Rare Earth Transition Metal Sulfides, $LnMS_3$*

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Ternary rare earth transition metal sulfides $LnMS_3$ with Ln = La, Nd, and Gd, and M = V and Cr; as well as Ln = La and M = Mn, Fe, Co, and Ni have been prepared and characterized. The vanadium and chromium sulfides crystallize in a monoclinic layer structure isotypic with $LaCrS_3$, while the other $LnMS_3$ sulfides crystallize in a hexagonal structure. Chemical shifts of the metal K-absorption edge and XPS binding energies of core levels indicate that the transition metal is trivalent in the V and Cr sulfides, while it is divalent in the Mn, Fe, Co, and Ni sulfides. Electrical and magnetic properties of the sulfides are discussed in terms of their structures and the electronic configurations of the transition metal ions.

1. Introduction

A large number of perovskite oxides of the general formula $LnMO_3$ (Ln = lanthanide metal and M = transition metal) exhibiting a variety of structures and electronic properties have been investigated in detail (1). In view of the limited information available on the analogous ternary sulfur compounds, we have taken up a systematic study of several members of the $LnMS_3$ family, where M is a first-row transition metal ion. In the literature, the preparation of only a few of the $LnMS_3$ members has been reported (2), while their characterization has been limited to a structural study of $LaCrS_3$ (3). In the present study, we have investigated the structures as well as electronic and magnetic and related properties

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of $LnMS_3$ compounds where M is V, Cr, Mn, Fe, Co, and Ni.

2. Experimental

The ternary sulfides $LnMS_3$ were prepared from the corresponding ternary oxides by reaction with H_2S or CS_2 vapor at elevated temperatures. $LnMS_3$ compounds with M = V and Cr were obtained by the H_2S reaction at 1200 and 1000°C, respectively (for a total period of ~150 hr). $LaMS_3$ with M = Mn, Fe, Co, and Ni were synthesized by passing dry oxygen-free nitrogen saturated with CS_2 vapor over the oxides kept at 1100°C. Each sample was repeatedly heated in the stream of CS_2/N_2 with intermittent grindings until the reaction was complete as indicated by its constant weight. It generally took around 150 hr of total reaction time for the reaction to be complete. Chemical analysis for Ln, M, and S, carried out by standard methods,

showed that the compositions of the
sulfides are very close to $LnMS_3$ in all the
cases studied. We must mention here that
great care had to be exercised in ensuring
the completion of sulfide formation and to
establish exact conditions for the prepara-
tions. We have taken over a year to prepare
these compounds reliably. The compounds
were stored in evacuated sealed tubes.

X-Ray powder patterns recorded with a
Philips diffractometer (vertical goniometer
type PW 1050/70 employing Ni-filtered
$CuK\alpha$ radiation) showed the compounds to
be monophasic with unique crystal struc-
tures (Table I).

Experimental procedures for the study of
metal K-absorption edges and X-ray photo-
electron spectra (XPS) have been described
elsewhere (4, 5). Electrical resistivities re-
ported here are from four-probe measure-
ments on pressed pellets carried out in an
atmosphere of dry oxygen-free nitrogen in
the temperature range 300–600 K; for the
iron compound, resistivity was measured
up to 800 K. The pellets were presintered
under the same conditions employed for the
preparation. Seebeck coefficients were also
measured on the same pellets (6). Magnetic
susceptibility measurements were carried
out down to 100 K under vacuum by the
Faraday method employing a Cahn electro-
balance.

3. Results and Discussion

3.1 Crystal Chemistry

X-Ray powder diffraction data show that
the $LnMS_3$ compounds studied by us crys-
tallize in two different structures (Table I).
The vanadium and chromium sulfides (of
La, Nd, and Gd) crystallize in a monoclinic
structure isotypic with $LaCrS_3$ (2), wherein
alternating layers of LaS and CrS_2 are
present. Other $LnMS_3$ compounds with Ln
= La and M = Mn, Fe, Co, or Ni are
isostructural, forming in a hexagonal struc-
ture with six formula units per cell. Powder
diffraction data of two typical compounds,
$LaMnS_3$ and $LaNiS_3$, are given in Table II.
The hexagonal cell appears to be in a way
related to the $2H$ hexagonal structure of
$CsNiCl_3$ (1). In order to determine the
oxidation state of the transition metal and
the nature of sulfur in these sulfides, we
have measured the chemical shifts in the K-
absorption edge of the transition metal as
well as the valence- and core-level binding
energies using XPS. In Table III, we have
listed the chemical shifts of the transition
metal K-absorption edges in $LaMS_3$ com-
pounds. The corresponding values of bi-
nary transition metal sulfides are also
shown in this table. We readily see that, in
the case of $LaCrS_3$, the shift is close to that
of Cr_2S_3 indicating that chromium in
$LaCrS_3$ is in the trivalent state. In the other
$LaMS_3$ sulfides, the chemical shifts of the
transition metal are close to those of the
monosulfides, indicating that the oxidation
state of transition metal is likely to be $2+$.

