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Preparation, Structure, and Magnetic Properties of Isostructural La_3MAlS_7 and La_3MFeS_7 (M = Mg, Mn, Fe, Co, Ni, or Zn)*

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A series of quaternary metal sulfides of the general formula $La_3MM'S_7$ (M = Mn, Fe, Co; M' = Al and M = Mg, Mn, Fe, Co, Ni; M' = Fe) consisting of linear chains of face shared MS_6 octahedra and isolated $M'S_4$ tetrahedra has been prepared and studied. The aluminium compounds La_3MAlS_7 (M = Mn, Fe, Co) exhibit linear chain antiferromagnetism. Magnetic behavior of other La_3MFeS_7 sulfides has been examined in detail. The magnetic susceptibility of La_3MgFeS_7 shows that tetrahedral site Fe^{3+} undergoes a transition from $S = \frac{5}{2}$ to $S = 2$ spin state around 150 K.

Introduction

Flahaut and co-workers (*1–3*) reported a family of metal sulfides of the general formula $Ln_3MM'S_7$ (Ln = rare earth, M = a divalent metal such as Mg, Mn, etc., and M' = Al or Ga). These sulfides crystallize in a hexagonal structure (space group $P6_3$) consisting of chains of MS_6 octahedra sharing faces along the c axis and isolated $M'S_4$ tetrahedra (Fig. 1). The structure appears to be stabilized by the tetrahedral site M' atoms that form strong covalent bonds with sulfur (*1*). It is apparent from Fig. 1 that magnetic interaction among the M ions in the octahedral chains can occur in only one dimension. With a view to investigate such a one-dimensional behavior, we have carried out a magnetic susceptibility study of sulfides of the formula La_3MAlS_7 where M = Mn, Fe, or Co. The study has indeed revealed linear chain antiferromagnetism in these novel sulfides.

Another interesting aspect of $La_3MM'S_7$ sulfides that we have investigated relates to the replacement of Al or Ga at the tetrahedral (M') sites by a paramagnetic ion. The obvious choice for a paramagnetic M' would be Fe^{3+} since this ion is known to exist in tetrahedral sulfur coordination in several sulfides such as $AFeS_2$ (A = K, Rb, Cs) (*4*), $BaFe_2S_4$ (*5*), $Ba_5Fe_4S_{11}$ (*6*), and Na_3FeS_3 (*7*). We have successfully prepared a series of sulfides of the general formula La_3MFeS_7 with M = Mg, Mn, Fe, Co, Ni, and Zn. These sulfides are isostructural with the La_3MAlS_7 series, but show distinctly different magnetic properties. In particular, La_3MgFeS_7 shows a transition involving the spin state of the Fe^{3+} ion from $S = \frac{5}{2}$ to $S = 2$ state which is likely to arise from an electron transfer from sulfur ($3p^6$) to iron ($3d^5$).

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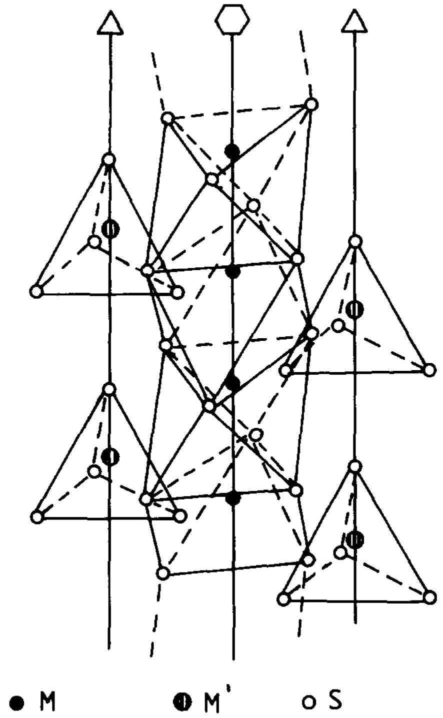

FIG. 1. Structure of $La_3MM'S_7$. Only MS_6 octahedra forming chains and isolated $M'S_4$ tetrahedra are shown (after Ref. (*1*)).

