Trivalent rare earths in layered $(LX)_{1.15}NbX_2$ chalcogenides

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The magnetic and electrical properties of the layered misfit compounds $(LX)_{1.15}NbX_2$ have been studied for the rare earths $L = $Ce, Sm, Gd, and Yb and the chalcogens $X = $S and Se, on single crystals grown by vapor transport. The compounds consist of double layers of LX, which are 111 rocksalt planes, inserted between layers of NbX_2. In spite of the fact that the LX rocksalt compounds SmS, SmSe, and YbS contain divalent lanthanides at atmospheric pressure, in the misfit compounds the lanthanides are trivalent. This may be due to a preference for a 1 electron per rare earth charge transfer to the NbX_2 layer.

INTRODUCTION

The Sm, Yb, Eu, and Tm monochalcogenides with NaCl structure have been the subject of many studies, due to their unusual divalent rare-earth valence under ambient conditions and pressure-induced valence transitions from the divalent to trivalent state.[1] In SmS, for example, a modest pressure of 6.5 kbar induces a first-order phase transition due to the change of the Sm valence from 2^+ to an intermediate valence state, accompanied by a semiconductor-to-metal transition. Many rare-earth compounds, especially those based on Ce, Sm, Tm, and Yb, are known for unusual magnetic behavior, distinct from that of fully localized $4f$ electrons with an integer f-electron count. Recently, the crystallography of $(LX)_{1.15}NbX_2$ layered "misfit" compounds and related materials has been studied extensively.[2-5] Some physical properties have also been reported.[2-8] These compounds are of particular interest to us in the context of rare-earth properties because their crystal structures consist of two (111) planes of rocksalt-type LX sandwiched between NbX_2 layers, allowing the effects of two dimensionality, and possibly charge transfer between layers, to be studied. The unusual stoichiometries arise because the (111) rocksalt layers have a slightly different in-plane lattice parameter than the NbX_2 layers, resulting in a structural "misfit" and small deviation from an ideal commensurate $1LX:1NbX_2$ chemical ratio.

Here we present the magnetic and electrical properties of $(SmX)_{1.15}NbX_2$, $(CeX)_{1.15}NbX_2$, and $(YbX)_{1.15}NbX_2$ for $X = $S and Se, and also for $(GdSe)_{1.15}NbSe_2$. The latter compound was of interest due to the possibility of frustrated magnetic interactions between the Gd^{3+} ions in the triangular arrangement of the (111) rocksalt plane. Studies were performed on small single crystals. Crystals of Tm- and Eu-based analogs could not be grown by our techniques. The results show the presence of trivalent lanthanides in all cases, even for Sm and Yb, which are divalent in their monochalcogenides. This may be due to a charge transfer of the additional f electron into states in the NbX_2 layer, a new type of rare-earth valence stabilization recently proposed to explain x-ray photoemis-

sion spectroscopy (XPS) spectra on $(CeS)_{1.15}NbS_2$ and $(SmS)_{1.15}NbS_2$.[9,10]

SYNTHESIS

Freshly shaved rare-earth metals, Nb-metal powder, and S or Se pieces were mixed in 2-g batches in stoichiometric ratios and sealed into evacuated quartz tubes. Initial reaction temperatures were 400 °C, with slow increases in temperature in 50° increments up to 700° over the period of 1 week, with intermediate shaking and/or grinding until all signs of chalcogen vapor and rare-earth metal were eliminated. The resulting powder was then sealed in a 10-mm-i.d. quartz tube, 7 in. in length, with 30 ± 5 mg $SeCl_4$ and heated in a gradient with a hot zone temperature of 1050 °C and a cool zone of 975 °C for 1 week. In some cases the $(LX)_{1.15}NbX_2$ crystals were transported to the cold end of the tube, and in some cases they grew on the powder in the hot end. The crystals were thin hexagonal plates, varying in size from 0.5 to 5 mm along an edge, depending on the rare earth and chalcogen. Crystals employed in physical property measurements were checked by energy-dispersive x-ray analysis (EDAX) in a scanning electron microscope (SEM) to ensure that they had the correct composition.

