Magnetic and structural properties of iron and manganese lanthanide spinels

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Abstract

Six compounds with the spinel structure were obtained for the system (Fe, Mn)(Yb, Lu)$_2$(S, Se)$_4$. The manganese spinels are normal and do not order magnetically in the applied temperature range. In the iron thiospinels some of the iron ions occupy the tetrahedral $16d$ and $16c$ sites and some of the lanthanide ions are partially transferred from $16d$ to $16c$ sites (but not to the tetrahedral positions as in inverted spinels). FeLu$_2$S$_4$, containing about 20% Fe at $16d$ positions, undergoes a magnetic transition at 8 K; FeYb$_2$S$_4$, with a smaller occupancy factor, remains paramagnetic down to 4.2 K. This suggests that the growing occupation of the $16d$ sites increases the ordering temperature. Measurements of high field magnetization for FeLu$_2$S$_4$ rule out a non-zero magnetic moment in the ordered phase and strongly support the hypothesis assuming antiferromagnetism.

1. Introduction

The spinel structure is widespread among the oxygen compounds of AB$_2$O$_4$ type. A lot of spinels crystallize in the normal structure where A^{2+} ions occupy the tetrahedral and B^{3+} ions the octahedral sites of the close-packed anion lattice. The lanthanides do not form oxygen spinels because their ionic radii are too large. The heavy lanthanides yttrium and scandium form spinel-type compounds with the larger anions (sulphur, selenium) and cadmium, magnesium, iron or manganese as a divalent cation. The thio- and selenospinels of manganese with lutetium and ytterbium and the thiospinel with thulium are known to exist. Iron forms only the thiospinels with lutetium and ytterbium [1].

The magnetic susceptibility of several cadmium and magnesium spinels has been studied down to liquid helium temperature [2–6]. Except for CdEr$_2$S$_4$ and CdEr$_2$Se$_4$, none of them was magnetically ordered. The magnetic properties of the iron and manganese spinels with lutetium were not investigated. The properties of the ytterbium compounds are better known, but in several cases the data come from the temperature range 77–300 K (see Table 1).

The aim of our work was to study the magnetic properties of lanthanide spinels with iron or manganese as a divalent cation. One can expect that the replacement of cadmium or magnesium by iron or manganese should

TABLE 1

Some magnetic data of the lanthanide thio- and selenospinels

Compound	Curie constant C		Weiss constant Θ (K)
	Exp.	Calc.	
$FeYb_2S_4$	8.03	8.14	−60
$FeYb_2S_4$ [7][b]	10.34	8.14	−83
$FeYb_2S_4$ [8][b]	8.6	8.14	−67
$FeYb_2S_4$ [13]	8.6	8.14	−30
$FeLu_2S_4$	3.63	3.00	−97
$MnYb_2S_4$	9.13	9.52	−37
$MnYb_2S_4$ [9]	9.52	9.52	−60
$MnYb_2S_4$ [7][b]	10.15	9.52	−30
$MnYb_2S_4$ [10][b]	10.0	9.52	−54
$MnLu_2S_4$	4.29	4.38	−15
$MnYb_2Se_4$	9.36	9.52	−50
$MnYb_2Se_4$ [7][b]	9.85	9.52	−23
$MnYb_2Se_4$ [8][b]	9.1	9.52	−22
$MnLu_2Se_4$	3.90	4.38	−16

[a]Calculated from the Yb^{3+} free-ion (4.54 μ_B) and the Me^{2+} spin-only moments (Fe^{2+}, 4.90 μ_B; Mn^{2+}, 5.92 μ_B).
[b]Studied in the temperature range 77–300 K.

increase the exchange interactions. Another problem of utmost importance is the complex cation distribution in the iron–lanthanide thiospinels [11–13], which is different from that occurring in the remaining lanthanide spinels which are normal. Some of the iron ions occupy the octahedral 16d and 16c positions whereas some of the lanthanide ions pass from the normally occupied 16d to the 16c positions (see Table 2). Such a cation distribution is different from that occurring in the inverse spinels, where the divalent ions and half of the trivalent ions change their tetrahedral 8a and octahedral 16d positions.