Experimental

La_3MFeS_7 (M = Mg, Mn, Fe, Co, Ni, or Zn) were prepared by sulfidation of oxide mixtures using CS_2 vapors at 1100°C. The oxide mixtures were prepared by mixing aqueous solutions of the nitrates of lanthanum, iron, and M in the required stoichiometry, concentrating to a small volume and decomposing it around 600°C. Graphite boats were used for sulfidation. Sulfide formation was found to be complete in about 6 days with two grindings in between. The sulfur content of the samples was determined gravimetrically as $BaSO_4$ after oxidizing the sulfide with Br_2 in CCl_4 and HNO_3. The procedure for the preparation of La_3MAlS_7 (M = Mn, Fe, Co) was similar except that slightly higher temperature (1150–1200°C) was required for sulfidation. Experimental procedures for recording X-ray powder diffraction patterns and measuring magnetic and electrical properties were the same as reported by us in a recent paper (*8*).

Results and Discussion

La₃MAlS₇

To characterize the magnetic behavior of paramagnetic M^{2+} ions at the octahedral sites of the Ln_3MAlS_7 structure (*1*), we have measured the susceptibilities of La_3MAlS_7 with M = Mn, Fe, or Co and the $\chi_m - T$ plots are shown in Fig. 2. All three sulfides show a broad maximum around 115–130 K indicating an antiferromagnetic ordering. The susceptibility increases sharply below 80 K. Magnetism in these sulfides consisting of linear chains of face-sharing MS_6 octahedra along the hexagonal c axis is comparable to that of Ba_2MS_3 (*9*). The linear chain antiferromagnetism of the latter series of sulfides has been attributed to a short-range magnetic ordering in the chains formed by corner-sharing MS_4 tetrahedra. The temperature dependence of the susceptibility of these sulfides has been analyzed on the basis of a reduced-spin model proposed by Emori *et al.* (*10*) for one-dimensional systems with $S \geq 1$. The susceptibility according to this model is given by

$$\chi = \frac{Ng^2\beta S(S+1)}{3kT} e^{J'/kT}$$

where $J' = \frac{4}{3}JS(S+1)$ and N, g, and β have the usual significance. A plot of $\log[3k\chi_m T/N\beta^2]$ against T^{-1} would be linear above the ordering temperature, the slope and the intercept giving J and μ_{eff} values. Such plots for La_3MAlS_7 are shown in Fig. 3 and the relevant data from the plots in Table I. The μ_{eff} and J/K values are comparable to those of Ba_2MS_3 indicating that M^{2+} in La_3MAlS_7 are in the high spin state and that these sulfides show linear chain antiferromagnetism

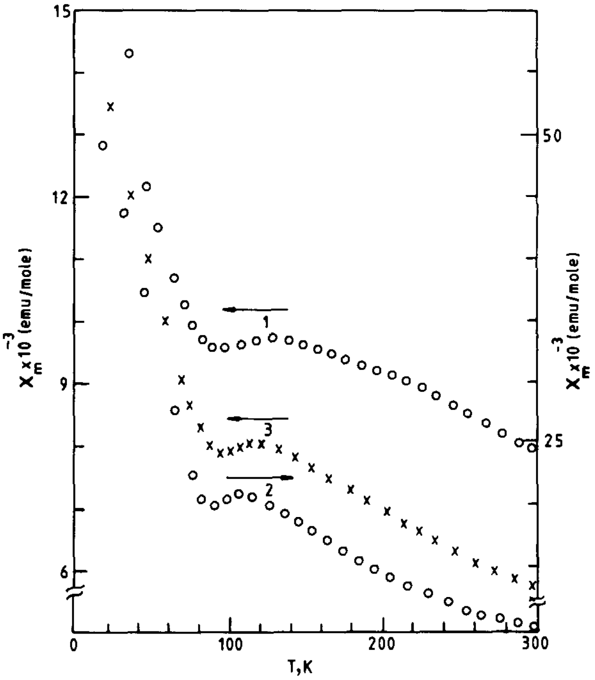

FIG. 2. $\chi_m - T$ plots of La_3MAlS_7: 1, M = Mn; 2, M = Fe; and 3, M = Co.

due to short-range ordering in the MS_6 octahedral chains. The sharp increase of susceptibility at low temperatures is seen in other linear chain antiferromagnetic systems such as $(NH_4)_2MnF_5$ and has been attributed by Emori *et al.* (*10*) to interchain interaction and end effects in the chain.

