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Stability and charge transfer in the misfit compound $(LaS)(SrS)_{0.2}CrS_2$: *Ab initio* band-structure calculations

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Local-density approximation *ab initio* band-structure calculations have been carried out on the misfit compound $(LaS)(SrS)_{0.2}CrS_2$. It appears that this phase can be regarded as an infinite two-dimensional intercalation compound. One electron is transferred from the LaS slab to the CrS_2 slab. For the $(LaS)(La_{2/3(1-y)}Sr_yS)_{0.2}CrS_2$ derivatives Sr atoms can substitute La atoms up to $y=1$. This study confirms the existence of La vacancies in the nondoped compound and is consistent with the observed nonmetallic character of this phase. [S0163-1829(97)02615-5]

I. INTRODUCTION

Misfit layered chalcogenides show a regular alternation of MX ($M=$Pb, Sn, Bi, Ln;$X=$S, Se) and TX_2 ($T=$Ti, V, Cr, Nb, Ta) slabs along a stacking direction which gives the c parameter. Each sublattice, MX (rock-salt structure) or TX_2 (CdI_2 or NbS_2 type structure), has two in-plane a and b parameters. So far the b parameters have been found to be equal, but the ratio of a parameters is an irrational number, i.e., these structures show incommensurability in one direction. The corresponding misfit is expressed through the $1+x$ factor in chemical formulations which appear as $(MX)_{1+x}TX_2$. The $1+x$ value $(1.08<1+x<1.28)$ can be calculated from the ratio of the a parameters taking into account the number of formula units in each subcell: $1+x=2a(TX_2)/a(MX)$.

Although a lot of work has been dealing with structure determinations and physical properties of misfit layer compounds,[1,2] the reason why these compounds exist still remains an open question. Why do they form preferentially to the two binaries MX and TX_2? Stability resulting from charge transfer has been hypothesized. In the case of a trivalent M cation (i.e., $M=$ Ln) an electronic transfer from LnX ($Ln^{3+}e^-X^{2-}$) slabs to TX_2 ones is responsible for the overall stability of the misfit compounds. With a divalent M cation (i.e., $M=$ Pb, Sn), such an electronic transfer is not very likely to be proposed, at least in the case of PbS. Indeed, Pb has never been found in a +4 oxidation state in sulfides. Nevertheless, there is an extrapopulation of the conduction band related to the TX_2 part. This is particularly obvious in the case of $(SnS)_{1.17}NbS_2$,[3] where 0.4 additional electrons are calculated in the $4dz^2$ band (a_1' band) of NbS_2. Precise chemical analyses on this compound have shown that there is an excess of niobium element which is very likely present as Nb^{3+} cations substituting for Sn^{2+} cations in the SnS layer.[4] This condition would lead to an excess of positive charge which is balanced by an equal quantity of Nb^{3+} ions in the NbS_2 slab. This model, which suggests an electrostatic interaction between layers, is still under discussion. But it is largely supported by a clear explanation of the electrical properties: each T^{3+} cation brings one additional electron to the TX_2 slabs in accordance with the increased electronic population.

The misfit chalcogenides with CrS_2 slabs are of particular interest. First of all there is no stable chromium disulfide binary phase whereas TiS_2,TaS_2,NbS_2, and even VS_2 are known. Indeed chromium at the +4 oxidation state cannot be stable in the presence of sulfur. The corresponding d level is too deeply engaged in the sp band of sulfur. CrS_2 slabs however exist in $NaCrS_2$,[5] where they are separated by layers of Na^+ ions. The arrangement is similar to the one in $NaTiS_2$ which is an intercalation compound of TiS_2 (α-$NaFeO_2$ structure), with one electron transferred from Na to the t_{2g} levels of Ti. $NaCrS_2$, which is prepared by high-temperature solid-state reactions, can also be regarded as an intercalation compound of sodium in an hypothetical CrS_2. Similarly, $(LnS)_{1+x}CrS_2$ phases appear as an infinite two-dimensional intercalation compound of LnS layers in this hypothetical CrS_2. From magnetic measurements chromium has been found at the +3 oxidation state,[6–8] which emphasizes the role of an electronic transfer from the LnS to CrS_2 slab. Misfit phases with PbS or SnS slabs for which no electronic transfer can be predicted, were never reported with CrS_2; this is consistent with the hypothesis of an electronic transfer between slabs that PbS or SnS slabs cannot provide.

