Enhanced Magnetocaloric Effect by the Rare Earth Polarization Due to the Exchange with a Transition Metal. Study of $GdCrO_4$

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Keywords: Magnetocaloric effect. Mean field. Magnetic refrigeration.

Abstract. The zircon polymorph of $GdCrO_4$ has a large magnetocaloric effect over a wide temperature range, with $|\Delta S_T| > 20$ J/kg·K from 6 K to 34 K, for a magnetic field of 9 T. This unusual behaviour is very interesting on magnetic refrigeration applications, for liquefying H_2 or natural gas. The mean-field approach explains that it is due to the weaker Gd-Cr magnetic exchange relative to the Cr-Cr one, while the Gd-Gd exchange is negligible. This possibility has not been sufficiently studied and opens an interesting strategy to design more efficient materials for magnetic refrigeration.

Introduction

Adiabatic demagnetization (used since the 1930's [1]) has revealed as an efficient method of liquefying gases like H_2 or natural gas, before transport or storage, and indeed some prototypes have been already developed [2,3]. The magnetocaloric material used for this purpose is: *a)* A magnetically dense material, paramagnetic in the temperature range of interest (*e.g.* $Gd_3Ga_5O_{12}$ (GGG), $Dy_3(Ga,Al)_5O_{12}$ (DGAG)); or *b)* A ferromagnetic material with T_C near the working temperature (*e.g.* $ErCo_2$). The main technical parameter to evaluate the cooling capacity of a material is the isothermal entropy change ΔS_T (usually negative) when a given magnetic field B is applied. In case *a)* the material has strong cooling capacity only at very low temperatures, below 10 K, whereas in case *b)* $|\Delta S_T|$ is only high near T_C. Liquefying gases requires efficient cooling methods over wide temperature ranges, and multi-stage systems are used. Therefore materials with high $|\Delta S_T|$ over a wide temperature range would be very interesting.

Recently, we proposed an idea for designing such materials [4], based on the fact that $|\Delta S_T|$ of a paramagnet for a given field increase ΔB is enhanced when a previous effective field B_i is already present. This is so because, in a paramagnet, when the magnetization is far from saturation (*i.e.* for low fields or relatively high temperatures, above 10 K), $|\Delta S_T|$ is proportional to $\Delta(B^2) = (B_i+B_f)(B_f-B_i) = (B_i+B_f)\Delta B$, being B_i, B_f the initial and final fields. In a compound containing a rare-earth R plus a transition-metal M, this case can occur if the R-R exchange interaction is very weak, the M-M exchange is very strong, and the R-M exchange is intermediate, of the order of working temperature. At the working temperature the magnetic moments of the M atoms are fully saturated and the R-M exchange acts as an external field polarizing the R atoms.

Actually, the idea comes from the 1970's [5] and in the 90's it was tested in RMO_3 perovskites, mainly in $NdFeO_3$ [6], where the experimental heat capacity and magnetization of the Nd sublattice match perfectly with the prediction for a single ion in a constant field, without any external applied field. The Fe sublattice orders antiferromagnetically at 690 K and the staggered polarizing field on the Nd sublattice does not produce any net magnetization, but could be observed by neutron diffraction. Therefore, this compound is not useful for magnetic refrigeration. Instead, the zircon polymorphs of $R\mathrm{CrO_4}$ compounds are usually ferromagnetic at low temperature. The polarization of the R atom by the exchange should produce a stronger influence on the magnetocaloric effect, as compared to other isostructural $RM\mathrm{O_4}$ compounds, when M is a non-magnetic atom. In a previous work, [4] we presented the experimental results for $\mathrm{GdCrO_4}$, that orders ferromagnetically at 21.3 K and has $|\Delta S_T| > 20$ J/kg·K for 9 T in the broad range, 6 K < T < 34 K, when other conventional materials, like $\mathrm{ErCo_2}$, exceeds this value only between 34 K and 46 K, the paramagnet GGG only below 14 K, and DGAG (used in prototypes) never reaches it. In that work we did not treat in detail the analysis of the mean-field model.

