

Magnetic order in sulfide spinels $\text{MnLu}_{1.8}\text{Me}_{0.2}\text{S}_4$ (Me = Ho, Er, Cr)

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Abstract

Magnetic properties of sulfide spinels derived from the lutetium manganese thiospinel MnLu_2S_4 are reported. In this first approach, we have partially substituted lutetium by other lanthanides or by some transition metal elements. The effective moment corresponds to Mn^{2+} ($5.69\mu_B$ and $\Theta = -15\text{ K}$, for MnLu_2S_4). Partial substitution of Lu by Er and Ho weakens the parameter Θ due to a larger separation of the Mn^{2+} ions, but it does not trigger any magnetic interaction. Inversely, 10% substitution of Lu by chromium generates long-range ferromagnetic interactions below $T_c = 67\text{ K}$, although the antiferromagnetic components still predominate, yielding a ferrimagnetic or AF-canted type state.

Keywords: Lanthanide thiospinels; Magnetic interactions; Ferrimagnetism

The spinel structure is rather common among ternary oxides. Many of them crystallize in the normal spinel structure, where the A cation occupies a tetrahedral T site and two B cations occupy the octahedral O positions. This structure is commonly denoted by $(\text{A})[\text{B}_2]\text{O}_4$. The lanthanides do not form oxygen spinels because their ionic radii are too large. However, the heavy lanthanides may form spinel-type compounds when the anion has a large ionic size (i.e. sulfur or selenium). Lutetium and ytterbium sulfide spinels (or thiospinels) $(\text{Me})[\text{RE}_2]\text{S}_4$ have been reported, mainly in connection with substitutions at the A site [1,2]. On the other hand, some transition metal thiospinels, like iron and manganese-based chromium sulfides FeCr_2S_4 and MnCr_2S_4 , have been recently well described because of multiple applications, for instance, in the domain of tunneling microscopy [3,4]. In this work we present magnetic results on the lutetium manganese thiospinel, of formula MnLu_2S_4 [1] and partially substituted $\text{Mn}(\text{Lu}_{1.8}\text{Me}_{0.2})\text{S}_4$, for Me = Er, Ho and Cr. In this way, we should be able to separate out the steric effects due to the size of the substituent, the magnetic effects due to the importance of

the effective moment of the substituent and valence effects due to possible differences in the oxydation states of both the substituent and the substituted cation.

The materials MnLu_2S_4 and $\text{Mn}(\text{Lu}_{1.8}\text{Me}_{0.2})\text{S}_4$ (Me = Er, Ho and Cr) were prepared by reaction of stoichiometric mixtures of the binary sulfides (MnS , Lu_2S_3 , Er_2S_3 , Ho_2S_3), chromium and sulfur. The mixtures were milled and pressed into pellets, placed in an alumina crucible and sealed in evacuated silica ampoules. The samples were then heated to $1100\text{ }^\circ\text{C}$ at the rate of $50\text{ }^\circ\text{C/h}$ and kept at this temperature for 6 days. Scanning electron microscopy, X-ray powder diffraction (XRD) and EDX analyses confirm the good homogeneity and the expected stoichiometry; absolutely no secondary phases were detected, within the limits of their experimental detection. The XRD patterns were fully indexed in the space group $\text{Fd}\bar{3}m$, and confirm that the partial substitution of metal cations results in phases whose crystalline structures are closely related to the MnLu_2S_4 structure type. The evolution of the lattice parameters in this series perfectly agree with the ionic size of the substitutes [5]. Magnetic measurements were performed using a Quantum Design MPMS XL5 SQUID magnetometer, between 2 and 300 K, under different applied fields.

