wiegiers, 1977). The average V—V distances of $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ are 3.576, 3.538 and 3.533 Å (see Table 6). Remarkably, the refinement shows that the largest modulation amplitude occurs on the V atoms (Table 4); the distances of one V atom to its six nearest-neighbour V atoms therefore show strong variation (Fig. 5), the largest being *ca* 0.63 Å (Table 6). From Fig. 5 one can see that the distances of the V—V pairs along the *a* direction change slightly compared with the V—V pairs along other directions. The V—Se(1) distances of the distorted octahedra are plotted against the superspace phase parameter *t* in Fig. 6; the largest variation is 0.15 Å. Part of the modulated structure of VSe_2 is depicted in Fig. 7 along the [001] direction. It can be seen from Table 5 that the largest variation of Se(1) occurs along *c*, while the V atoms

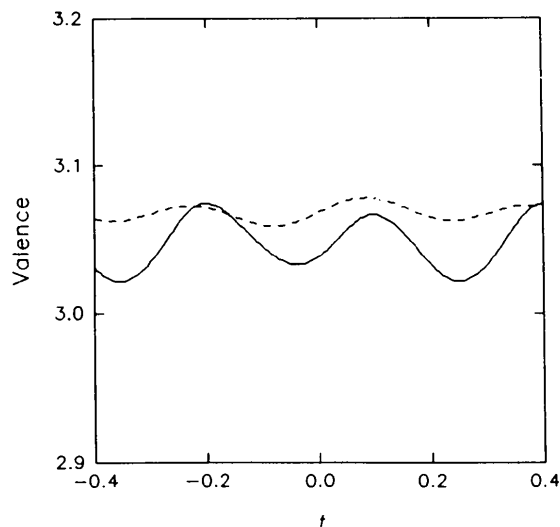


Fig. 4. Variation of the bond valence of La as a function of *t*. The dashed and solid lines are for the basic and modulated structure, respectively.

show the largest variation in the ab plane. It may be noted that for lanthanoid compounds $(\text{LnX})\text{TX}_2$, with $T = \text{Nb}$ or Ta , the largest displacive modulation is on the Ln and X atoms, while the modulation of Nb or Ta is negligibly small. With respect to the average V—V distance in $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$, one expects metallic-type conduction for this compound in view of the relation between V—V distances and the electronic properties of the sodium intercalates Na_xVSe_2 . However, in Fig. 7 one can see that the V atoms form clusters with short V—V distances; between clusters the V—V distances are longer. Thus, electron localization has presumably taken place by the mutual modulation-induced formation of the long V—V distances, separating the V—V clusters.

6. Concluding remarks

In conclusion, the complete structure of the misfit layer compound $(\text{La}_{0.95}\text{Se})_{1.21}\text{VSe}_2$ has been determined using a $(3+1)$ -dimensional superspace-group approach. This is the first example of the V-based rare-earth misfit layer compounds, whose structure is fully described. The puzzle about the semiconducting behaviour of this compound is uncovered by its modulated structure involving *ca* 5% La vacancies in the LaSe layers: The La vacancies lead to no excess electrons remaining in the LaSe layers, while the large modulation in the V—V distances induces V atom clusters with short V—V distances separated by large V—V distances, which cause Mott localization in the VSe_2 sandwiches. Non-stoichiometry of the rare-earth double layers may occur for all lanthanoid misfit layer compounds.

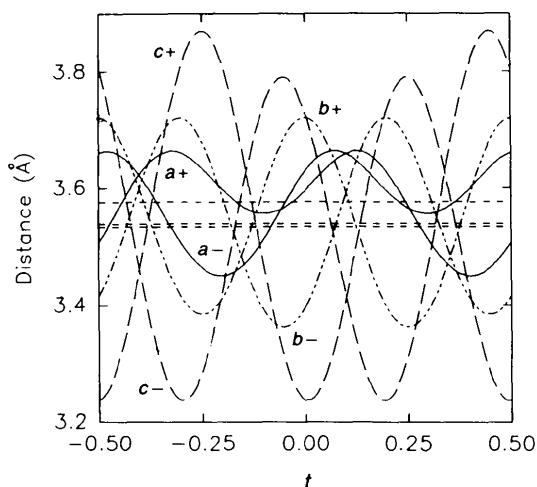


Fig. 5. Variation of the V—V distances of the subsystem VSe_2 , plotted as a function of t . The basic structure distances (see Table 6) are the dashed horizontal lines. The distances including the modulation are the wavy lines and the curve marks refer to Table 6.

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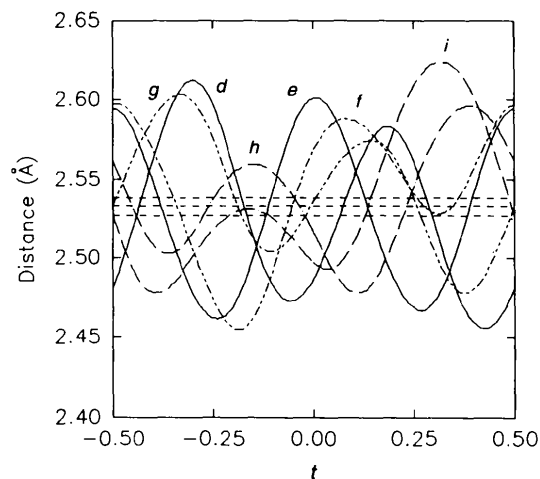


Fig. 6. Coordination of V ($v = 1$) by Se(1) of the same subsystem VSe_2 , plotted as a function of t . The dashed horizontal lines represent the V—Se(1) distances without modulation. The wavy lines show the V—Se(1) distances for the modulated structure and the curve marks refer to Table 6.

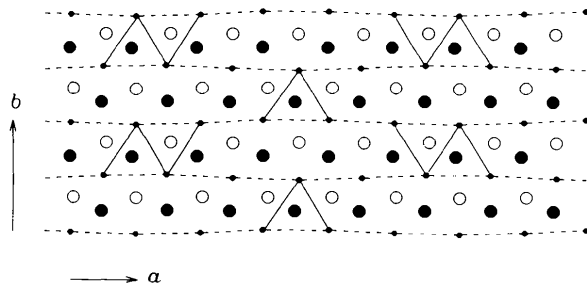


Fig. 7. Part of the modulated structure of VSe_2 projected along the $[001]$ direction. Small filled circles are V atoms and open filled large circles denote the Se(1) atoms at different heights.

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