2. Experimental details

2.1. Syntheses

The syntheses of the iron thiospinels carried out in flowing H_2S give non-stoichiometric materials [11, 13]. In order to attain the required composition, the compounds were synthesized in a closed system by solid state reactions. Stoichiometric amounts of the lanthanide chalcogenides Ln_2X_3 and the iron or manganese monochalcogenides were pressed into pellets and heated to 1200 K for several days. The crude materials were crushed, pressed again and sealed in double quartz ampoules containing 200 mmHg of argon in the outer tube to prevent oxygen diffusion through the walls. The samples

TABLE 2

Crystallographic parameters and cation distribution in several thiospinels

Compound	Lattice constant a (nm)	Anionic parameter u	Site	Occupancy	Temperature factor B (Å^2)
FeLu$_2$S$_4$	1.0786	0.380	8a	0.70 Fe	0.6
			16d	0.85 Lu, 0.10 Fe	
			16c	0.15 Lu, 0.05 Fe	
FeLu$_2$S$_4$ [2]	1.0808	0.378	8a	0.71 Fe	_a
			16d	0.84 Lu, 0.095 Fe	
			16c	0.16 Lu, 0.05 Fe	
FeYb$_2$S$_4$	1.0839	0.380	8a	0.59 Fe	1.3
			16d	0.87 Yb, 0.01 Fe	
			16c	0.13 Yb, 0.19 Fe	
FeYb$_2$S$_4$ [2]		0.378	8a	0.80 Fe	_a
			16d	0.88 Yb, 0.045 Fe	
			16c	0.12 Yb, 0.05 Fe	
FeYb$_2$S$_4$ [3]	1.0828	0.378	8a	0.80 Fe	–
			16d	0.84 Yb, 0.10 Fe	
			16c	0.16 Yb	
MnLu$_2$S$_4$	1.0919	0.381	8a	0.98 Mn	0.4
			16d	0.99 Lu	
			16c	0.005 Lu, 0.01 Mn	

a Anisotropic temperature factor employed.

were heated to 1580 K for 1 h and then rapidly cooled in cold water. The compounds obtained in this way showed the pure spinel structure without any additional X-ray lines.

2.2. X-ray studies

Powder X-ray measurements were performed on a DRON-2 diffractometer with Cu Kα radiation. The lattice constants and other structural parameters of the compounds studied are shown in Table 2. The occupancy factors and the anion parameters u were determined with the aid of our computer programme using the peaks with 2θ ranging from 20° to 90°. The scattering factors for neutral atoms [14, 15] and average temperature factors were applied. The (111) peak ($2\theta \approx 14°$) was excluded from the refinement; including it in the calculations increased the R factor significantly ($R = \Sigma |I_{obs} - I_{calc}| / \Sigma I_{obs}$) and always gave the anion parameter $u < 0.375$.

2.3. Magnetic measurements

The magnetic susceptibility was measured by the Faraday method in the temperature range 4.2–300 K. Measurements of the FeLu$_2$S$_4$ magnetization in high magnetic fields (up to 14 T) were carried out at the International Laboratory of High Magnetic Fields and Low Temperatures in Wrocław.

Figures 1–3 present the results of the magnetic measurements. Only one compound, $FeLu_2S_4$, orders magnetically at 8 K. The remaining five compounds are paramagnetic down to 4.2 K. Our results do not confirm the statement of Tomas et al. [16] about a magnetic ordering in $FeYb_2S_4$. The parameters of the Curie–Weiss equation are summarized in Table 1. The Curie constants C and the Weiss constants Θ were determined from the high temperature parts (200–300 K) of the $1/\chi(T)$ plots because the ytterbium compounds do not satisfy the Curie–Weiss law at lower temperatures. We prefer to use the Curie constants rather than the effective magnetic moments ($\mu_{eff}^2 = 8C$) because the value of the moment is not informative in compounds containing two kinds of paramagnetic ions.