La_3MFeS_7

We have prepared a new series of $La_3MM'S_7$ sulfides with M' = Fe and M = Mg, Fe, Co, Ni, or Zn by reaction of the corresponding oxide mixtures with CS_2 vapors around 1100°C. Chemical analysis of sulfur and X-ray diffraction data (Table II) reveal that stoichiometric La_3MFeS_7 are formed for all the M investigated. The Mn, Fe, Co, and Ni sulfides are isostructural crystallizing in the hexagonal structure of La_3MAlS_7 (*1–3*). The *c* parameter remains nearly constant but the cell volume shows a slight decrease along the series Mn–Ni as expected. The M = Mg and Zn compounds show a distortion to orthorhombic symme-

TABLE I

MAGNETIC DATA ON La_3MAlS_7 (M = Mn, Fe, Co)

Compound	T_N (K)	θ (K)	μ_{eff} (BM) from χ_m^{-1} vs T plot	μ_{eff} (BM) = $[g^2S(S+1)]^{\frac{1}{2}}$	J/K	M–M distance (Å)
La_3MnAlS_7	115	−515	6.80	5.72	−14	3.01
La_3FeAlS_7	110	−48	5.65	5.62	−6.2	3.01
La_3CoAlS_7	130	−260	4.90	4.30	−21	3.01

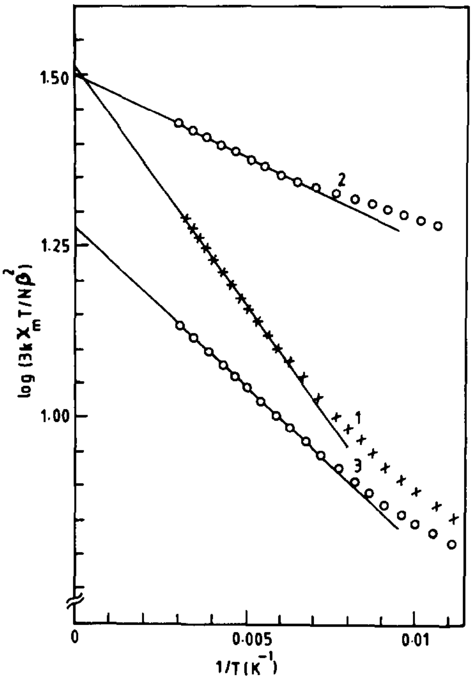

FIG. 3. Analysis of magnetic susceptibility data of La_3MAlS_7 according to the reduced-spin model: 1, M = Mn; 2, M = Fe; and 3, M = Co.

try with $a_o \simeq a_h$, $b_o \simeq \sqrt{3}\, a_h$, and $c_o = c_h$, where a_h and c_h denote the hexagonal cell parameters of $La_3MM'S_7$ cell. A comparison of the unit cell parameters of La_3MFeS_7 series with those of the corresponding La_3MAlS_7 (*2*) reveals that the c/a ratio is significantly smaller in the iron series (c axis particularly smaller). Flahaut and Laruelle (*1*) have remarked that the c parameter is principally determined by the tetrahedral site M' atom. The distinct shortening of the c parameter in the La_3MFeS_7 series as compared to the aluminium series may be taken as an indication of strong covalent Fe–S bonds in the FeS_4 tetrahedra.