PROPERTIES

The temperature dependence of the magnetic susceptibility was measured between 2 and 300 K in a field of 1 kOe in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Representative data are shown in Figs. 1 and 2. The data are fit well to the Curie-Weiss form with some temperature-independent susceptibility: $\chi - \chi_0 = c/(T - \theta)$, where c is the Curie constant, θ the Curie-Weiss temperature, and χ_0 the temperature-dependent susceptibility. Magnetic characteristics extracted from the fits are presented in Table I. Only the Gd compound showed magnetic ordering, at 5.4 K. Our data for $(CeS)_{1.15}NbS_2$ are not in agreement with one set published earlier, which showed a magnetic transition at 3.4 K (Ref. 6) or another set show-
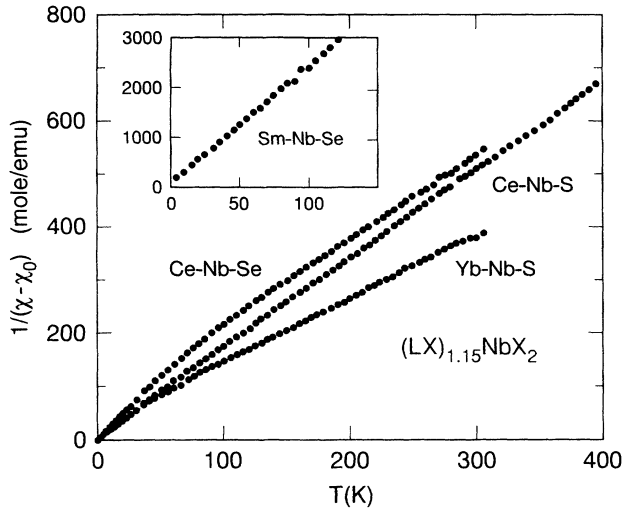
FIG. 1. Magnetic susceptibilities of $(CeS)_{1.15}NbS_2$, $(CeSe)_{1.15}NbSe_2$, $(YbS)_{1.15}NbS_2$, and $(SmSe)_{1.15}NbSe_2$ (inset) plotted as $1/(\chi - \chi_0)$ vs temperature. Fitting parameters in Table I. The rare earths are in the trivalent state.
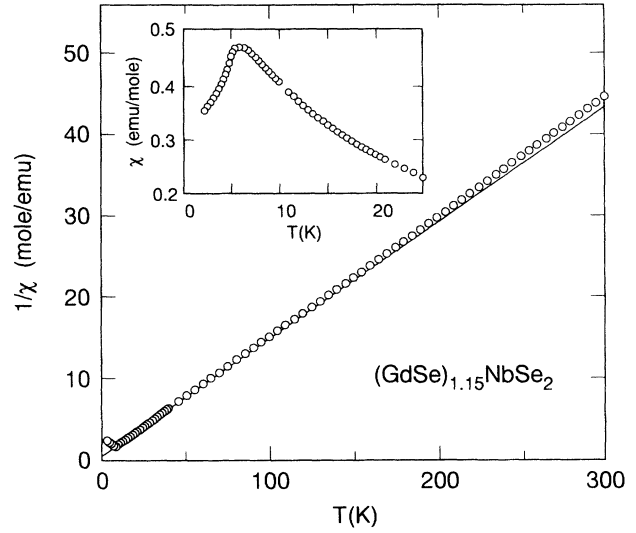

