Electrical transport and magnetic properties of the misfit layer compound $(LaS)_{1.14}NbS_2$

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Abstract. $(LaS)_{1.14}NbS_2$ is a misfit layer compound built of alternate double layers of LaS with La in square pyramidal coordination with sulphur and sandwiched with NbS_2 as occurs in $2H\text{-}NbS_2$. The electrical transport properties and magnetic properties were determined using single crystals and powder compacts. The compound is a p-type metal (Hall coefficient R_H and Seebeck coefficient positive) with a strong anisotropy of the electrical resistivity: $\rho_{\perp c}/\rho_{\|c} = 5 \times 10^{-5}$. The electrical transport properties are interpreted as being due to holes in $4d_{z^2}$ band of the NbS_2 part of the structure. The $4d_{z^2}$ band which is half-filled in the case of $2H\text{-}NbS_2$ contains 0.12 hole/Nb atom. This corresponds to a donation of 0.88 electron/ Nb atom from the LaS part, the charge of La being +2.8. The magnetic properties are interpreted as being due to the LaS part. In the temperature region 40–300 K the curve of reciprocal magnetic susceptibility (not corrected) against T is linear with a Curie constant C of $1.4 \times 10^{-6}\,m^3\,K\,(mol\,La)^{-1}$ corresponding to 0.14 4f electron at La, 0.86 electron being donated to the $4d_{z^2}$ band of the NbS_2 part. Down to 4 K there are no signs of super-conductivity.

1. Introduction

It was found recently (Meerschaut *et al* 1989, Wiegers *et al* 1989b) that the compound with the assumed composition $LaNbS_3$ (Donohue 1975) is a misfit layer compound with real composition $(LaS)_{1.14}NbS_2$. The compound is built of alternate double layers of LaS and sandwiches of NbS_2 as also occur in $2H\text{-}NbS_2$. The structure of this so-called composite crystal is described by two orthorhombic unit cells and space groups, respectively, for the LaS and the NbS_2 parts of the structure. The unit-cell dimensions are $a = 5.834\,\text{Å}$, $b = 5.801\,\text{Å}$ and $c = 11.902\,\text{Å}$ for the LaS part and $a = 3.313\,\text{Å}$, $b = 5.801\,\text{Å}$ and $c = 23.807\,\text{Å}$ for the NbS_2 part. The corresponding a, b and c axes are parallel, and the c axes are perpendicular, to the layers. Along the c axis of length $23.807\,\text{Å}$, four units LaS and NbS_2 alternate. The axes can be related as follows to those of the parent compounds LaS and $2H\text{-}NbS_2$. The b axis of the NbS_2 part corresponds to $a\sqrt{3}$ of $2H\text{-}NbS_2$ $(a = 3.324(3)\,\text{Å}$, $c = 11.95(2)\,\text{Å}$; space group, $P6_3/mmc$ (Fisher and Sienko 1980)); for the LaS part the a and b axes correspond approximately to the cell edge of solid LaS (NaCl type structure; $a = 5.860\,\text{Å}$ (Bergmann 1983)). The a axis of the NbS_2 part corresponds to the hexagonal a of $2H\text{-}NbS_2$. The structures are described in space group $Cm2a$ for the LaS part and $Fm2m$ for the NbS_2 part. The composition of the compound is determined by the number of formula units per unit cell ($Z = 4$ for LaS
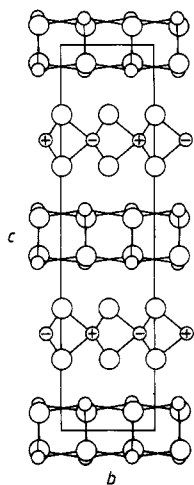
Figure 1. Projection of the structure of $(LaS)_{1.14}$ NbS_2 along the misfit axes; the large circles are S atoms. In order to demonstrate the F centring of the NbS_2 part, Nb atoms at $z = \frac{1}{4}$ and $z = \frac{3}{4}$ in the same plane parallel (100) have the same symbol (+ or $-$); Nb atoms ($\frac{1}{2}$) A apart have different symbols. Double layers of LaS with the midplane at $z = 0$ and $z = \frac{1}{2}$ are related by a translation over ($\frac{1}{2}$) c.
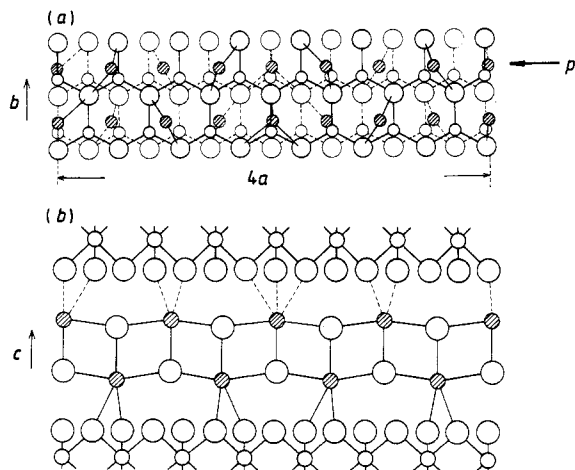
Figure 2. (*a*) Projection of the structure of $(LaS)_{1.14}NbS_2$ along the [001] axes. Large and small open circles are S and Nb, respectively. La atoms are indicated by broken circles. Along the misfit axes a length corresponding to four unit cells of the LaS part is given. S atoms of the LaS part are not drawn for clarity. (*b*) A projection along the [010] axes showing the coordination of La in a double layer of LaS. Only La atoms along the row indicated by p in 2*a* are shown. 'Bonds' between La and S of NbS_2 are indicated by full and broken lines, respectively.