We have refined the atomic position parameters of La_3MnFeS_7 in the space group $P6_3$ using X-ray powder diffraction intensities and the program POWDER (*11*). The observed and calculated intensities are given in Table III and the corresponding atomic positions in Table IV. The refinement shows that La_3MnFeS_7 is indeed isostructural with the La_3MAlS_7 series. The bond lengths indicate that the coordination of Mn is octahedral with two sets of Mn–S bonds (2.81 and 2.77 Å). The FeS_4 tetrahedron is distorted with one short (2.11 Å) and three long (2.22–2.23 Å) bonds. These bond lengths are believed to be accurate only within ±0.01 Å since the values are obtained from a refinement of limited number of powder diffraction intensity data. The average Fe–S distance is usually around 2.233 Å in tetrahedrally coordinated Fe^{3+} sulfides (*12*). A similarly distorted

TABLE II

UNIT CELL PARAMETERS AND SULPHUR ANALYSIS DATA OF La_3MFeS_7

Compound	a (Å)	c (Å)	c/a	Unit cell volume V (Å^3)	S (%) Exp.	S (%) Calc.
La_3MnFeS_7	10.323(5)	5.803(3)	0.5620	803.4	29.95	29.85
$La_3Fe_2S_7$	10.321(6)	5.804(4)	0.5623	803.2	29.85	29.80
La_3CoFeS_7	10.321(5)	5.804(4)	0.5622	802.8	30.60	29.70
La_3NiFeS_7	10.322(6)	5.802(3)	0.5621	803.0	28.25	29.70
La_3MgFeS_7	a = 10.297(7) b = 18.020(1)	5.807(5)	0.5640	808.0	31.06	31.11
La_3ZnFeS_7	a = 10.286(8) b = 18.050(1)	5.802(5)	0.5640	808.0	29.30	29.44

TABLE III

X-RAY POWDER DIFFRACTION DATA OF La_3MnFeS_7

hkl	d_{obs} (Å)	d_{cal} (Å)[a]	I_{obs}	I_{calc}[b]
101	4.87	4.86	22.00	21.80
200	4.48	4.47	21.30	20.44
201	3.54	3.54	100.00	102.54
210	3.380	3.380	35.90	35.24
211	2.921	2.920	14.60	10.96
002	2.894	2.901	17.30	17.38
301	2.652	2.651	26.40	24.50
220	2.585	2.581	50.10	49.88
112	2.529	2.529	31.50	31.60
310	2.480	2.479	49.80	49.92
212	2.196	2.201	31.60	31.61
321 222	1.933	1.934 1.928	21.20	24.31
312 103	1.880	1.884 1.890	31.60	30.14
411	1.848	1.849	23.60	24.26
402 203	1.771	1.770 1.775	18.60	18.43
501	1.709	1.709	8.00	9.25
331	1.650	1.649	12.20	11.37
412 421 303	1.618	1.619 1.622 1.622	15.40	14.47

[a] The unit cell parameters are given in Table II.

[b] The atomic position parameters are given in Table IV.

AlS_4 tetrahedron with three long and one short Al–S bonds is found in the corresponding aluminium sulfides (*1*).

The inverse magnetic susceptibility–temperature plots for La_3MFeS_7 sulfides are shown in Fig. 4. We see two linear regions with a break or plateau in the region 150–180 K in most cases. The magnetic behavior of La_3MgFeS_7 is expected to be the simplest arising from tetrahedral site Fe^{3+}. Indeed, the high temperature linear region of the $X_m^{-1} - T$ plot of La_3MgFeS_7 gives a μ_{eff} of 5.85 B.M. ($\theta = -50$ K) which is consistent with high spin ($S = \frac{5}{2}$) Fe^{3+}. The moment in the low-temperature region is, however, 4.90 B.M. ($\theta = -10$ K), which indicates a $S = 2$ state for iron. It is difficult to understand the origin of lower moment of iron in terms of the structure of La_3MFeS_7 because there seems to be no possibility of direct Fe–Fe interaction as the FeS_4 tetrahedra are isolated. Ba_3FeS_5 in which the formal valency of iron is 4+ possesses similar isolated FeS_4 tetrahedra and exhibits a $S = 2$ spin state for iron (*13*). Occurrence of $S = 2$ iron in this sulfide has been explained as arising from coupling of a hole in the S : $3p^6$ band with Fe : $3d^5$ configuration resulting in a net spin of $S = 2$ at iron (*14*). It is likely that in La_3MgFeS_7 the $Fe^{3+} : 3d^5$ state overlaps with the $S^{2-} : 3p^6$ band states at lower temperatures resulting in creation of holes in the S(3*p*) band and a $S = 2$ state for iron. Na_3FeS_3 is an example of Fe(III) sulfide consisting of a pair of FeS_4 tetrahedra sharing a common edge $(Fe_2S_6)^{6-}$ wherein iron is in the $S = 2$ state (*7*). La_3ZnFeS_7 gives a μ_{eff} of 4.60 B.M. and the value does not change significantly at low temperatures. It appears that in this compound iron is present in the $S = 2$ state even at room temperature.