However if we assume the LnX part to be $Ln^{3+}e^-X^{2-}$, as in simple rare-earth monochalcogenides themselves, there are $1+x$ electrons that could be transferred. A part of electrons (x) could remain in the LnX slab to maintain a metallic behavior (at least for the first rare-earth elements in the series where they are delocalized in $5d$- or $4f$-based bands). But, $(LnS)_{1+x}CrS_2$ phases are semiconductors. How can this be? A very accurate chemical analysis of the $(LaS)_{1+x}CrS_2$ phase detected less La than expected;[9] this result can be described by metal-atom vacancies in the LaS slab. The correct formulation of this phase is not $(LaS)_{1.2}CrS_2$ but rather a $(La_{0.94}[\ ]_{0.06}S)_{1/2}CrS_2$ abbreviated as $\sim LaCrS_3$ in this paper. This formulation leads to an exact charge balance between La^{3+}, Cr^{3+}, and S^{2-}. The electron transfer from the LaS to the CrS_2 layer is such that no excess electron remains in the LaS slab.

In the present work band-structure calculations have been

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performed to examine the electronic structure and then to correlate the results with the observed physical properties. We also examined the role of vacancies by preparing phases doped with a cationic species that would not take part in any electronic transfer. The $\sim LaCrS_3$ compound was thus chosen as it represents the most appropriate model material, i.e., no magnetic properties coming from the LaS layer, one electron on a $5d$ level. The filling of the vacancies was tempted with Sr^{2+} which has a comparable ionic size and which should behave as an inert component regarding charge transfer (of course the ''substitution'' scheme implies that 3 Sr^{2+} replace 2 La^{3+} and that one vacancy is filled). Such a substitution (La/Sr) has already been done for the $\sim LaVS_3$ phases.[10]

II. EXPERIMENT

To clearly express what has been done, the above formulation $(La_{0.94}[\ ]_{0.06}S)_{1.2}CrS_2$ can be decomposed into (LaS) $(La_{2/3}[\ ]_{1/3}S)_{0.2}CrS_2$. The introduction of Sr^{2+} will lead to $(LaS)(SrS)_{0.2}CrS_2$ for the upper limit when all vacancies are filled up, and for any intermediate situation, the general formulation $(LaS)(La_{2/3(1-y)}[\ ]_{1/3(1-y)}Sr_yS)_{0.2}CrS_2$ is abbreviated as $\sim(La,Sr)CrS_3$ in this paper. The preparation of these compounds with $0<y\leqslant 1$ was performed by sulfurization of appropriate amounts of $SrCrO_3$, $LaCrO_3$, and La_2O_3 with H_2S gas at 1300 °C during 6 h in a graphite crucible. The products were annealed subsequently in evacuated silica tubes at 1050 °C for ten days. The samples are characterized by means of powder x-ray diffraction and chemical analysis with an energy dispersion spectroscopy (EDS) equipped scanning electron microscope. Magnetic measurements were performed on powder samples with a SQUID magnetometer between 5 and 300 K. Electrical transport measurements were made on a single crystal by the standard four-probe method with silver point contacts.

III. EXPERIMENTAL RESULTS

The x-ray powder-diffraction patterns of the obtained products are very similar to the pattern of $\sim LaCrS_3$. Because of the composite character of these compounds, and two triclinic unit cells, it is difficult to index the x-ray-diffraction patterns. Refinement of (La,Sr)S cell parameters has been performed for $y=0.00$, 0.25, 0.50, 0.75, and 1.00 using the full pattern matching mode with the use of the FULLPROF program.[11] The variations of these parameters versus y are shown in Figs. 1 and 2. Some differences between our refined cell parameters for $y=0$ and those given by Kato[12] are observed. The quasilinear variation of the c parameter (versus y) certifies that the substitution really takes place up to $y=1$ as is consistent with the chemical analysis. The fact that the cell volume does not increase gradually up to $y=1$ but varies drastically from $y=0$ to 0.25 and then much more smoothly up to $y=1$ could be related with the filling of La vacancy sites. This should induce a large variation of the a parameter at the first step of the ''substitution'' process. Indeed in that direction (misfit axis) structural constraints are the weakest. Then, the difference in the ionic size ($r_{La^{3+}}=1.03$ Å, $r_{Sr^{2+}}=1.18$ Å) could lead to a smaller regular increase of the parameters up to $y=1$.