Further evidence for the oxidation state
of M and the nature of sulfur is provided by
XPS of $LaMS_3$ compounds. XPS binding
energies of valence and core levels are
listed in Table IV. For purposes of compar-
ison, we have listed the binding energies of
the corresponding ternary oxides (7) in the
same table. We see that the binding ener-
gies of the transition metal levels are
slightly lower in the sulfides than in the

TABLE I

UNIT CELL PARAMETERS OF $LnMS_3$

Compound	a (Å)	b (Å)	c (Å)	β (°)	Unit cell volume, V (Å³)
$LaVS_3$	5.985	16.854	11.158	89.7	1125
$NdVS_3$	5.886	16.800	10.958	89.3	1083
$GdVS_3$	5.847	16.372	10.866	89.4	1040
$LaCrS_3$	5.970	17.110	11.033	87.5	1126
$NdCrS_3$	5.889	16.446	10.859	87.8	1051
$GdCrS_3$	5.838	16.205	10.703	86.9	1011
$LaMnS_3$	10.370	—	5.772	—	537.5
$LaFeS_3$	10.314	—	5.806	—	534.9
$LaCoS_3$	10.318	—	5.776	—	532.5
$LaNiS_3$	10.295	—	5.762	—	528.9

TABLE II

X-Ray Powder Diffraction Data of $LaMnS_3$ and $LaNiS_3$[a]

hkl	LaMnS$_3$			LaNiS$_3$		
	I/I_0	d_{obs} (Å)	d_{calc} (Å)	I/I_0	d_{obs} (Å)	d_{calc} (Å)
101	25	4.87	4.86	30	4.84	4.84
200	25	4.51	4.49	25	4.46	4.46
111	50	3.870	3.857	60	3.839	3.839
201	100	3.555	3.544	100	3.527	3.526
210	40	3.401	3.394	45	3.373	3.370
211	10	2.929	2.926	15	2.912	2.909
002	20	2.885	2.886	20	2.876	2.881
301	35	2.659	2.657	20	2.638	2.641
220	30	2.595	2.592	35	2.574	2.574
112	25	2.522	2.522	30	2.514	2.514
310	50	2.493	2.491	65	2.475	2.473
202	40	2.428	2.428	40	2.417	2.420
311	65	2.288	2.287	60	2.272	2.272
212	40	2.201	2.199	30	2.189	2.190
{401	—	—	—			2.079
{302	—	—	—	8	2.078	2.069
312	30	1.883	1.886	30	1.873	1.876
411	50	1.853	1.856	30	1.842	1.843
311	20	1.656	1.656	15	1.645	1.644

[a] Unit cell parameters are given in Table I.

oxides due to the higher covalency of the former compounds. The lanthanum levels in LaMS$_3$ are similar to those in LaMO$_3$ showing $4d$ and $3d$ peaks with characteristic satellites (7). A comparison of the core level binding energies of transition metals in the LnMS$_3$ compounds with the values

TABLE III

Chemical Shifts of Transition Metal (M) K-Absorption Edges in LaMS$_3$

Compound	K-absorption edge energy (± 0.5 eV)	Chemical shift[a] ΔE (eV)
LaCrS$_3$	5996.25	7.4[b] (5.0)
LaMnS$_3$	6543.80	5.80 (5.0)
LaFeS$_3$	7118.49	7.0 (6.5)
LaCoS$_3$	7717.68	8.0 (7.4)
LaNiS$_3$	8337.10	5.9 (5.3)

[a] ΔE values for the corresponding transition metal monosulfides are shown in parentheses.