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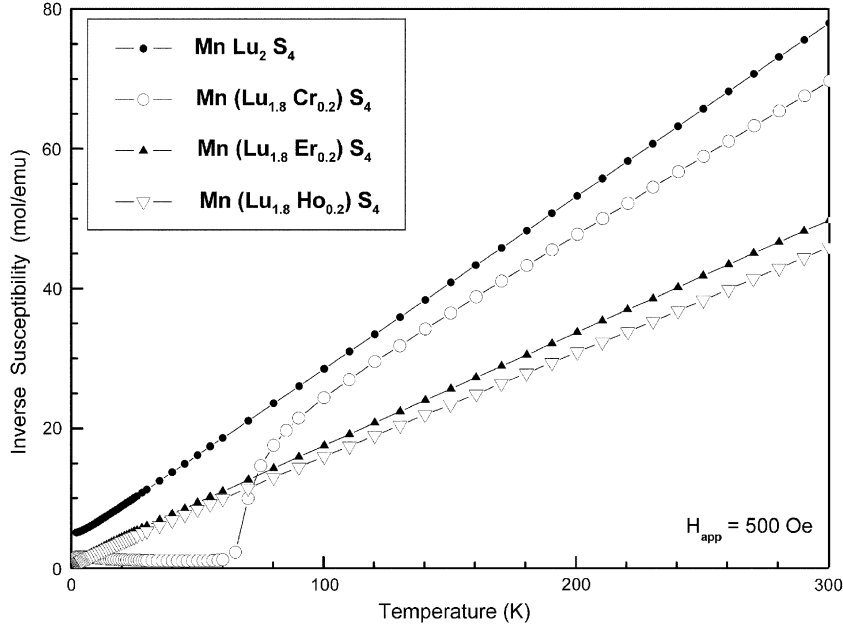


Fig. 1. Inverse magnetic susceptibility of MnLu_2S_4 and its substituted compounds $\text{Mn}(\text{Lu}_{1.8}\text{Me}_{0.2})\text{S}_4$, $\text{Me} = \text{Cr}, \text{Er}$ and Ho .

Fig. 1 shows the inverse susceptibility of all samples, measured under an applied field of 500 Oe, between 2 and 300 K, with increasing temperature. For the non-substituted spinel MnLu_2S_4 , an effective moment of $5.69 \pm 0.07 \mu_{\text{B}}$ per formula unit and a Weiss parameter Θ of -15 K was found, similar to reported values on MnLu_2X_4 ($\text{X} = \text{S}, \text{Se}$) [1]. Since lutetium is a non-magnetic element, the magnetic moment is strictly due to the manganese contribution (either $3d^5 \text{Mn}^{2+}$, $3d^4 \text{Mn}^{3+}$ or $3d^3 \text{Mn}^{4+}$, with their respective moments of 5.92 , 4.90 and $3.87 \mu_{\text{B}}$). A default composition ($0.93 \text{ MnS}:\text{Lu}_2\text{S}_3$, instead of one-to-one ratio) can be considered within the experimental errors, and we may state that the experimental moment is basically due to manganese Mn^{2+} in its high-spin state.

The substitution of lutetium by Er or Ho does not significantly modify the paramagnetic behaviour, showing a Curie-Weiss law down to low temperature. The effective moment increases (Table 1) due to the presence of 0.2 mol of erbium or holmium ($\mu_{\text{eff}} = 9.58$ and $10.61 \mu_{\text{B}}$, for Er^{3+} and Ho^{3+}). No magnetic interactions are observed between lanthanides since ions are statistically spread inside the structure and the lanthanide-lanthanide exchange is considered to be weak [1]. The Weiss parameter Θ decreases from -15 K in MnLu_2S_4 down to -8 and -6.5 K for $\text{Me} = \text{Er}$ and Ho , respectively, suggesting that the antiferromagnetic-type interactions between Mn^{2+} ions slightly weaken: one possible mechanism of such a decrease could be the larger separation between Mn^{2+} atoms due to the substitution of lutetium by elements having larger ionic radii. Assuming that Er and Ho behave as free ions, we evaluated their contributions and subtracted it from the total effective moment. The resulting

Table 1
Magnetic parameters of MnLu_2S_4 and $\text{MnLu}_{1.8}\text{Me}_{0.2}\text{S}_4$

Compound	$\mu_{\text{eff}} (\mu_{\text{B}}/\text{f.u.}) \pm 0.07$	$\Theta (\text{K}) \pm 2$	$\mu (\mu_{\text{B}}/\text{Mn}^{2+}) \pm 0.12$
MnLu_2S_4	5.69	-15	5.69
$\text{MnLu}_{1.8}\text{Cr}_{0.2}\text{S}_4$	6.01	-15	5.76
$\text{MnLu}_{1.8}\text{Er}_{0.2}\text{S}_4$	7.04	-8	5.58
$\text{MnLu}_{1.8}\text{Ho}_{0.2}\text{S}_4$	7.32	-6.5	5.57

moment per manganese ion is similar to the one obtained for MnLu_2S_4 (Table 1).