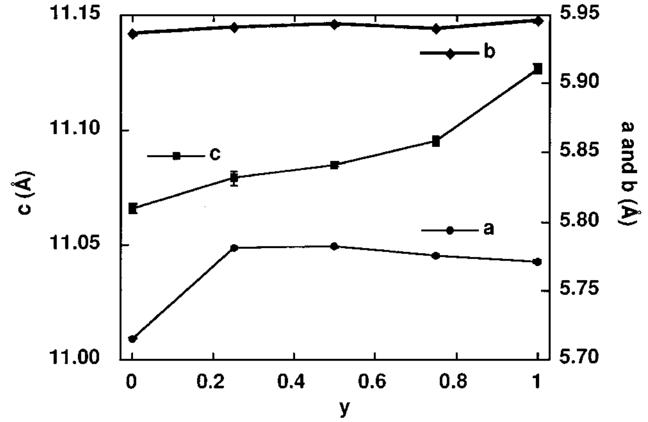

FIG. 1. Variation of (La,Sr)S cell parameters versus y for (LaS) $(La_{2/3(1-y)}Sr_yS)_{0.2}CrS_2$ compounds.

During the preparation of the oversubstituted $(La_{0.9}Sr_{0.3}S_{1.2})CrS_2$ compound, a small amount of SrS was observed in the obtained product, and the refined lattice parameters are nearly the same as for $y=1.0$. This observation leads to the conclusion that the substitution is limited to $y\leqslant 1$.

Preliminary magnetic and electrical measurements clearly indicate that the behavior of $\sim(La,Sr)CrS_3$ ($0.25\leqslant y \leqslant 1.00$) is close to that of $\sim LaCrS_3$. For temperatures above 150 K the susceptibility obeys a Curie-Weiss law which confirmed the expected valency states of chromium (Cr^{3+}) and of lanthanum (La^{3+}).[6–8] Likewise the temperature dependence of the resistivity for these compounds shows a nonmetallic behavior as for $\sim LaCrS_3$.

IV. BAND-STRUCTURE CALCULATIONS

A. Description of the structure

In order to obtain more information about the electronic structure, we performed local-density approximation (LDA), *ab initio* band-structure calculations. So far, no computer program exists to treat modulated crystals lacking three-

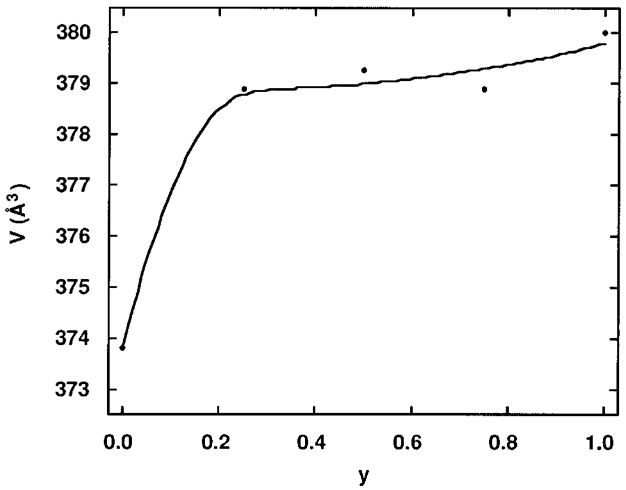

FIG. 2. Variation of (La,Sr)S cell volume versus y for (LaS) $(La_{2/3(1-y)}Sr_yS)_{0.2}CrS_2$ compounds.