[b] ΔE of Cr$_2$S$_3$ is 7.6 eV.

in the corresponding transition metal monosulfides (8) indicates that the metal is trivalent in LaVS$_3$ and LaCrS$_3$ and divalent in the other LnMS$_3$ compounds. From the XPS data we also see that LaVS$_3$ and LaCrS$_3$ show single sharp peaks for the sulfur ($3s$) and ($2s$) levels, whereas the other LaMS$_3$ (M = Mn, Fe, Co, Ni) compounds show two S($3s$) peaks and broad S($2s$) peaks suggesting presence of two types of sulfur anions. We have similarly found presence of two sulfur anions, S^{2-} and S$_2^{2-}$, in the case of CuS (8). The results from XPS and K-absorption edge measurements are consistent with the following formulation of the LnMS$_3$ compounds: (i) $Ln^{3+}M^{3+}3S^{2-}$ in the case of M = V and Cr and (ii) $La^{3+}M^{2+}2S^{2-} 0.5(S_2^{2-})$ in the case of M = Mn, Fe, Co, and Ni.

3.2 Electron Transport Properties

Results of our measurements of electrical

TABLE IV

XPS Binding Energies (eV) of LaMS₃ᵃ

Compound	M levels		S levels		La levels	
LaVS₃	$3d$ 0.1	(1.0)	$3p$ 4.5		$5p$ 17.8	
	$3p$ 38.9	(40.7)	$3s$ 13.2		$4d_{5/2}$ 102.1 (102.7)	
	$2p_{3/2}$ 514.6	(516.6)	$2p$ 161.3		$3d_{5/2}$ 836.5 (834.5)	
	$2p_{1/2}$ 522.1	(524.1)	$2s$ 225.3			
LaCrS₃	$3d$ 2.0	(2.4)	$3p$ 3.8, 5.0		$5p$ 17.6	
	$3p$ 43.0	(43.2)	$3s$ 14.0		$4d_{5/2}$ 102.3 (101.1)	
	$2p_{3/2}$ 575.8	(576.0)	$2p$ 161.2		$3d_{5/2}$ 836.4 (834.4)	
	$2p_{1/2}$ 585.3	(586.1)	$2s$ 225.1			
LaMnS₃	$3d$ 1.2	(1.0, 3.5)	$3p$ 3.5, 7.8		$5p$ 17.6	
	$3p$ —	(48.3)	$3s$ 11.0–13.5		$4d_{5/2}$ 102.3 (101.5)	
	$2p_{3/2}$ 639.2	(640.9)	$2p$ 161.4		$3d_{5/2}$ 836.7 (834.1)	
	$2p_{1/2}$ 650.0	(652.9)	$2s$ 225.4			
LaFeS₃	$3d$ 0.3, 3.1	(2.0, 4.0)	$3p$ 4.6		$5p$ 17.8	
	$3p$ —	(55.2)	$3s$ 10.5, 13.0		$4d_{5/2}$ 102.6 (101.2)	
	$2p_{3/2}$ 706.6	(710.5)	$2p$ 161.4		$3d_{5/2}$ 836.7 (833.7)	
	$2p_{1/2}$ 719.9	(724.0)	$2s$ 225.4			
LaCoS₃	$3d$ 0.2, 1.5	(—)	$3p$ 3.8, 7.7		$5p$ 17.8	
	$3p$ —	(60.6)	$3s$ 10.5, 13.7		$4d_{5/2}$ 102.3 (101.5)	
	$2p_{3/2}$ 778.3	(779.6)	$2p$ 161.3		$3d_{5/2}$ 836.7 (833.6)	
	$2p_{1/2}$ 793.4	(795.2)	$2s$ 225.6			
LaNiS₃	$3d$ 1.1, 2.8	(1.0, 2.8)	$3p$ 4.5, 7.4		$5p$ 17.7	
	$3p$ 67.1	(67.1)	$3s$ 11.5, 14.0		$4d_{5/2}$ 102.2 (101.1)	
	$2p_{3/2}$ 852.7	(—)	$2p$ 161.1		$3d_{5/2}$ 836.8 (833.8)	
	$2p_{1/2}$ 869.8	(—)	$2s$ 225.5			

ᵃ Values in parentheses are those found in the corresponding oxides, LaMO₃ (from Ref. (7)).