and NbS_2) and the ratio of the lengths of the a axes. A projection of the structure along the misfit a axes is shown in figure 1. Each La atom is coordinated by five S atoms of the LaS lattice, these S atoms lying approximately on the corners of a square pyramid, and by two or three S atoms (at larger distances) of the NbS_2 lattice (figure 2). The variation in coordination of La by S of the NbS_2 lattice is due to the incommensurate character of the structure along the [100] axes. The Nb–S distances in the NbS_2 sandwiches, 2.479 Å (the average of 2.487(8) Å (2×) and 2.475(6) Å (4×)), are close to those found in

(SnS)$_{1.17}$NbS$_2$, 2.473(2) Å (Meetsma *et al* 1989). This description of the structure (Wiegers *et al* 1989b) supersedes the structure determination in terms of a large supercell (Meerschaut *et al* 1989). So far structure determinations using single crystals were performed for (LaS)$_{1.14}$NbS$_2$ (Meerschaut *et al* 1989, Wiegers *et al* 1989b), (SnS)$_{1.17}$NbS$_2$ (Meetsma *et al* 1989), (PbS)$_{1.14}$NbS$_2$ (Wiegers *et al* 1989a, b), (PbS)$_{1.13}$TaS$_2$ (Wulff *et al* 1989), (CeS)$_{1.16}$NbS$_2$, (CeS)$_{1.15}$TaS$_2$ and (SmS)$_{1.19}$TaS$_2$ (Wiegers *et al* 1989d). In all cases, centred orthorhombic unit cells were found; the differences between the various compounds concern the stacking of structural units. Recent progress in the understanding of the crystallographic description of misfit layer structures has been discussed in papers by Van Smaalen (1989). A review of the structures determined so far is given in a paper by Wiegers *et al* (1989c).

In this paper we report the electrical transport and magnetic properties of (LaS)$_{1.14}$NbS$_2$.

2. Experimental details

'LaNbS$_3$' crystals suitable for physical measurements can be obtained by vapour transport in a temperature gradient from 1110 to 760 °C. About 5–10 mg of (NH$_4$)$_2$PbCl$_6$ was added to about 200 mg of starting compound. (NH$_4$)$_2$PbCl$_6$ decomposes at high temperatures into Cl$_2$, PbCl$_2$ and NH$_4$Cl; we assume chlorine to be the transport agent. The crystals grow on the low-temperature side of the quartz tube as thin platelets with a diameter of up to 3 mm. X-ray powder data (Cu Kα_1 radiation) on crushed crystals were obtained using a Guinier–Hägg camera (Jungner Instruments). The in-plane electrical resistivity $\rho_{\perp c}$ and Hall coefficient R_H were measured using the four- and five-point contact method on crystal platelets cut into a rectangular shape. Contacts were made on the edges using platinum paste. For R_H the magnetic field was along the c axis. The resistivity $\rho_{\|c}$ along the c axis was measured using a two-contact method. The thickness of the crystal used was 24 μm. The Seebeck coefficient α was measured on a powder compact. The magnetic susceptibility was measured on a powder compact using a Faraday balance (Oxford Instruments) equipped with a superconducting magnet. Details of the physical measurements have been described in a previous paper (Wulff *et al* 1989).