FIG. 2. Magnetic susceptibility of $(GdSe)_{1.15}NbSe_2$ plotted as $1/\chi$ vs temperature. Inset: χ vs T in the vicinity of the antiferromagnetic ordering at 5.4 K.
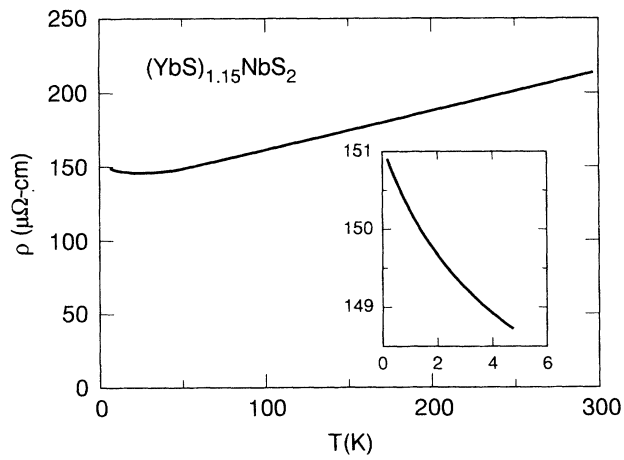

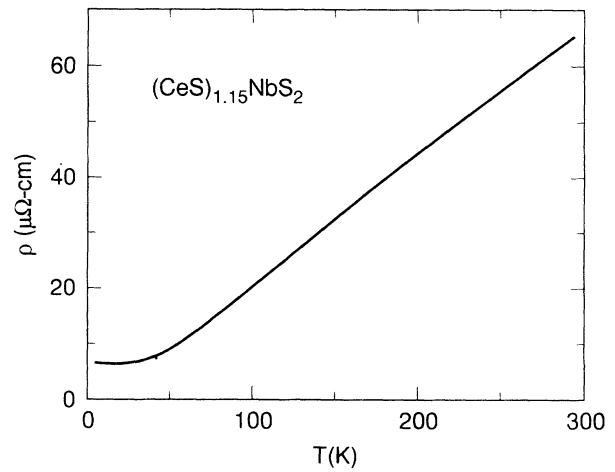FIG. 3. Basal-plane resistivity of $(YbS)_{1.15}NbS_2$ between 325 and 4.2 K and (inset) below 4.2 K.

FIG. 4. Basal-plane resistivity of $(CeS)_{1.15}NbS_2$ between 325 and 4.2 K.

TABLE I. Electrical and magnetic characterization of $(LX)_{1.15}NbX_2$.

Compound	$\rho(300)$ ($\mu\Omega$ cm)	$\dfrac{\rho(300)}{\rho_{min}}$	T_{min} (K)	$\dfrac{\rho_{LT,max} - \rho_{min}}{\rho_{min}}$	Effective moment (μ_B)		
					Low T	High T	θ (K)
$(SmS)_{1.15}NbS_2$	60	1.90	19	0.0101	0.40(1)		$-3.4(1)$
$(SmSe)_{1.15}NbSe_2$	127	2.46	14	0.0123	0.580(2)		$-5.0(1)$
$(YbS)_{1.15}NbS_2$	212	1.46	28.5	0.0350	2.08(5)	2.65(5)	$-2.3(1)$
$(YbSe)_{1.15}NbSe_2$	127	1.52	21.6	0.0268	a		
$(CeS)_{1.15}NbS_2$	64	9.9			2.15	2.23	-1.8
$(CeSe)_{1.15}NbSe_2$	90	3.12			1.76	2.30	$-1.0(1)$
$(GdSe)_{1.15}NbSe_2$ [b]	1040	1.81	14	0.0032	7.57(8)		$-6.42(2)$

[a] Crystals too small to measure $\chi(T)$.
[b] $T_N = 5.4$ K for $(GdSe)_{1.15}NbSe_2$.

ing a distinct change in slope of $1/\chi$ at 40 K.[5] In all cases the data clearly show the magnetic signature of the corresponding trivalent rare earth, with temperature-dependent effective moments due to the crystal-field splitting of $4f$ multiplets. The low values of θ are characteristic of weak antiferromagnetic interactions.