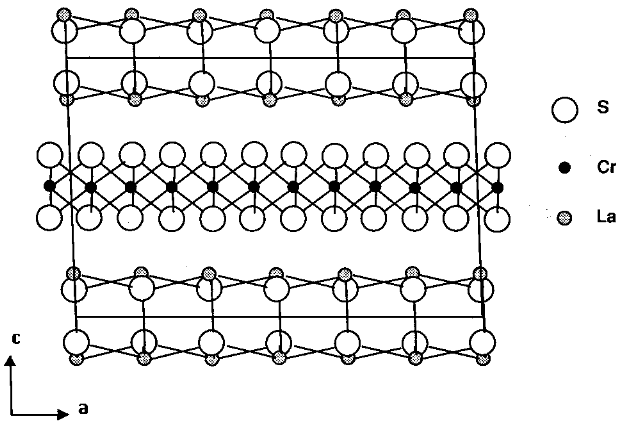

FIG. 3. Projection of the structure of $(\mathrm{LaS})_{1.2}\mathrm{CrS}_2$ along [010] in the commensurate approximation.

dimensional translational symmetry. The common method to do such calculations is to approximate the incommensurate structure by considering a commensurate supercell. For $\sim\mathrm{LaCrS}_3$ the x value is nearly 0.2, so we could form a superstructure by using 3 LaS units and 5 CrS_2 units along the incommensurate lattice direction a as shown in Fig. 3. Taking the vacancies into account is not possible with this approximation, since this would lead to a unit cell too large for reasonable computation time. Thus, band-structure calculations of $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$ have been performed assuming that the Sr atom does not affect the structural geometry.

The structure of $\sim\mathrm{LaCrS}_3$ has been described in the triclinic symmetry (space group $C\bar{1}$) with the lattice constants taken from Kato:[12] $a_{(\mathrm{LaS})}=5.752$ Å, $a_{(\mathrm{CrS}_2)}=3.435$ Å, $b_{(\mathrm{LaS})}=b_{(\mathrm{CrS}_2)}=5.936$ Å, $c_{(\mathrm{LaS})}=c_{(\mathrm{CrS}_2)}=11.04$ Å, $\alpha_{(\mathrm{LaS})}=95.42°$, $\alpha_{(\mathrm{CrS}_2)}=95.29°$, $\beta_{(\mathrm{LaS})}=90.21°$, $\beta_{(\mathrm{CrS}_2)}=93.29°$, $\gamma_{(\mathrm{LaS})}=\gamma_{(\mathrm{CrS}_2)}=90°$. For the commensurate approach we used the angle β from the CrS_2 part, since this is the more rigid one. $C\bar{1}$ is not a conventional space group so we have changed the unit cell to obtain the correct symmetry $P\bar{1}$ as shown in Fig. 4. By substitution of one La by Sr, leading to the cell content $\mathrm{La}_5\mathrm{SrCr}_5\mathrm{S}_{16}$, the center of inversion is lost and the symmetry becomes $P1$. For the calculations the following unit cell was used: $a=9.086$ Å, $b=11.04$ Å, $c=5.936$ Å, $\alpha=95.3°$, $\beta=109.07°$, $\gamma=86.1°$. In this approximation, the geometry of the CrS_2 part corresponds to the experimental values (except the modulation), whereas the LaS slab is slightly distorted due to the difference in the β angle, but differences in the interatomic distances are small (less than 0.002 Å) and therefore negligible.

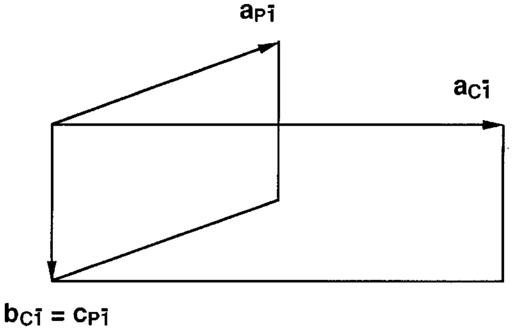

FIG. 4. Relationship between the unit cells used for band-structure calculations ($P\bar{1}$) and for commensurate structure description ($C\bar{1}$).

TABLE I. Input parameters for the band-structure calculation of $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$. Positions and radii of the ASA spheres of Sr, La, Cr, and S.