3. Electrical transport properties of (LaS)$_{1.14}$NbS$_2$

The curve of in-plane resistivity $\rho_{\perp c}$ against temperature of (LaS)$_{1.14}$NbS$_2$ shows (figure 3) metallic type of conduction as was also found by Meerschaut *et al* (1989). The resistivity along the c axis is shown in figure 4. It is seen that the resistivity is strongly anisotropic with a $\rho_{\perp c}/\rho_{\|c}$ ratio of 5×10^{-5} at 4 K. The Hall coefficient is positive (figure 5), indicating conduction by holes; R_H is 5.5×10^{-9} m^3 C^{-1} at 300 K, and the curve shows a slight increase in R_H with decreasing temperature. One calculates from R_H (=1/pe, where p is the number of holes per cubic metre and e is the electron charge) that $p = 1.13 \times 10^{27}$ m^{-3} which corresponds to 0.12 hole/Nb atom at 300 K. It may be remarked that the error in R_H is estimated to be 10–20% because of the difficulty in measuring the thickness of the very thin crystals accurately. The Seebeck coefficient is positive and equal to +50 μV K^{-1} at 300 K (figure 6).
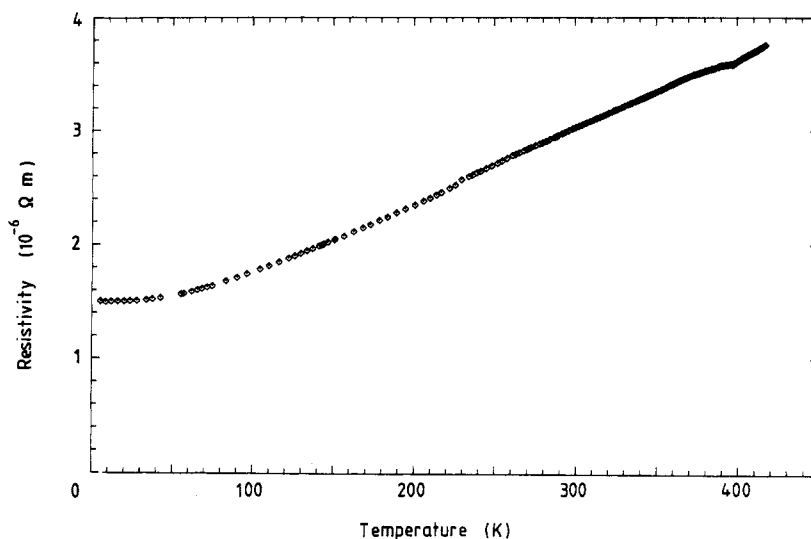
Figure 3. The in-plane resistivity $\rho_{\perp c}$ against temperature T of $(LaS)_{1.14}NbS_2$.

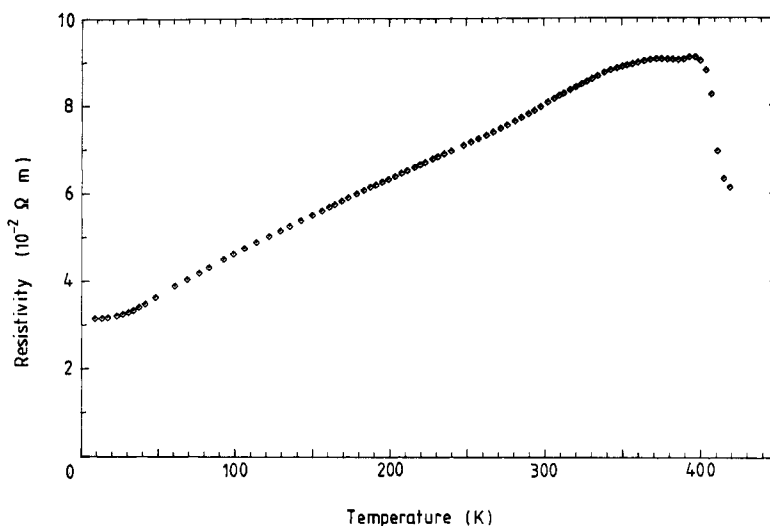**Figure 4.** The resistivity $\rho_{\parallel c}$ along the c axis against temperature T of $(LaS)_{1.14}NbS_2$.

