Enhanced magnetocaloric effect in $Gd_3Ga_{5-x}Fe_xO_{12}$

R. D. McMichael,[a] J. J. Ritter, and R. D. Shull
National Institute of Standards and Technology, Gaithersburg, Maryland 20899

The working refrigerant material in the majority of magnetic refrigerators has been $Gd_3Ga_5O_{12}$ (GGG) which has an upper temperature limit near 15 K. In this paper we report on the field-induced adiabatic magnetic entropy change, $\Delta S_m(H,T)$, of a series of iron-substituted gadolinium garnets (GGIG) $Gd_3Ga_{5-x}Fe_xO_{12}$ which have the potential to increase the working temperature range or to reduce the field requirements of cryogenic magnetic refrigeration. Depending on Fe concentration, x, the entropy change of these materials at applied fields of 0.9 and 5.0 T is much greater than that of GGG, especially at temperatures above 15 K. At low Fe concentrations, the results are consistent with formation of magnetically ordered clusters of spins at low temperatures. Room temperature electron paramagnetic resonance measurements show that Fe^{3+} ions mediate exchange interactions which are responsible for clustering at low temperatures.

INTRODUCTION

When a material is magnetized by application of a magnetic field, the entropy associated with the magnetic degrees of freedom, S_m, is changed as the field changes the magnetic order of the material. Under adiabatic conditions, ΔS_m must be compensated for by an equal but opposite change in the entropy associated with the lattice, ΔS_l, resulting in a change in temperature of the material, ΔT. This temperature change, the magnetocaloric effect, has been used for many years to achieve millikelvin temperatures in laboratory systems through adiabatic demagnetization of paramagnetic materials.[1–4]

More recently, cyclic magnetic refrigerators have been designed to operate in the temperature range of 1.2–15 K for use in liquefying He.[5–7] The magnetic refrigerant material most commonly used has been gadolinium gallium garnet, $Gd_3Ga_5O_{12}$ (GGG). Oriented single crystal $Dy_3Al_5O_{12}$ has been demonstrated to have superior properties at temperatures above 15 K, but its useful temperature range is still limited to temperatures less than $\sim$20 K.[6,8] Because of their special magnetic properties, the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials have desirable thermodynamic properties which are quite promising for their development as magnetic refrigerant materials for magnetic cryocoolers above 15 K.

In this paper, we report on the magnetocaloric properties of $Gd_3Ga_{5-x}Fe_xO_{12}$ as a function of Fe concentration, x, temperature, T, and applied field, H. $Gd_3Ga_5O_{12}$ (GGG) is a paramagnetic material with only very weak ($\sim$1 K) interactions between Gd spins; gadolinium iron garnet, $Gd_3Fe_5O_{12}$ (GdIG) is a ferrimagnetic material with a Curie temperature of 564 K. Molecular field coefficients have been determined for the $Gd_3Ga_{5-x}Fe_xO_{12}$ system under the assumption of collinear spin arrangements, and the strongest exchange interactions are between Fe atoms on octahedral sites and Fe atoms on tetragonal sites, with the coupling between the Gd atoms and the Fe sublattices being relatively weak.[9,10]

For low Fe concentrations, (i.e., for Fe concentrations low enough that percolation of the Fe sublattices does not occur), it may be more useful to approach the behavior from the dilute limit. Consider the behavior of Gd^{3+} ions near a single Fe^{3+} ion substituting for a single Ga^{3+} ion in GGG. Depending on whether the Fe^{3+} is located on a tetrahedral or an octahedral lattice site, neighboring Gd^{3+} moments would be expected to align either parallel or antiparallel to the moment of the Fe^{3+} ion, forming a superparamagnetic cluster in either case. Larger clusters are expected to form with increasing Fe^{3+} concentration until the cluster size diverges at the percolation threshold.

THEORETICAL ANALYSIS

The magnetocaloric effect can be related to the magnetic properties of the material through a thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H. \tag{1}$$

Using this relation, the isothermal entropy change of a material can be calculated from the magnetic properties;

$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'. \tag{2}$$

For magnetization measurements made at discrete temperature intervals, ΔS_m can be approximated by

$$\Delta S_m \approx \frac{1}{\Delta T}\left[\int_0^H M(T+\Delta T,H')dH' - \int_0^H M(T,H')dH'\right], \tag{3}$$

[a]National Research Council Postdoctoral Research Associate.