Atom	X	Y	Z	R (Å)
Sr	−0.3334	0.1624	−0.3892	1.8670
La1	0.0000	0.1624	0.2775	1.8775
La2	0.0000	−0.1624	−0.2775	1.8776
La3	0.3334	−0.1624	0.3892	1.8669
La4	0.3334	0.1624	−0.0558	1.8557
La5	−0.3334	−0.1624	0.0558	1.8554
Cr1	−0.1000	0.5000	0.2000	1.3811
Cr2	0.1000	−0.5000	−0.2000	1.3811
Cr3	0.3000	0.5000	0.4000	1.3810
Cr4	−0.3000	−0.5000	−0.4000	1.3808
Cr5	0.5000	−0.5000	0.0000	1.3811
S1	0.0000	0.1030	−0.2325	1.5255
S2	0.0000	−0.1030	0.2325	1.5256
S3	0.3334	−0.1030	−0.1008	1.5352
S4	−0.3334	0.1030	0.1008	1.5349
S5	0.3334	0.1030	0.4342	1.5150
S6	−0.3334	−0.1030	−0.4342	1.5149
S7	0.1080	0.3775	0.1161	1.4004
S8	−0.1080	−0.3775	−0.1161	1.4002
S9	−0.2910	0.3775	−0.0834	1.3930
S10	0.2910	−0.3775	0.0834	1.3929
S11	−0.0910	0.3775	−0.4834	1.3929
S12	0.0910	−0.3775	0.4834	1.3930
S13	0.3088	0.3775	−0.2835	1.3944
S14	−0.3088	−0.3775	0.2835	1.3944
S15	0.4910	−0.3775	−0.3166	1.3933
S16	−0.4910	0.3775	0.3166	1.3931

B. Computation methods

Self-consistent, *ab initio*, band-structure calculations were performed using the tight-binding–linear muffin-tin orbital–atomic-sphere-approximation (ASA) method[13,14] in its scalar relativistic version.[15] A detailed description may be found elsewhere,[16] so only the main data used in our calculations are given. All reciprocal space integrations were performed with the tetrahedron method[17] using 128 irreducible k points within the Brillouin zone. Due to the magnetic properties, all calculations were carried out assuming spin-polarized conditions. The basis sets consisted of $6s$, $6p$, $5d$, and $4f$ orbitals for La; $5s$, $5p$, $4d$,$4f$ for Sr; $4s$, $4p$, $3d$ for Cr and $3s$, $3p$, and $3d$ for S. The La $6p$, Sr $5p$ and $4f$, as well as the S $3d$ orbitals were treated by the downfolding technique.[18] To achieve space filling within the atomic sphere approximation, interstitial spheres are introduced. Their positions and radii were calculated using an automatic procedure.[18] We do not allow an overlap of more than 17% for any two atom-centered spheres. The resulting atom positions and sphere radii are listed in Tables I and II.

TABLE II. Input parameters for the band-structure calculation of (LaS)(SrS)$_{0.2}$CrS$_2$. Positions and radii of the ASA spheres for the empty spheres.

Empty sphere	X	Y	Z	R (Å)
$E1$	0.1665	0.0008	0.0918	1.2164
$E2$	−0.1666	−0.0008	−0.0920	1.2166
$E3$	−0.1668	−0.0008	0.4249	1.2174
$E4$	0.1668	0.0008	−0.4250	1.2171
$E5$	−0.0878	0.2965	−0.1628	1.2170
$E6$	0.0879	−0.2965	0.1630	1.2168
$E7$	−0.1123	−0.3081	0.2347	1.1320
$E8$	0.1123	0.3081	−0.2350	1.1325
$E9$	−0.2673	0.2935	0.2315	1.1084
$E10$	0.2673	−0.2935	−0.2315	1.1086
$E11$	0.3128	0.3022	0.3715	1.0606
$E12$	−0.3128	−0.3022	−0.3715	1.0604
$E13$	0.2139	0.2315	−0.4221	1.0553
$E14$	−0.2139	−0.2315	0.4221	1.0549
$E15$	0.4858	−0.2790	0.1659	1.0252
$E16$	−0.4858	0.2790	−0.1659	1.0252
$E17$	−0.0985	0.4490	−0.1806	1.0228
$E18$	0.0991	−0.4490	0.1809	1.0229
$E19$	−0.4998	0.0000	0.2449	0.9827
$E20$	0.4998	0.0000	−0.2449	0.9824
$E21$	0.1059	0.4339	0.4590	1.0254
$E22$	−0.1059	−0.4339	−0.4590	1.0254
$E23$	0.3060	0.4337	0.0586	0.9027
$E24$	−0.3060	−0.4337	−0.0586	0.9027
$E25$	0.3127	−0.4435	−0.2552	0.8392
$E26$	−0.3127	0.4435	0.2553	0.8392
$E27$	0.4939	−0.4337	0.3413	0.7867
$E28$	−0.4939	0.4337	−0.3413	0.7867