The substitution of lutetium by chromium basically modifies the magnetic behavior. Fig. 1 shows a ferrimagnetic transition at about 65 K, even if only 10% of the Lu sites have been replaced by Cr. The paramagnetic regime is characterized by a Curie-Weiss law above 150 K, with an effective moment ($6.01 \mu_{\text{B}}$) larger than the one observed for LuMn_2S_4 , while Θ remains unchanged to -15 K . The fact that Θ remains constant is due to the small ionic radius of Cr^{3+} , and so it does not affect much the separation between Mn^{2+} ions responsible for the antiferromagnetic interactions observed in MnLu_2S_4 . We have subtracted the chromium contribution (Cr^{3+} ; $3d^3$; $\mu_{\text{eff}} = 3.87 \mu_{\text{B}}$), resulting into an overall moment of $5.76 \mu_{\text{B}}$ for the Mn-based sublattice, in good agreement with the 2+ state for manganese.

Contrary to the partial substitution of lutetium by the heavy lanthanides, the presence of 0.2 atoms of chromium immediately triggers long-range magnetic interactions, with transition temperatures as high as 65 K or more. In order to investigate deeper this ordered regime, we performed magnetization loops at 5, 40 and 80 K, sweeping the field

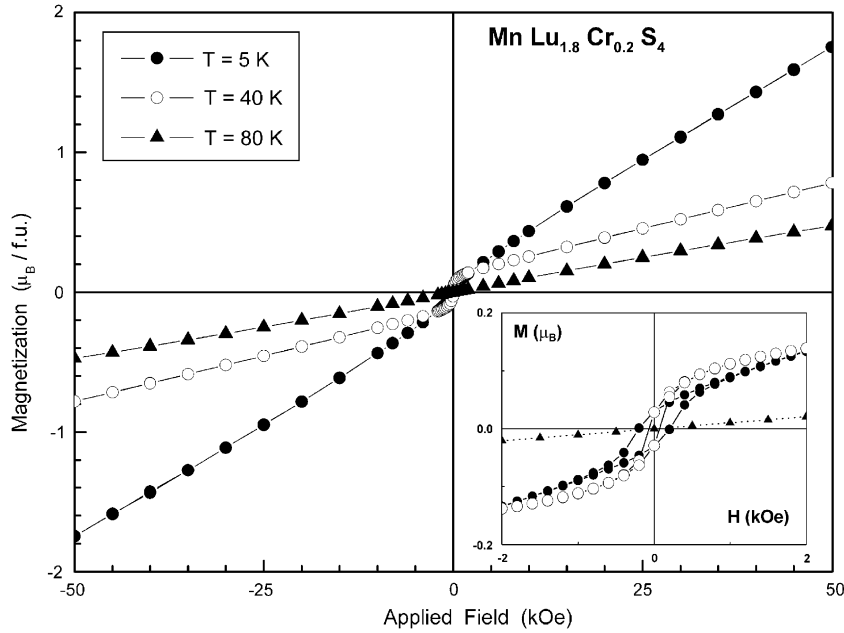


Fig. 2. Magnetization loops at given temperatures for $\text{MnLu}_{1.8}\text{Cr}_{0.2}\text{S}_4$.