properties of $LnMS_3$ compounds are summarized in Table V. Among the isostructural $LnVS_3$ and $LnCrS_3$ compounds possessing layer structures, the vanadium compounds show low resistivities and small positive Seebeck coefficients. While LaVS₃ clearly shows metal-like temperature dependence of resistivity, NdVS₃ and GdVS₃ do not show this behavior (Fig. 1). Electron transport in $LnVS_3$ may arise from holes in the S($3p$) band created by the partial overlap of V($3d$) states with the top of S($3p$) bonding states; this model is similar to the type (e) band model proposed by Jellinek (9) for transition metal chalcogenides. In contrast to the behaviour of $LnVS_3$, the isostructural $LnCrS_3$ compounds are insula-

tors with resistivities of the order of 10⁶ ohm · cm at 300 K. The activation energy, E_a, for electrical conduction varies in the order Gd > Nd > La just as in the oxides (6). The large negative Seebeck coefficient of $LnCrS_3$ at 300 K suggests the presence of a small sulfur deficiency which can be shown as $LnCr^{3+}_{1-x}Cr^{2+}_{x}S_{3-x/2}$. The sharp change in the electron transport properties of $LnMS_3$ compounds on passing from $M =$ V to $M =$ Cr is reminiscent of the behavior in LaMO₃ perovskites (1), where LaTiO₃ is a metal, LaVO₃ is a semiconductor with a small activation energy, and LaCrO₃ is an insulator. In $LnMO_3$ the changes have been explained by Goodenough (10) on the basis of the varying M–O covalent interaction

TABLE V

ELECTRICAL AND MAGNETIC PROPERTIES OF $LnMS_3$

Compound	μ_{eff}[a] (μ_B)		Θ[b] (K)	Resistivity at 300 K ρ (ohm · cm)	Seebeck coefficient at 300 K, α (μV/deg)	Activation energy E_a (eV)
	Expt.	Calcd.				
LaVS$_3$	Pauli para-magnetic	2.83	—	3×10^{-3}	+9	Metallic
NdVS$_3$	4.24	4.59	−180	5×10^{-3}	+10	—
GdVS$_3$	8.37	8.43	−50	10×10^{-3}	+10	—
LaCrS$_3$	3.70	3.87	−350	5×10^6	−800	0.48
NdCrS$_3$	5.00[c]	5.30	−140[c]	6×10^6	−300	0.50
GdCrS$_3$	9.40	8.83	−50	7×10^6	−200	0.56
LaMnS$_3$	5.50	5.92	−300	1.0	+22	0.05
LaFeS$_3$	4.00	4.90	+450	0.3	+19	0.08
LaCoS$_3$	2.32	1.73	−110	4.0×10^{-2}	−10	Metallic
LaNiS$_3$	1.35	2.83	25	1.0×10^{-2}	−11	Metallic

[a] μ_{eff} for the transition metal, M.

[b] Paramagnetic Curie temperature.

[c] μ_{eff} from Cr^{3+} contribution alone is 3.55 in agreement with the spin-only value of Cr^{3+}; the corresponding Θ is −300 K.

across the transition metal series. It is also to be noted that in the isostructural $NaMS_2$

FIG. 1. Temperature dependence of electrical resistivity of $LnMS_3$ sulfides: (a) 1, LaVS$_3$ and 2, NdVS$_3$; (b) 1, LaCoS$_3$ and 2, LaNiS$_3$; (c) 1, LaMnS$_3$ and 2, LaFeS$_3$.

series, NaTiS$_2$ is a metal, NaVS$_2$ a good conductor, and NaCrS$_2$ an insulator (11).

Among the LaMS$_3$ sulfides with M = Mn, Fe, Co, or Ni, the cobalt and nickel compounds are definitely metallic with small negative Seebeck coefficients (Fig. 1). The manganese and iron compounds, on the other hand, are p-type semiconductors with small activation energies (Fig. 1). It is interesting to compare the electronic properties of pyrite disulfides of Mn, Fe, Co, and Ni (12) with those of the LaMS$_3$ compounds. MnS$_2$ shows localized electron behavior similar to LaMnS$_3$, which is characteristic of octahedral-site high-spin $Mn^{2+}:3d^5$. In the other pyrites, covalent interaction between the metal and sulfur is stronger than in the manganese compound creating a narrow σ^* band from the metal e_g orbitals. Electronic properties of FeS$_2$, CoS$_2$, and NiS$_2$ have been explained in terms of electron correlation and occupancy of the σ^* band. Although LaFeS$_3$ is a semiconductor similar to FeS$_2$, the magnetic properties are different (as can be
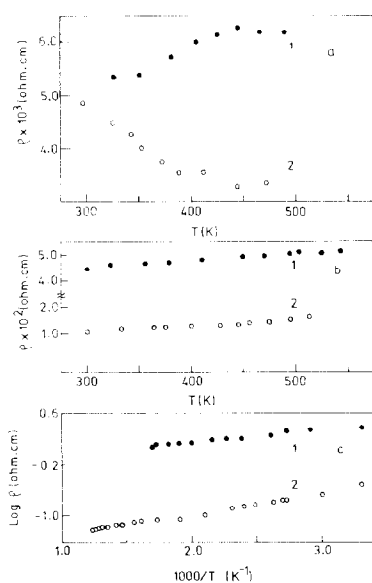
seen in the next section); Fe^{2+} is in the high-spin state in $LaFeS_3$ unlike in FeS_2. The result seems to indicate that covalent interaction between iron and sulfur in $LaFeS_3$ is not strong enough to give rise to the low-spin state of Fe^{2+}. A definite interpretation of electronic properties of this isostructural $LaMS_3$ series must await determination of their detailed crystal structures.