V. RESULTS OF THE LMTO CALCULATIONS

The total spin projected density of state (DOS) of (LaS)(SrS)$_{0.2}$CrS$_2$ is shown in Fig. 5. We find the S $3s$ states at -13 eV and the $3p$, hybridized with the Cr $3d$ states, extending from -6 to -1 eV. The La $4f$ band is placed 4 eV above the Fermi level. No La or Sr contribution is found below E_F, i.e., both atoms are completely ionized to the $+3$ and $+2$ state, respectively. As seen from the spin-projected DOS in Fig. 6, the 3 Cr $3d$ electrons are fully polarized on $t_{2g}(\uparrow)$ and the difference of the spin densities $[n(\uparrow)-n(\downarrow)]$ leads to a magnetic moment of $3\mu_B$ in agreement with the magnetic measurements. The lack of occupied La states and the $+3$ oxidation state of Cr implies, indeed,

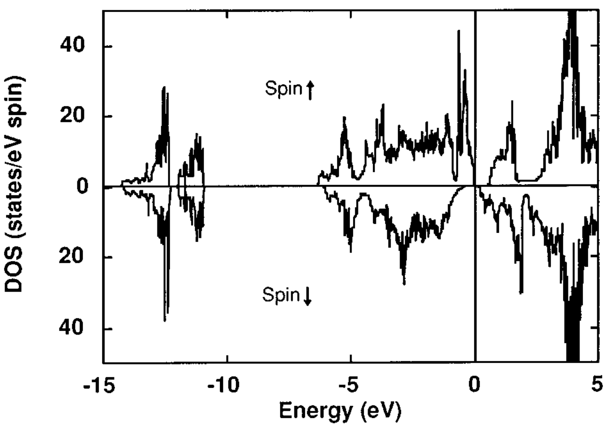

FIG. 5. Total spin projected DOS of (LaS)(SrS)$_{0.2}$CrS$_2$.

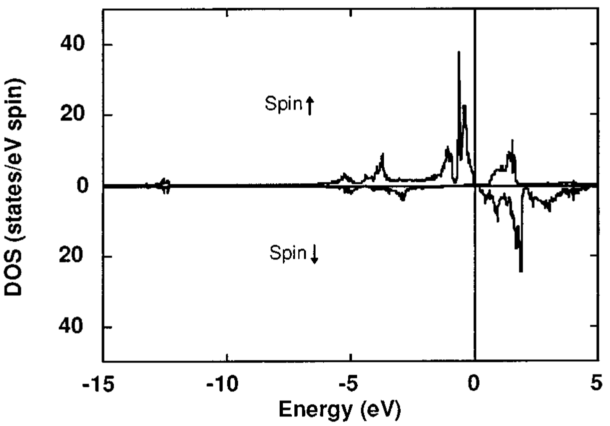

FIG. 6. Spin projected DOS of the Cr $3d$ orbitals.