3. Results and discussion

The X-ray analysis confirmed the unusual cation distribution in the iron spinels (Table 2). The estimated occupancy factors differ slightly from the
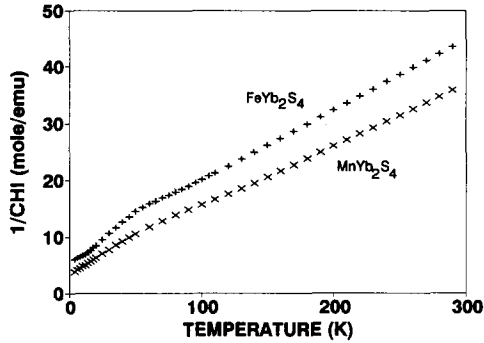

Fig. 1. Reciprocal molar susceptibility vs. temperature for $FeYb_2S_4$ and $MnYb_2S_4$.

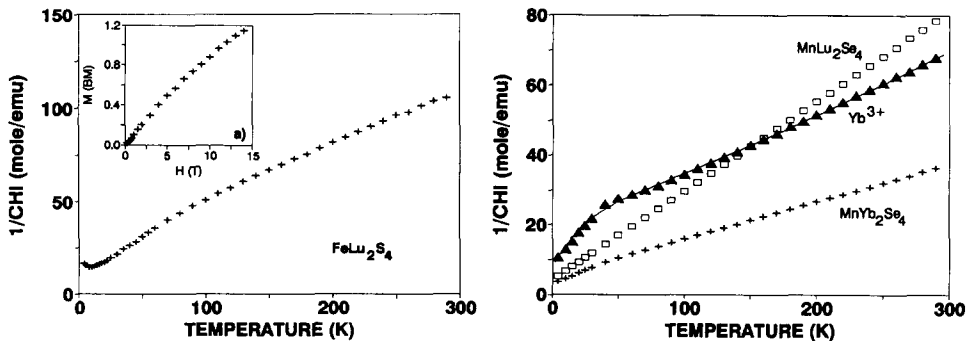
Fig. 2. Reciprocal molar susceptibility vs. temperature and (a) high field magnetization for $FeLu_2S_4$.

Fig. 3. Reciprocal molar susceptibility vs. temperature for $MnLu_2Se_4$ and $MnYb_2Se_4$. Full triangles represent the reciprocal of susceptibility difference $1/(\chi_{MnYb2Se4} - \chi_{MnLu2Se4})$ and the solid curve was calculated using the parameters mentioned in the text.

literature values, especially in the case of $FeYb_2S_4$. Undoubtedly, the main reason is the different method of synthesis, especially the annealing temperature and the quenching rate. A cation distribution a little different from that existing in the normal spinels was found also for $MnLu_2S_4$, but the deviation is much smaller than that observed in the iron compounds and appears not to exceed the accuracy of the powder measurements. The site occupancies in the remaining manganese spinels were not examined.

All the spinels are paramagnetic at room temperature. The susceptibilities of the lutetium compounds (except $FeLu_2S_4$) follow the Curie–Weiss law down to liquid helium temperature. The ytterbium spinels reveal a deviation from this rule typical of the Yb^{3+} ion below about 150 K as a result of the crystalline field influence. The plots of the reciprocal susceptibilities below about 20 K are deformed compared with the pure paramagnetic case, which is probably an effect of short-range exchange interactions near the ordering temperature. Only $FeLu_2S_4$ shows a magnetic phase transition above 4.2 K ($T_N = 8$ K).

There are three possible types of magnetic interactions in AB_2X_4 spinels: B–B, A–B and A–A. Their strength usually changes in accord with the respective interionic distances: the first of them is strongest and the last weakest in transition metal spinels (the A–A distance is 22% longer than B–B).