The properties of $(LaS)_{1.14}NbS_2$ and also those of $(SnS)_{1.17}NbS_2$ and $(PbS)_{1.14}NbS_2$ reported previously (Wiegers *et al* 1988, 1989a) are strongly related to those of $2H-NbS_2$; the properties of $2H-NbS_2$ and intercalated $2H-NbS_2$ are therefore briefly reviewed. Band-structure calculations of $2H-NbS_2$ (see for a review Doni and Girlanda (1986)) have shown that owing to the trigonal–prismatic coordination of Nb, the 4d band is split up into a lower-lying half-filled band which is mainly of $4d_{z^2}$ character of Nb and an upper-lying empty 4d band. The $4d_{z^2}$ band overlaps the valence band which is mainly of S 3s, 3p character. The Hall coefficient of $2H-NbS_2$ (Naito and Tanaka 1982) is positive
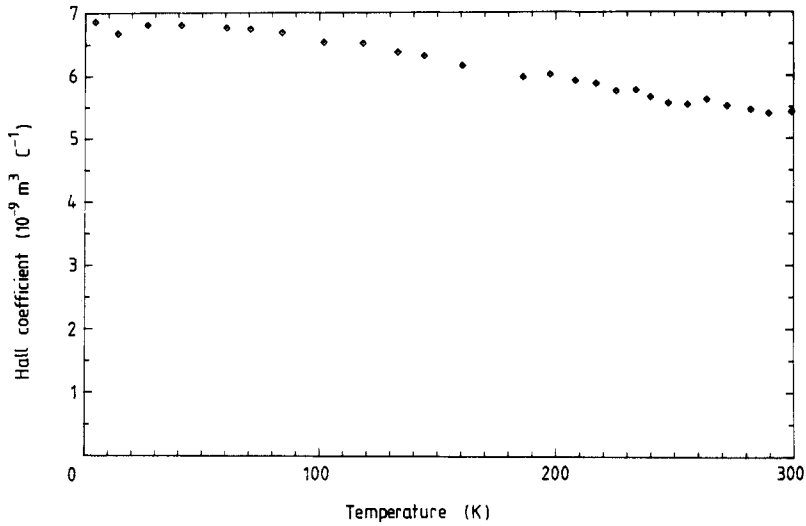
Figure 5. The Hall coefficient R_H against temperature T of (LaS)$_{1.14}$NbS$_2$.

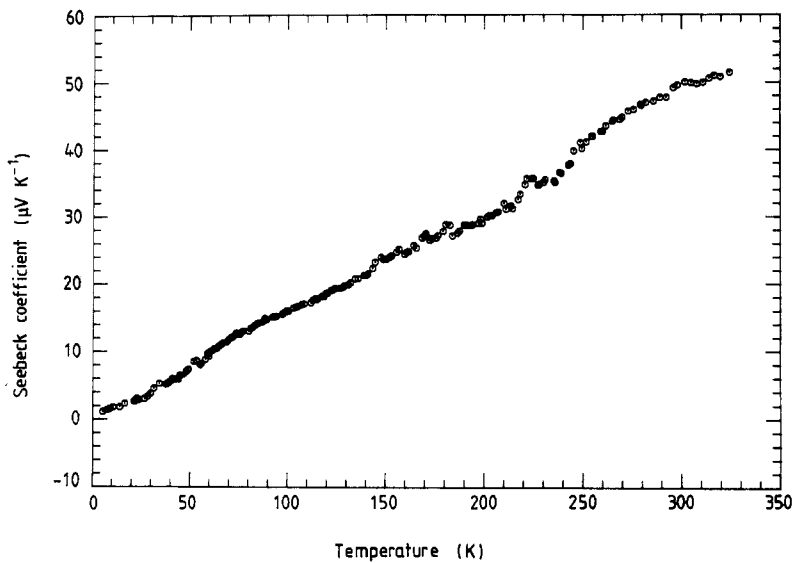**Figure 6.** The Seebeck coefficient of (LaS)$_{1.14}$NbS$_2$ against temperature T.