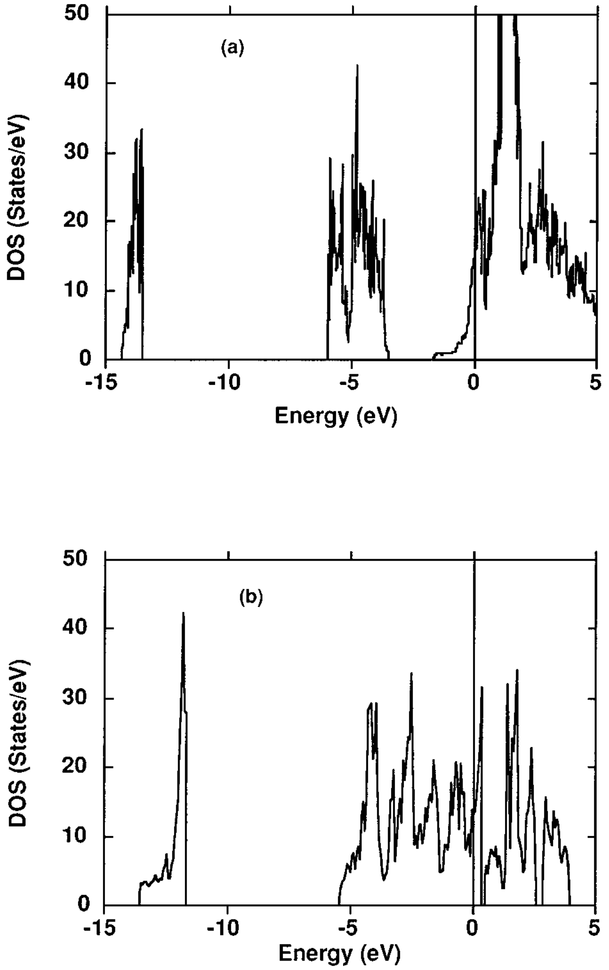

FIG. 7. DOS of the hypothetical (La,Sr)S (a) and CrS$_2$ (b) isolated layers.

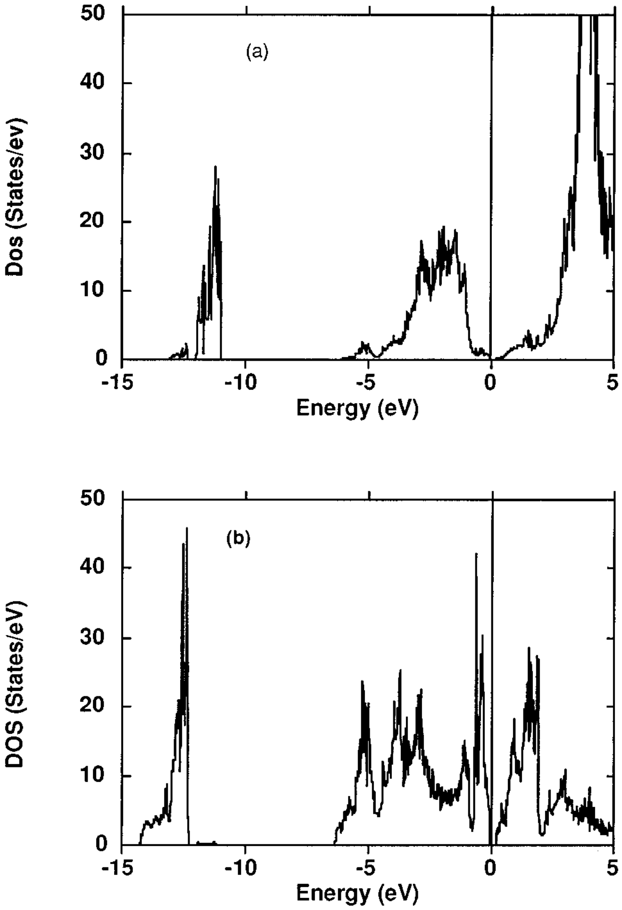

FIG. 8. Partial DOS of the (La,Sr)S layer (a) and CrS_2 layer (b) in $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$.

one electron per Cr atom has been transferred from the LaS to the CrS_2 slab.