3.3 Magnetic Properties

Magnetic properties of $LnMS_3$ compounds are summarized in Table V. $LaVS_3$ (Fig. 2) has a small molar magnetic susceptibility, χ_m ($\sim350 \times 10^{-6}$ cgs units) which is nearly independent of temperature down to 200 K; at low temperatures, the susceptibility develops a "Curie tail," similar to that found in VO_x (13) and VS_x (14). In order to see whether the magnetic properties of $NdVS_3$ and $GdVS_3$ are similar to $LaVS_3$, we subtracted the rare earth ion contribution

from the measured susceptibility and plotted the reciprocal of the difference susceptibility, $\Delta\chi_m^{-1}$, against temperature (Fig. 2). We find the behavior to be similar to $LaVS_3$ except that $\Delta\chi_m$ is higher ($\sim820 \times 10^{-6}$ cgs units for $NdVS_3$) indicating a greater degree of localization of $V(3d)$ electrons in $NdVS_3$ and $GdVS_3$ than in $LaVS_3$. This behavior is consistent with electrical properties of these vanadium sulfides.

$LnCrS_3$ compounds show Curie–Weiss paramagnetism at high temperatures in all the three cases studied (Fig. 3). The effective magnetic moments, μ_{eff}, obtained from the linear region of the χ_m^{-1}–T plots are in fair agreement with the values calculated assuming spin-only contribution for Cr^{3+} and spin and orbital contribution for Ln^{3+} (Table V). The paramagnetic Curie temperatures, Θ, are negative, the absolute values varying in the order La > Nd > Gd. The χ_m^{-1}–T plots do not, however, show a Néel temperature; instead, the plots deviate from the Curie–Weiss law at low tempera-
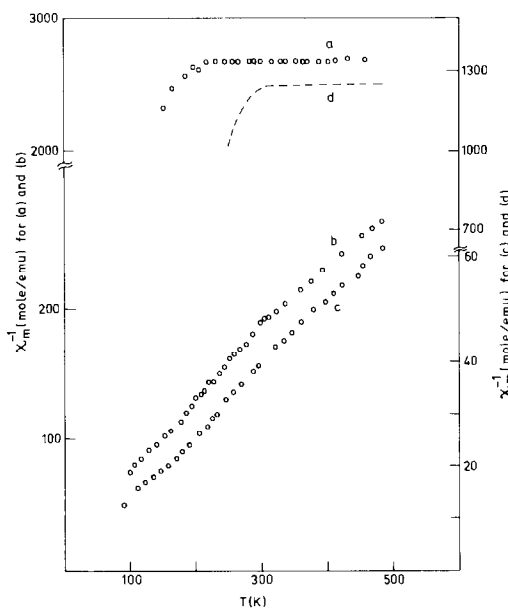

FIG. 2. χ_m^{-1}–T plots of (a) $LaVS_3$, (b) $NdVS_3$, and (c) $GdVS_3$; plot of vanadium contribution in the case of $NdVS_3$ is shown by the broken curve (d).
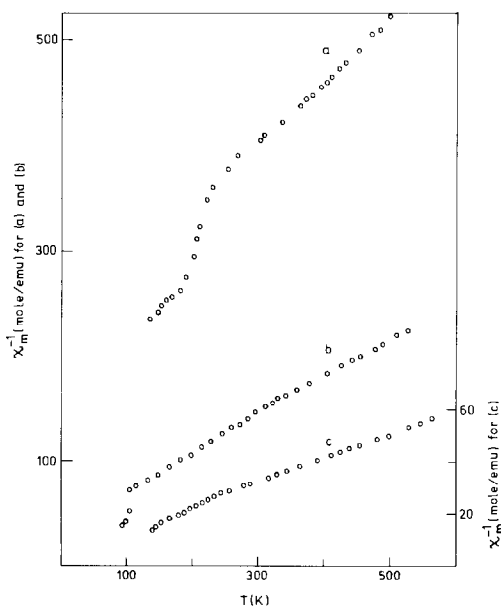