Mean Field Model (MF)

The energy per chemical unit in the MF approximation is

$$\frac{E}{k_B} = -z_R J_{RR}\langle s_R\rangle^2 - z_M J_{MM}\langle s_M\rangle^2 - z_{RM} J_{RM}\langle s_M\rangle\langle s_R\rangle - \frac{\mu_B}{k_B}\left(g_R\langle s_R\rangle + g_M\langle s_M\rangle\right)B\,, \tag{1}$$

where B is the external field, z_j the numbers of nearest neighbours, s_j the spins and J_i the exchange constants between R atoms, M atoms, and between R and M atoms. The interesting case occurs when $J_{RR} \ll J_{RM} < J_{MM}$, otherwise, if these exchange constants are comparable, both sublattices order simultaneously as in a conventional ferromagnet. For $\mathrm{GdCrO_4}$, J_{RR} is weak (Gd orders at T_N = 4.8 K) but antiferromagnetic and a MF model should consider several sublattices for the R atoms. For simplicity, we neglect the small exchange J_{RR}. The mean fields at the R and M sublattices are:

$$B_M = B + \frac{k_B}{\mu_B g_M}\left(z_M J_{MM}\langle s_M\rangle + z_{RM} J_{RM}\langle s_R\rangle\right);\; B_R = B + \frac{k_B}{\mu_B g_R} z_{RM} J_{RM}\langle s_R\rangle \tag{2}$$

The average moments of the sublattices, $\mu_R = g_R\mu_B\langle s_R\rangle$ and $\mu_M = g_M\mu_B\langle s_M\rangle$, are obtained by solving the system of coupled equations:

$$\frac{\langle s_R\rangle}{s_R} = B_{s_R}\left(\frac{z_{RM} J_{RM}\langle s_M\rangle}{T} + \frac{\mu_B g_R s_R B}{k_B T}\right);\; \frac{\langle s_M\rangle}{s_M} = B_{s_M}\left(\frac{z_{RM} J_{RM}\langle s_R\rangle + z_M J_{MM}\langle s_M\rangle}{T} + \frac{\mu_B g_M s_M}{k_B T}B\right) \tag{3}$$

where $s_R = 7/2$ for $\mathrm{Gd^{3+}}$, $s_M = 1/2$ for $\mathrm{Cr^{5+}}$, and $B_s(x)$ is the Brillouin function for spin s, defined as

$$B_S(x) = \frac{2s+1}{2s}\coth\left[\frac{(2s+1)x}{2s}\right] - \frac{1}{2s}\coth\left[\frac{x}{2s}\right]. \tag{4}$$

The canonical partition function is: $$Z = \sum_{m_R=-s_R}^{s_R}\exp\left(\frac{g_R\mu_B m_R B_R}{k_B T}\right)\times\sum_{m_M=-s_M}^{s_M}\exp\left(\frac{g_T\mu_B m_M B_M}{k_B T}\right). \tag{5}$$

Finally, the molar thermodynamic functions (in eq. (6) $R = N_A k_B$ is the ideal gas constant) are obtained in the usual way,

$$U = N_A E;\;\; F = -RT\ln Z;\;\; S(T,B) = (-F+U)/T = R\ln Z + U/T;\;\; C_B(T,B) = T\left(\frac{\partial S}{\partial T}\right)_B. \tag{6}$$

For the $\mathrm{GdCrO_4}$ zircon phase, $R = \mathrm{Gd^{3+}}$, $M = \mathrm{Cr^{5+}}$, $z_{RM} = 2$, $z_M = z_R = 4$, $g_R = g_M = 2$. The exchange constants $J_{MM} = 12.5$ K , $J_{RM} = 10$ K give $T_C = 30$ K and values for $M(T)$ and $|\Delta S_T|$ similar to the experimental results (see below).

Fig. 1, left panel, shows the magnetization of the R and M sublattices for applied fields $B = 0$ and 5 T. The M sublattice saturates quickly for $T < T_C$, but the moment of the R sublattice increases much more slowly, reaching only 4 μ_B (quite below the saturation value) at $T = 20$ K = 2/3 T_C for B = 0 T. This leaves room to increase μ below T_C when an external field is applied, involving an entropy decrease. Fig. 1, right panel, shows the entropy increments deduced from the model. For T

<< T_C the M sublattice is saturated and the exchange interaction R-M acts as a constant effective field $B_{ex} = k_B z_{RM} J_{RM} \langle s_M \rangle / (\mu_B g_R)$ on the R sublattice, giving the entropy change represented by the pink line, computed for a constant $B_{ex} = 7$ T .