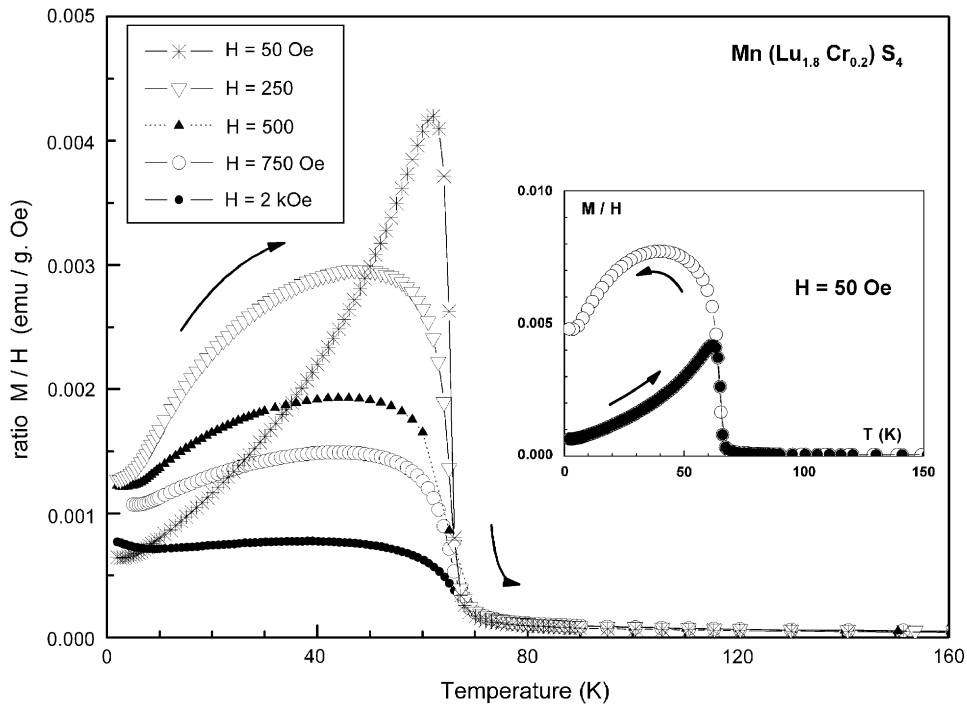


Fig. 3. Temperature dependence of ZFC magnetization, for $\text{MnLu}_{1.8}\text{Cr}_{0.2}\text{S}_4$. Inset shows the ZFC/FC cycle under 50 Oe.

between -50 and $+50\text{ kOe}$ (Fig. 2). At low temperatures, two different behaviors superpose: one due to a ferromagnetic component (inset) and the other due to an anti-ferromagnetic-like linear variation of M with H . The value reached at 50 kOe and 5 K is small compared to the expected saturation value of $5\mu_B$ for Mn^{2+} , even if the chromium spins were oriented opposite to the manganese spins. This situation differs with the one observed in pure MnCr_2S_4 , where an antiparallel collinear arrangement

between the Cr and Mn spins has been reported [6]; this means that in our case we have to consider the statistical distribution of the chromium ions inside the lutetium sublattice.

The intrinsic duality existing in an antiferromagnetic canted-type ordering, with a very weak ferromagnetic component superposed to largely predominant antiferromagnetic interactions, becomes apparent by performing a thermal cycle ZFC/FC under low applied fields. The inset

of Fig. 3 shows results taken at 50 Oe. A pronounced peak is observed in the magnetization during the warming branch, characteristic of AF-type ordering, with a maximum at $T_{\max} = 62$ K, abruptly decreasing afterwards and reaching the paramagnetic regime at $T_c = 67$ K. During cooling, magnetization reversibility is observed in the paramagnetic region, followed by the sudden increase of $M(T)$ at T_c , reaching a broad maximum typical of AF canting. The decrease observed at lower temperature indicates that antiferromagnetic interactions are still important at low applied fields.

Several ZFC/FC cycles were then performed at different fields. Fig. 3 shows only the zero-field-cooled branches. No change in T_c occurred with applied field. The sharp maximum observed at $T_{\max} = 62$ K, becomes wide and slightly decreases with increasing field, transforming into a plateau at $H_{\text{app}} = 2$ kOe or above. The low-temperature irreversibility which occurs during the ZFC/FC cycle (inset) disappears almost completely for fields above 500 Oe (not shown), in accordance with the very low coercive fields (less than 100 Oe at 5 K) found for this compound. Here again, the case discussed in this work differs from the results obtained in single crystals of MnCr_2S_4 having a 100% Cr network: our results show a broad maximum below T_c for low applied fields, while Tsurkan et al. [6] show a rather constant $M(T)$ for equivalent fields. Since the magnetic state below T_c is related to the ferromagnetic order of the chromium sublattice [6], it is expected that the magnetic dilution of

chromium by lutetium should affect the temperature dependence of the magnetization, $M(T)$, below T_c , as observed in our samples.

A systematic upturn of the magnetization is observed below 10 K (Fig. 3). This anomaly, also observed in MnCr_2S_4 , was interpreted by other authors as due to the onset of a canted antiferromagnetic order of the transverse component of the Mn sublattice, in a Yafet–Kittel-type magnetic transition [6]. Since in our case, the magnetic dilution in the chromium sublattice should not affect the behavior of the Mn sublattice, similar phenomena may be expected in the $\text{MnLu}_{1.8}\text{Cr}_{0.2}\text{S}_4$ compound. This effect is just sharper and more pronounced in Ref. [6] because it was obtained in oriented single crystals.

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