and equal to 3.9×10^{-10} m^3 C^{-1}; the number of holes calculated from R_H, 1.6×10^{28} m^{-3}, is in good agreement with 1 d electron/Nb in the $4d_{z^2}$ band as expected from the band structure (1.77×10^{28} Nb atoms m^{-3}). The in-plane resistivity at 300 K is 1.1×10^{-6} Ωm (Naito and Tanaka 1982). The magnetic properties are those of a high-density-of-states narrow-band Pauli paramagnetic metal (Fisher and Sienko 1980). 2H-NbS$_2$ does not show a periodic lattice distortion–charge density wave (PLD–CDW) type of transition like

the other Vb transition-metal dichalcogenides with 2H structure; it becomes super-conducting at about 6 K (see the review on the superconduction of layered transition-metal dichalcogenides and their intercalates by Frindt and Huntley (1976)).

The electrical transport properties of the intercalates of 2H-NbS$_2$ and 2H-TaS$_2$ are reasonably well explained by the rigid-band approximation (see for a review Friend and Yoffe (1987)). Intercalation leads to donation of electrons from the intercalated species to the 4d$_{z^2}$ and 5d$_{z^2}$ band of 2H-NbS$_2$ and 2H-TaS$_2$, respectively. On intercalation of 2H-NbS$_2$, one expects therefore conduction by holes in a more than half-filled 4d$_{z^2}$ band; a decrease in the density of states at E_F may become visible in the magnetic susceptibility ($\chi \sim N(E_F)$). For silver and copper intercalates of 2H-NbS$_2$ (Bouwmeester 1988, Paulus et al 1989) and 2H-TaS$_2$ (Diedering et al 1989) it was found that the Seebeck coefficient α is negative. This can be understood from the LCAO band structure of the related compound 2H-NbSe$_2$ (Bullett 1978). The Fermi surface consists of two approximately cylindrical surfaces with the axes along the Γ–A direction. The states between the inner and outer cylinder are filled, the carriers being electrons and holes on the outer and inner side, respectively. On donation of electrons the ratio of parts of the Fermi surface with electron and hole character change, the heavy electrons being manifest especially in the Seebeck coefficient.

(SnS)$_{1.17}$NbS$_2$ and (PbS)$_{1.14}$NbS$_2$ were found to be p-type metals. The number of holes per Nb atom calculated from R_H measurements on thin crystals amounts to approximately 1.1 and 0.24 for (SnS)$_{1.17}$NbS$_2$ and (PbS)$_{1.14}$NbS$_2$, respectively (Wiegers et al 1988a,b). The Seebeck coefficient of both compounds is negative, about $-15\ \mu$V K^{-1} at 300 K, as the copper and silver intercalates of 2H-NbS$_2$ mentioned above. The properties of (LaS)$_{1.14}$NbS$_2$ are in agreement with a large donation of electrons from the LaS to the NbS$_2$ part of the structure. The number of holes per Nb atom is 0.12, which indicates a donation of 0.88 electron/Nb atom. The Seebeck coefficient is positive, indicating that the electron parts of the Fermi surface have disappeared. The Fermi energy calculated using

$$\alpha = (\pi^2/3)(k/e)(kT/E_F)$$

is 0.38 eV. An approximate value for the effective mass assuming a spherical band can be obtained from

$$E_F = (h/2\pi)^2 (3\pi^2 p)^{2/3}/2m^*$$

using the hole concentration p from the Hall data and E_F from the Seebeck coefficient; the result is $m^* = 2.7m_0$. The mobility of the holes at 300 K is 1.8×10^{-3} m^2 V^{-1} s^{-1}.