TABLE IV

CRYSTALLOGRAPHIC DATA OF La_3MnFeS_7 (COMPOSITION: La_3MnFeS_7: SPACE GROUP: $P6_3$ ($Z = 2$))

		Atomic coordinates		
Atom	Position	*x*	*y*	*z*
La	6*c*	0.361(1)	0.128(2)	0.250(3)
Fe	2*b*	$\frac{1}{3}$	$\frac{2}{3}$	0.164(4)
Mn	2*a*	0	0	0.015(8)
S(I)	6*c*	0.263(6)	0.091(7)	0.758(5)
S(II)	6*c*	0.525(8)	0.421(5)	0.523(4)
S(III)	2*b*	$\frac{1}{3}$	$\frac{2}{3}$	0.528(4)

Residual factor $R = 3.5\%$

Selected bond distances (Å)

	Fe–S	Mn–S
	2.11	2.81(3×)
	2.22(2×)	2.77(3×)
	2.23	
Average	2.19	2.79

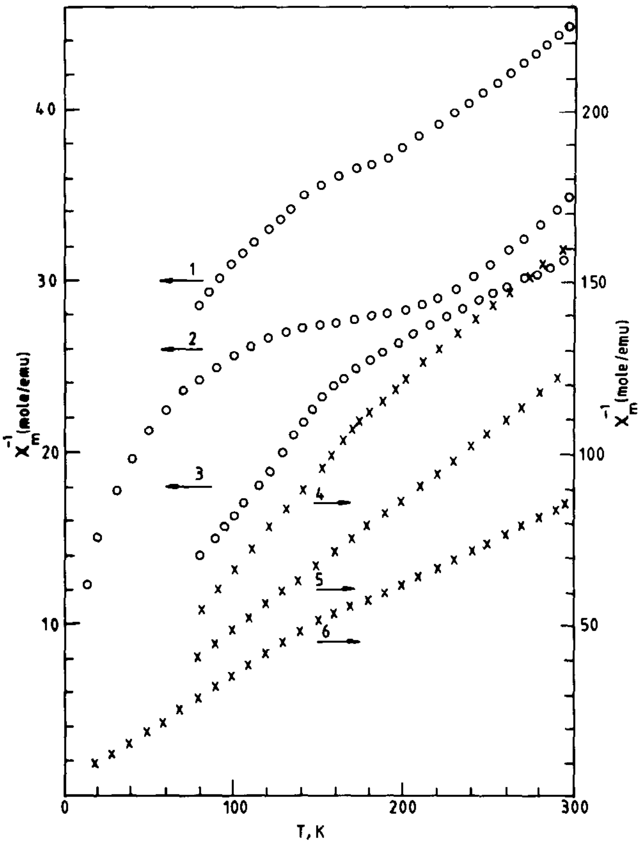

FIG. 4. $\chi_m^{-1} - T$ plots of La_3MFeS_7: 1, M = Mn; 2, M = Fe; 3, M = Co; 4, M = Ni; 5, M = Zn; and 6, M = Mg.