FIG. 3. χ_m^{-1}–T plots of (a) $LaCrS_3$, (b) $NdCrS_3$, and (c) $GdCrS_3$.

tures towards larger susceptibility values. In the $LaCrS_3$ structure consisting of alternating rocksalt-like LaS and CdI_2-like CrS_2 layers (3), two types of magnetic interaction between chromium ions are possible: antiferromagnetic Cr–Cr interaction and a ferromagnetic 90° Cr–S–Cr interaction between the edge-shared CrS_6 octahedra in the CrS_2 layers. While the negative Weiss constant suggests antiferromagnetic interaction, the deviation from the Curie–Weiss law at low temperatures may arise from a short-range ferromagnetic interaction within the CrS_2 layers. Similar weak ferromagnetism is shown by $Ln$$CrSe_3$ crystallizing in the (NH_4) $CdCl_3$ structure (15).

The χ_m^{-1}–T plots (Fig. 4) of $LaMnS_3$, $LaCoS_3$, and $LaNiS_3$ show Curie–Weiss law behavior with negative Weiss constants. A μ_{eff} value of 5.5 μ_B found for the manganese compound is consistent with the 2+ oxidation state of manganese ($3d^5$). The μ_{eff} value (2.32 μ_B) found in $LaCoS_3$ is slightly higher than the value expected for

octahedral-site low-spin Co^{2+} ion. The CoS_2–$CoSe_2$ system where divalent cobalt is in the low-spin state, also has a similar μ_{eff} (16). The susceptibility of $LaNiS_3$ at room temperature is quite small ($\sim$690 × 10^{-6} cgs units) and shows a weak temperature dependence, the behavior being consistent with its metallic nature. The magnetic property of $LaNiS_3$ is roughly comparable to that of $NiSe_2$ (17).

$LaFeS_3$ shows a sharp magnetic transition around 620 K (Fig. 4). Above the transition temperature, the susceptibility seems to follow Curie–Weiss law behavior with μ_{eff} of about 4 μ_B which is close to that expected from high-spin Fe^{2+} ions. Because of thermal hysterisis it was not possible to obtain an exact value of μ_{eff}. At the transition temperature, the susceptibility increases by more than an order of magnitude and thereafter remains almost constant down to 150 K. Similar transitions to weak ferromagnetic state occur in α-Fe_2O_3 and $LaFeO_3$ (18). We are unable to ascribe the observed behavior of $LaFeS_3$ to oxide impurities since $LaFeS_3$ prepared by us was monophasic with a distinct crystal structure and exhibited very low resistivity and a relatively small Seebeck coefficient unlike Fe_2O_3 or $LaFeO_3$.
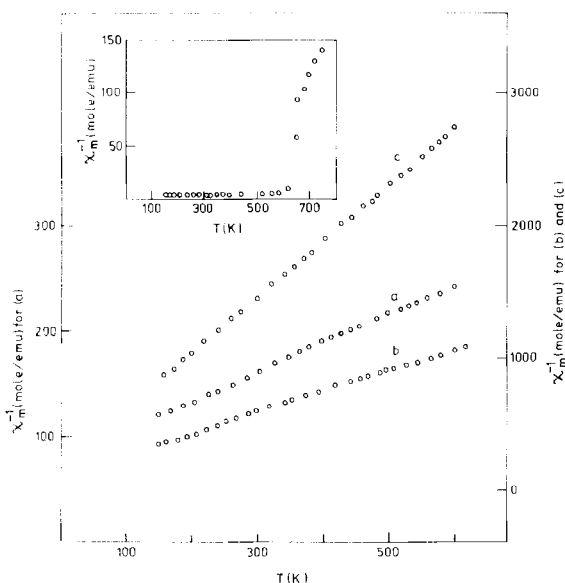
FIG. 4. χ_m^{-1}–T plots of (a) $LaMnS_3$, (b) $LaCoS_3$, and (c) $LaNiS_3$. The χ_m^{-1}–T plot of $LaFeS_3$ is shown in the inset.

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