The difference between (SnS)$_{1.17}$NbS$_2$ and (PbS)$_{1.14}$NbS$_2$ on the one hand and (LaS)$_{1.14}$NbS$_2$ on the other hand can be understood from the properties of SnS, PbS and LaS. It may be noted that SnS does not adopt a NaCl-type structure like PbS and LaS; the high-temperature structure of SnS is, however, closely related to the NaCl structure (Wiegers et al 1988). SnS and PbS are semiconductors with Sn and Pb in the +2 state with two 5s and 6s electrons, respectively, as a lone pair. The high electronic conductivity of LaS has been explained by the promotion of a 4f electron of La to the 5d conduction band; the compound is therefore characterised by the scheme (La^{3+}S^{2-})e$^-$. The magnetic susceptibility of LaS is of a temperature-independent Pauli paramagnetic type; χ-values of 3.53×10^{-9} and 0.65×10^{-9} m^3 mol^{-1} were reported (Bergmann 1983).

The results of the electrical transport properties of (LaS)$_{1.14}$NbS$_2$ indicate that La has a charge of about +2.8, 0.8 (=0.88/1.14) of the valence electron of La being transferred to the NbS$_2$ part of the structure. The strong anisotropy in the conduction,
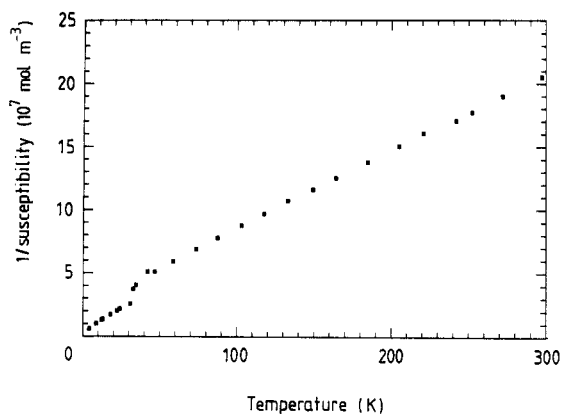
Figure 7. The reciprocal uncorrected magnetic susceptibility $1/\chi_{\|c}$ of (LaS)$_{1.14}$NbS$_2$ against temperature T, measured at a field of 0.875 T.

the conductivity along the c axis being much smaller than the in-plane conductivity, indicates that the band structure of the NbS$_2$ part is hardly disturbed by the presence of the LaS part of the structure.

4. Magnetic properties of (LaS)$_{1.14}$NbS$_2$

The magnetic susceptibility was measured using a powder compact which showed strong preferred orientation of the powder particles. The susceptibility was therefore measured with the magnetic field parallel and perpendicular to the axis of preferred orientation (the c axis). The measured susceptibilities in the two directions did not show significant differences. The stronger temperature dependence and the much higher values of the susceptibility compared with those of the Pb and Sn compounds are interpreted as owing to 4f electrons of La. The curve of $1/\chi$ against T curve (figure 7) (given only for $\chi_{\|c}$ and not corrected for diamagnetism and the Pauli susceptibility of the NbS$_2$ part) is linear in the temperature range 40–300 K with a Curie constant of 1.6×10^{-6} m^3 K mol^{-1} which corresponds to $1.6 \times 10^{-6}/1.14 = 1.4 \times 10^{-6}$ m^3 K (mol La)$^{-1}$. The contribution of the Pauli susceptibility of the NbS$_2$ part to the measured susceptibility is difficult to estimate. For 2H-NbS$_2$, the magnetic susceptibility, not corrected for diamagnetism, is 2.5×10^{-9} m^3 mol^{-1} at 300 K (Fisher and Sienko 1980); in this case the 4d$_{z^2}$ band is half-filled and the density of states is a maximum. For the Li intercalate of 2H-TaS$_2$, 2H-Li$_{0.99}$TaS$_2$, the 5d$_{z^2}$ band is almost filled and the diamagnetic susceptibility of the intercalate, -5.5×10^{-10} m^3 mol^{-1} (Murphy *et al* 1976), is close to the value of -7.3×10^{-10} m^3 mol^{-1} for semiconducting MoS$_2$ (Geertsma and Haas 1973). For (LaS)$_{1.14}$NbS$_2$ it follows from the Hall coefficient that the 4d$_{z^2}$ band contains 0.12 hole band/Nb atom; so the Pauli susceptibility is expected to be small. Correction of the measured susceptibilities of (LaS)$_{1.14}$NbS$_2$ for diamagnetism only, -6.5×10^{-10} m^3 mol^{-1} for NbS$_2$ and -7.9×10^{-10} m^3 mol^{-1} for (LaS)$_{1.14}$, assuming the Pauli susceptibility to be negligible, shows in the curve of reciprocal susceptibility against temperature T as a linear behaviour in the temperature range 120–300 K with a Curie constant of 2.4×10^{-6} m^3 K mol^{-1} (compared with 1.6×10^{-6} m^3 K mol^{-1} for the un-