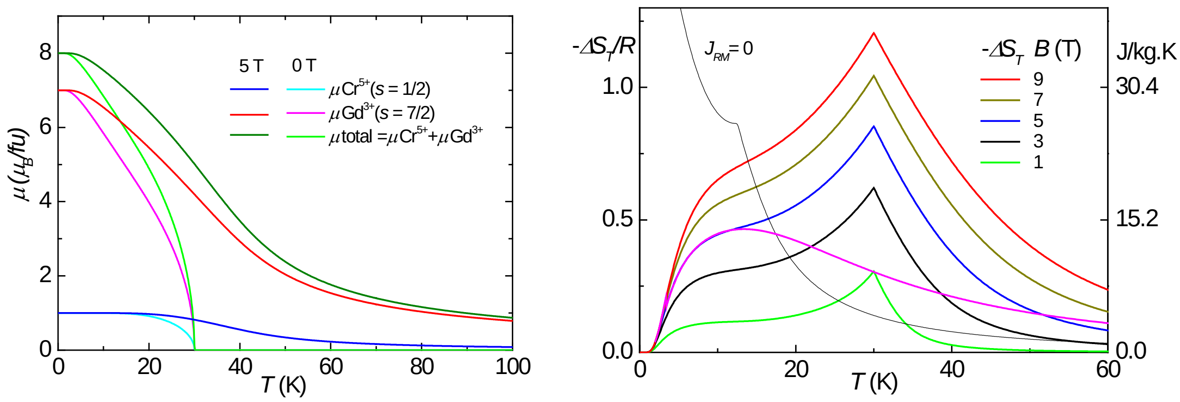

Figure 1. Left: Magnetization of the R and T sublattices, and total for the mean-field model with $J_{MM} = 12.5$ K, $J_{RM} = 10$ K. Right: Isothermal entropy increments $|\Delta S_T|$ from zero to several applied fields, deduced from the model. Pink line: entropy change for a spin 7/2 for $B = 5$ T with a constant effective exchange field $B_{ex} = 7$ T. Black line: Entropy change for two non-interacting sublattices R and M, for $B = 5$ T and the same J_{MM} value.

The effect of B_{ex} produces a shoulder in the curve $|\Delta S_T|$ *vs.* T for a given external field and the blue line in Fig. 1 right collapses with the pink line. For $T \sim T_C$, B_{ex} is proportional to $\langle s_M \rangle$, which in turn is easily polarized by an external field. Fig. 1, left panel, shows that at $T_C = 30$ K, $\langle s_M \rangle$ is 82% of the saturation value for $B = 5$ T. But the spin of Gd^{3+} is 7/2 while that of Cr^{5+} is only 1/2, therefore the entropy increment is higher than expected for Gd^{3+} in a constant B_{ex} (pink line) and much higher than for Cr^{5+} alone, which could only reach $|\Delta S_T|/k_B = \ln 2$, for infinite field. The black line shows the calculation for non-interacting R and M sublattices with the same J_{MM} value and $B = 5$ T. As expected, the R sublattice produces the typical $|\Delta S_T|$ curve for a paramagnet, increasing at very low temperatures. The M sublattice alone would produce the $|\Delta S_T|$ of a usual ferromagnet, with a peak near its corresponding $T_C = J_{MM} = 12.5$ K, but quite low due to the small Cr^{5+} spin, 1/2, which saturates for fields much lower than 5 T. The R-M interaction increases T_C but, more importantly, increases $|\Delta S_T|$. This can be understood since, for instance at T_C and zero field the R and M sublattices are unpolarized, but an applied field of 5 T saturates almost completely the Cr^{5+} sublattice ($|\Delta S_T| \cong k_B \ln 2$) and acts on the Gd^{3+} sublattice as a total effective field $B_{eff} = B + B_{ex} = 12$ T, giving $\mu_{Gd} = 4.2\ \mu_B$. As a result, $|\Delta S_T|$ is high in a wide temperature range. A key detail is that J_{RM} should not be too strong because, in such a case, $|\Delta S_T|$ would be high only near T_C, but would decay quickly at lower temperatures, since the mean field would saturate the magnetization even without any external field, as happens in a typical ferromagnet.