The energy gap at the Fermi level agrees with the insulating properties of this material. It is well known that LDA calculations produce too small gaps, i.e., the experimental E_G is expected to be larger than the calculated value of 0.2 eV. The gap is opened between the $t_{2g}(\uparrow)$ and $t_{2g}(\downarrow)$ orbital set of chromium. Thus, if any additional electrons should exist, they would fill the $t_{2g}(\downarrow)$ orbital, which is substantially higher in energy. This would destabilize the structure and reduce the magnetic moment. Hence the compound ‘‘$(\mathrm{LaS})_{1.2}\mathrm{CrS}_2$’’ does not form.

We have also calculated the band structures of the hypothetical isolated $(\mathrm{La,Sr}_{0.2})\mathrm{S}$ and CrS_2 layers separately, but with the same geometry for each as in the misfit compound. The resulting DOS diagrams are shown in Figs. 7(a) and 7(b). Compared with the partial DOS of the two layers calculated from the complete structure shown in Figs. 8(a) and 8(b), the most significant difference is the shift of the LaS part towards higher energies when both layers are present. The LaS slab alone would be metallic with the excess electron in the $5d$ band. Also, the lower-lying Cr t_{2g} levels are not fully occupied, leading to a reduced magnetic moment. We can describe the electronic structure of this misfit layer compound as a superposition of the band structures of the LaS and CrS_2 parts, stabilized by the charge transfer.

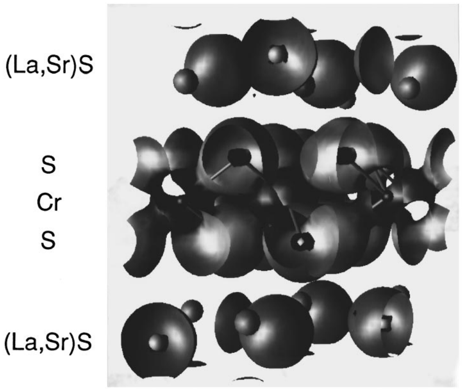

FIG. 9. Charge density of $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$, the isosurface corresponds to a density of $0.04e^-/a_0^3$.

A further question is raised up whether or not the stability of the misfit compounds is due to covalent bonding between La and the S atoms of the CrS_2 slab, as stated for $(\mathrm{SnS})_{1.17}\mathrm{NbS}_2$ and $(\mathrm{SnS})_{1.2}\mathrm{TiS}_2$.[3,19] To investigate this, we have calculated the charge density and the electron localization function of $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$. The isosurface which corresponds to a density of $0.04e^-/a_0^3$ is shown in Fig. 9. In this figure, the charge around the S atoms of the LaS part are nearly spherical, indicating an ionic behavior. In the CrS_2 slab, we find slightly covalent bonding between S and Cr. No significant charge density is found between the S atoms of the CrS_2 layer and the La atoms of the LaS slab. On the contrary, the ‘‘lone pairs’’ of the S atoms in the CrS_2 layer point towards the free space but not to the La atoms of the adjacent layer. Thus, the cohesion of the layers in this misfit compound is due to ionic interactions resulting from charge transfer from the LaS slab to the CrS_2 layer.

VI. CONCLUDING REMARKS

One electron has to be transferred to the CrS_2 slab to reach a stable configuration for chromium. It is not possible to give more electrons, since the CrS_2 slab would be strongly destabilized. On the other hand, the La atoms are fully ionized to the $+3$ oxidation state. Consequently, in order to maintain the necessary charge equilibrium in $\sim\mathrm{LaCrS}_3$, the formation of La vacancies in the LaS slab is the only possibility to avoid the x excess electrons. In this case the ideal composition with $x=0.2$ would be $(\mathrm{La}_{0.94}[\ ]_{0.06}\mathrm{S})_{1.2}\mathrm{CrS}_2$. Indeed we have shown recently,[9] from an accurate microprobe analysis, that this is the correct composition of the material. Filling the La vacancies by divalent Sr atoms, the electrovalent composition is then $(\mathrm{LaS})(\mathrm{SrS})_{0.2}\mathrm{CrS}_2$ and it is not possible to substitute more Sr. This agrees well with the present experimental results. Just before submitting this manuscript C. Fang sent us his thesis where a chapter is devoted to band-structure calculations on $(\mathrm{LaS})_{1.2}\mathrm{CrS}_2$ of which we were previously not aware.

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