corrected susceptibility). For free $La^{2+}(4f^1)$ ions, one expects a Curie constant of $1.01 \times 10^{-5} \, m^3 \, K \, mol^{-1}$ (Smart 1966). For CeS with one 4f electron, the other 4f electron being promoted to the 5d band, the Curie constant is about $0.95 \times 10^{-5} \, m^3 \, K \, mol^{-1}$ (Hulliger *et al* 1978). From the ratio $1.40 \times 10^{-6}/(1.01 \times 10^{-5}) = 0.14$ (no correction applied), one calculates a transfer of 0.86 4f electrons/La atom, in good agreement with the charge transfer found from the Hall coefficient. This means that 14% of the La atoms are in the $4f^1$ state. The Curie constant after correction for diamagnetism only corresponds to a smaller transfer, about 0.80 4f electrons/La atom. The linearity of the reciprocal uncorrected susceptibility in the temperature range 40–300 K suggests that the Pauli susceptibility of the NbS_2 part and the diamagnetic susceptibility are about the same absolute value, from which it follows that the Pauli susceptibility of the NbS_2 part is about $1.5 \times 10^{-9} \, m^3 \, K \, mol^{-1}$. The asymptotic Curie temperature for the uncorrected reciprocal susceptibility against T curve is about -35 K, indicating antiferromagnetic exchange. We have no explanation for the transition which occurs at about 40 K; it is evidently not due to antiferromagnetic ordering.

5. Conclusions

Electrical transport measurements and magnetic measurements have shown that $(LaS)_{1.14}NbS_2$ may be considered as an intercalate of $2H\text{-}NbS_2$. The electrical transport properties and the magnetic properties are ascribed to the NbS_2 and the LaS parts of the structure, respectively. Preliminary physical measurements on other rare-earth (Ce and Sm) misfit layer compounds with NbS_2 and TaS_2 sublattices are in line with those found for $(LaS)_{1.14}NbS_2$. Our conclusion for a transfer of electrons from the LaS part to the NbS_2 part is also supported by structural studies on $(SmS)_{1.19}TaS_2$ (Wiegers *et al* 1989c). Single-crystal x-ray diffraction showed the compound to be isostructural with $(PbS)_{1.13}TaS_2$ (Wulff *et al* 1989). The a and b axes of the SmS part of the structure ($a = 5.552(3)$ Å, $b = 5.679(4)$ Å, $c = 22.50(4)$ Å; space group Fm2m) point to a charge of $+3$ for Sm and not to $+2$ as for Sm in semiconducting SmS (NaCl-type structure; $a = 5.970$ Å (Bergmann 1983)). The TaS_2 part of the structure (unit-cell dimensions, $a = 3.293(1)$ Å, $b = 5.679(4)$ Å, $c = 22.50(4)$ Å; space group, Fm2m) is similar to that of $(PbS)_{1.13}TaS_2$.

In $(LaS)_{1.20}CrS_2$ with alternate NaCl-type units LaS and sandwiches CrS_2 with Cr in distorted octahedral coordination of sulphur (Kato *et al* 1973, Otera Diaz *et al* 1985; Williams and Hyde 1988), it is most likely that La has a charge of $+2.9$ and Cr a charge of $+3$ (CrS_2 does not exist in a stable state; trigonal and rhombohedral Cr_2S_3 are semiconductors with Cr^{3+} ions).

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