Experimental

The experimental data of ΔS_T [4] were obtained in 3 ways: a) From magnetization, via the Maxwell equation, b) From heat capacity at constant field, and c) Directly measured by an original method, based on considerations given in [7]. All the three methods agreed. The small differences between data from magnetization and calorimetry were due to the different demagnetization factors of the samples used. The parameters J_{RR} and J_{RM} were chosen to fit the experimental magnetization, heat capacity and ΔS_T at low temperatures (*i.e.* B_{ex}). The J_{MM} value was chosen from the magnetic energy, given in Eq. 1, compared to the experimental value $\int_0^\infty C_m(T, B=0)dT = 258\ \text{J/mol}$ obtained from the C_m data shown in Ref. [4]. With this choice, the experimental T_C is lower than the MF prediction, as happens in lattices with small number of nearest neighbours. Fig. 2 shows the experimental and MF data of ΔS_T versus the reduced temperature T/T_C.

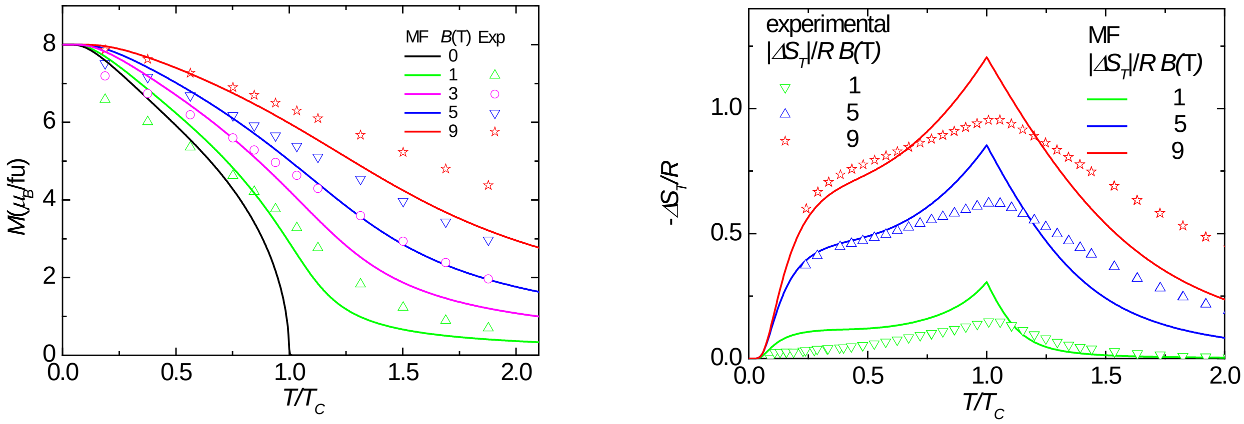

Figure 2: Left: Experimental magnetization of $GdCrO_4$ and MF calculations *vs.* reduced temperature. Right: Experimental $|\Delta S_T|$ and calculated curves with the MF model.

The computed data agree quantitatively with the experimental values in the low temperature region, when the Cr^{5+} moment is saturated. Data for B = 5 and 9 T match with the simplification of taking a constant B_{ex} = 7 T, as occurred in the case of $NdFeO_3$. The values for B = 1 T do not agree, probably because the demagnetizing field affects significantly the experimental results. At higher temperatures the MF model does not give a quantitative agreement with experimental data, but shows the same general features. There is a shoulder in the low temperature region, a maximum at $T_{C,}$ and a slow decrease for $T > T_C$. This shoulder produces a wide T range in which $|\Delta T_S|$ is high.

Conclusion

The mean-field approach gives a qualitative, easily understandable description of the magnetism in zircon $GdCrO_4$, although there is not a detailed quantitative agreement due to the small number of nearest neighbours. The Cr^{5+} sublattice orders ferromagnetically via exchange interaction at T_C = 21.3 K and polarizes the Gd^{3+} atoms below this temperature due to a weaker Gd-Cr exchange. This second exchange acts on Gd^{3+} as an additional effective field, enhancing the magnetocaloric effect at temperatures above 5 K, as compared with isostructural compounds where Cr is replaced by another non-magnetic atom, like in $GdVO_4$ or $GdAsO_4$. This mechanism provides a high $|\Delta S_T|$ over a wide temperature range, between 6 K and 34 K, which is of interest regarding to applications in magnetic refrigerators designed for liquefying H_2 or natural gas, where the efficiency of other methods decay.

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