The μ_{eff} and θ values of the other La_3MFeS_7 (M = Mn, Fe, Co, Ni) are given in Table V. The high temperature moments are higher than the moments at low temperatures in all the cases except the nickel compound. The high temperature moments are also higher than the spin-only values calculated assuming that M^{2+} and Fe^{3+} ions are in the high spin state. It is likely that there is some interaction between the octahedral site M and tetrahedral site Fe in these phases. The magnetic behavior of La_3NiFeS_7 deserves special mention. Both the high temperature and low temperature moments are lower than the spin-only moment of Fe^{3+}; it appears that there is no contribution from Ni^{2+} to the magnetic susceptibility. This is consistent with the presence of itinerant electron conduction in this compound arising from the face-shared NiS_6 octahedral chains.

La_3MFeS_7 sulfides are p-type semiconductors except for the nickel compound (Table V and Fig. 5). Both the activation energy for electrical conduction and the resistivity, measured using sintered pellets, decreases in the order Mg ~ Zn > Mn > Fe ~ Co > Ni; resistivity of the nickel compound is the lowest (~10^{-2} ohm-cm) and is nearly temperature-independent in the region 300–100 K. It is reasonable to assume that variation of electrical conductivity in the series arises from a variation of M–S–M covalent interaction in the octahedral

TABLE V

MAGNETIC AND ELECTRICAL PROPERTIES OF La_3MFeS_7 (M = Mg, Mn, Fe, Co, Ni, Zn)

	μ_{eff} (BM)						
	Exp.			θ (K)			
Compound	Low temp. range	High temp. range	Spin-only moment	Low temp. range	High temp. range	ρ at 300 K (ohm-cm)	E_a (eV)
La_3MgFeS_7	4.90 (20–180 K)	5.85 (180–300 K)	5.92 (Fe^{2+} hs)	−10	−50	3×10^3	0.30
La_3MnFeS_7	9.00 (80–150 K)	10.30 (180–300 K)	6.17 (Mn^{2+} ls) 8.37 (Mn^{2+} hs)	−210	−300	5×10^2	0.15
$La_3Fe_2S_7$	6.24 (20–70 K)	10.40 (225–300 K)	5.92 (Fe^{2+} ls) 7.67 (Fe^{2+} hs)	−50	−140	2×10^2	0.11
La_3CoFeS_7	7.88 (80–160 K)	12.80 (180–300 K)	6.12 (Co^{2+} ls) 8.35 (Co^{2+} hs)	−30	−300	1×10^2	0.10
La_3NiFeS_7	3.65 (80–180 K)	4.44 (180–300 K)	6.38 —	−15	−100	7×10^{-2}	—
La_3ZnFeS_7	—	4.60 (80–300 K)	5.92 —	—	−20	2×10^3	0.26

chains since the discrete FeS_4 tetrahedra are common to all the phases. The increasing conductivity in the Mn, Fe, Co, and Ni series with the nickel compound showing almost itinerant conduction is consistent with increasing M–S–M covalent interaction across the series as it occurs in the MS and MS_2 (M = Mn, Fe, Co, Ni, Cu) sulfides (*15*).

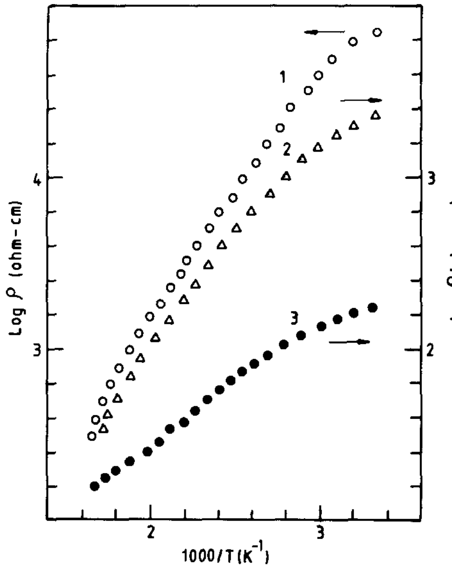

FIG. 5. Temperature dependence of electrical resistivity of some $La_3MM'S_7$: 1, La_3FeAlS_7; 2, La_3ZnFeS_7; and 3, $La_3Fe_2S_7$.

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