The electrical resistivity of single crystals was measured in the basal plane with dc current in a four-terminal configuration. Contacts were evaporated Au. Measurements were made between 0.3 and 300 K in a He_3/He_4 cryostat. Representative data are shown in Figs. 3 and 4. Metallic conductivity was observed in the plane of the layers in all cases. The resistivity ratios $(R_{300}/R_{4.2})$ for all materials with the exception of those for $CeXNbX_2$ were relatively low. This suggests either that the samples' resistivities are dominated by impurity scattering or that the incommensurate periodic strain which results from the mismatch in periodicity of the LX and NbX_2 layers is an effective scatterer of the conduction electrons, in which case the strain would be inferred to be lowest for $(CeS)_{1.15}NbS_2$. In addition, most of the materials show a weak upturn in resistivity at low temperatures: at 19 and 14 K for Sm-Nb sulfide and selenide, respectively, and 29 and 22 K for Yb-Nb sulfide and selenide, respectively. The upturns cannot be due to magnetic transitions in the LX layers, as none are observed. For $(GdSe)_{1.15}NbSe_3$, where a magnetic transition is observed, there is no effect in the resistivity, which is temperature independent in the vicinity of 5 K. The resistive upturns may be due to localization of carriers in the NbX_2 layers at low temperatures as a result of scattering from the strain of the layer misfits. For some samples, weak resistive drops were observed below 2 K, suggesting the presence of small amounts of intergrown superconducting NbX_2 layers.

CONCLUSIONS

The $(LX)_{1+\delta}NbX_2$ family of layered compounds consists of physically distinct rare earth chalcogenide-niobium chalcogenide layers, offering the possibility of complex electronic and magnetic behavior. We have found that the rare earths Ce, Sm, and Yb, chosen due to their tendency to form a variety of f-electron counts in chalcogenides, all occur in the 3^+ state in this family. This is in spite of the fact that the double (111) LX layers are the same geometry as those found in the Sm and Yb monochalcogenides where the rare earths are divalent. NbS_2 and $NbSe_2$ themselves are superconducting in the bulk at 6.2 and 7.3 K, respectively. The lack of superconductivity in $(LX)_{1+\delta}NbX_2$ supports our hypothesis that one electron per LX unit is transferred to the NbX_2 layers (two electrons are transferred to X within the LX layers): The greatly changed electron count suppresses the superconductivity.[11] Band-structure calculations on layered NbX_2 (Ref. 12) show that two additional electrons per formula unit could be put into the Nb d bands at the Fermi level. In some sense, then, $(LX)_{1.15}NbX_2$ is analogous to the intercalation compounds, e.g., $LiNbX_2$, with one electron transferred to the Nb d states per LX intercalate. Our conclusions are in agreement with the interpretation of the XPS spectra for $(SmS)_{1.15}NbS_2$ and $(CeS)_{1.15}NbS_2$ (Refs. 9,10). For the present materials, magnetic ordering of rare-earth moments was observed only for $(GdSe)_{1.15}NbSe_2$, which showed an antiferromagnetic transition (T_N) at 5.4 K, very close to the interaction temperature $\theta=6.42$ K, showing negligible frustration of the spins. Of the rare earths, the greatest tendency toward divalency is encountered for Eu chalcogenides. It would be of considerable interest to synthesise $EuXNbX_2$ and measure their physical properties. The results of this study on Ce-, Sm-, and Yb-based layered $(LX)_{1.15}NbX_2$ compounds show the presence of at least a moderately powerful force for trivalent rare-earth stabilization through electron transfer to a partially filled niobium-$4d$-dominated electronic band. The study of the physical properties of rare-earth chalcogenides has been largely limited to binary compounds; it would be of interest to learn how general the phenomenon of valence stabilization via charge transfer in fact may be for ternary or more complex lanthanide chalcogenides.

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