In the lanthanide spinels the Ln–Ln exchange is weak. This is clearly seen in $FeYb_2S_4$, which is paramagnetic down to 4.2 K in contrast to the lutetium analogue which orders at 8 K. This difference does not seem to be a result of the small change in lattice constant. The reason for the relatively high ordering temperature of $FeLu_2S_4$ may be strong exchange between iron ions in the octahedral $16d$ positions. The results of the X-ray investigations presented in Table 2 confirm that this position in the lutetium spinel is much more occupied by iron ions (about 20% of the total iron content) than in $FeYb_2S_4$ (less than 10%). Moreover, this hypothesis may explain the divergence in the magnetic data for $FeYb_2S_4$ (our compound does not order magnetically, in contrast to the literature results): it is seen from Table 2 that the iron occupation of the $16d$ sites is greater in the spinel obtained by Tomas *et al.* [16] than in the compound described in this work.

Direct cation–cation exchange interactions in the ionic compounds are usually weak and dominated by indirect exchange. Two kinds of superexchange between the magnetic ions occupying octahedral positions in the spinels are possible: the so-called 90° and 180° cation–anion–cation interactions. The first should have a ferromagnetic and the second an antiferromagnetic character for the high spin d^6 configuration [17]. We could not exclude *a priori* the possibility of ferrimagnetic ordering (for instance the existence of two sublattices containing octahedrally and tetrahedrally coordinated iron ions with non-zero net moment). The temperature dependence of the magnetic susceptibility of $FeLu_2S_4$ (Fig. 2) near 10 K suggests an antiferromagnetic transition. On the other hand, the entire $\chi^{-1}(T)$ plot is distinctly curved, which is the characteristic feature of ferrimagnets. In an attempt to explain

the nature of the magnetic ordering in $FeLu_2S_4$, we measured the high field magnetization at 4.2 K (Fig. 2(a)). The character of the $M(H)$ plot seems to exclude the existence of a permanent magnetic moment (ferro- and ferrimagnetism). There is some irregularity in the magnetization plot at the lowest fields but it lies within the range of experimental error. In conclusion, we consider that the phase transition found at 8 K in $FeLu_2S_4$ leads to an antiferromagnetic ordering of Fe^{2+} ions in the octahedral $16d$ positions caused by the strong Fe–S–Fe superexchange. An unequivocal explanation of the nature of this transition, however, requires neutron-scattering experiments.

Analysis of the magnetic properties of the compounds containing both d and f electron ions is complicated. The separation of their contributions to the magnetic susceptibility is not straightforward even under the assumption of purely ionic bonds and insignificant interionic interactions. There are several reasons for the difficulties in treating the iron and manganese spinels: (a) the strong deviation from the Curie–Weiss law in the case of Yb^{3+}; (b) incomplete quenching of the orbital moment in Fe^{2+} ions; (c) the unusual cation distribution in the iron spinels, influencing the symmetry of the lanthanide environment; (d) significant exchange interactions. The influence of the last factor is visible in the $\chi^{-1}(T)$ plot for $FeLu_2S_4$, which is non-linear over the whole temperature range.

We attempted to separate the susceptibility of the ytterbium in the spinel lattice by subtracting the susceptibilities of the pair $M^{2+}Yb_2X_4$–$M^{2+}Lu_2X_4$ ($X \equiv S$, Se). All three pairs of compounds were examined but only the data obtained for the manganese selenospinels gave satisfactory results (Fig. 3). This is not a surprise because the exchange interactions are expected to be weaker in selenides than in sulphide compounds.

The crystalline field parameters were obtained by fitting the calculated values of the Yb^{3+} susceptibility to the difference in the $MnYb_2Se_4$ and $MnLu_2Se_4$ susceptibilities. Assuming octahedral symmetry of the ytterbium environment, we obtained $x = -0.93$ and $W = 15.4$ cm^{-1} (Lea, Leask and Wolf's notation). The ground level is the Γ_6 doublet and the excited Γ_7 and Γ_8 levels lie at 205 and 470 cm^{-1} respectively. The splitting of the ground term $^2F_{7/2}$ is a little less than the value obtained for $MgYb_2Se_4$ [3].

The results of the present investigation show that substitution of iron or manganese for the diamagnetic cations (Cd^{2+}, Mg^{2+}) does not raise the magnetic ordering temperature in the lanthanide chalcogenide spinels significantly. Exchange interactions in these compounds are still much weaker than in ternary oxides.

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