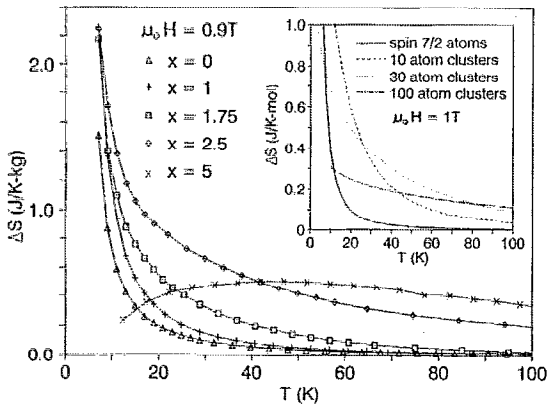

FIG. 1. Measured values of ΔS_m vs T in $Gd_3Ga_{5-x}Fe_xO_{12}$ for $0 \leqslant x \leqslant 5$ for a maximum applied field of $\mu_0 H = 0.9$ T. In comparison with $Gd_3Ga_5O_{12}$, significant increases in ΔS_m are obtained over the entire temperature range investigated and especially between 15 and 20 K. Inset: Calculated values of ΔS_m for individual atoms and clusters of perfectly aligned spins with an applied field of 1 T.

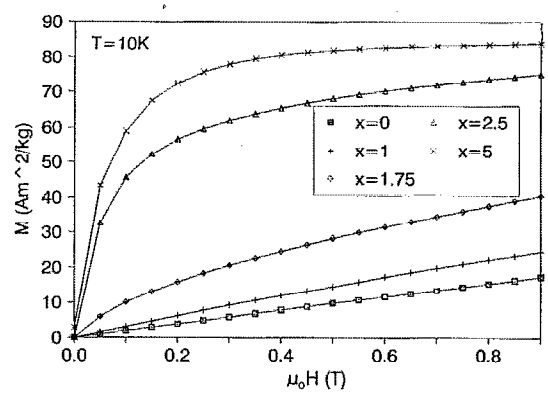

FIG. 2. Magnetization vs field curves of $Gd_3Ga_{5-x}Fe_xO_{12}$ for $x=0$, 1, 1.75, 2.5, and 5 at 10 K. The curvature of the $x=1$ data is even more apparent at 6 K.

which is the area between two magnetic isotherms divided by the temperature difference between the isotherms. This formulation is useful for graphical or numerical calculations of ΔS_m from magnetization data.

In the classical limit, the magnetization of an ensemble of noninteracting magnetic moments with amplitude $m(T)$, is given by

$$M = M_0 L\left(\frac{m(T)H}{kT}\right), \tag{4}$$

where M is the magnetization of the ensemble, M_0 is the saturation moment of the ensemble, and $L(x) = \coth(x) - 1/x$ is the Langevin function. If $m(T)$ is temperature independent, the magnetization measured at a variety of temperatures and fields should fall on a single line when plotted as a function of H/T, and such a plot is a common test for superparamagnetic behavior. If, however, $m(T)$ depends on temperature, as it would in a two-phase superparamagnetic material with a temperature dependent magnetic phase, the magnetization data will not be expected to fall on a single line. Because of the strong temperature dependence of bulk ferrimagnetic GdIG [$M_s(T=100\text{ K}) < \frac{1}{2} M_s(T=0\text{ K})$], if the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials are regarded as a two-phase system of particles of GdIG in GGG, the moments, m, of the GdIG particles will have a strong temperature dependence, and the magnetization data would not be expected to fall on a single line when plotted vs H/T.

Previous theoretical results[11–13] have shown that the formation of superparamagnetic clusters can enhance ΔS_m. The isothermal entropy change of an ensemble of superparamagnetic particles is given by[13]

$$\Delta S_m = \frac{M_0 H}{T}\frac{1}{x}\left[1 - x\coth(x) + \ln\left(\frac{\sinh(x)}{x}\right)\right], \tag{5}$$

where $x = mH/kT$. This expression is graphed in the inset of Fig. 1 for several values of m created by assuming individual Gd atoms and perfect alignment of moments within clusters of 10, 30, and 100 Gd atoms.

EXPERIMENTAL RESULTS

The samples were prepared by complexing the mixed metal nitrates with an excess of tartaric acid in water solution. After thermally removing the solvent at temperatures between 200 and 325 °C, the garnets were formed by heating the resultant precursors in air at 950 °C. Formation of the garnet materials was confirmed by x-ray diffraction.

Values of magnetization were measured at discrete intervals of H and T in an automated vibrating sample magnetometer. Magnetization versus field data for the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials at 10 K are shown in Fig. 2. The $x=2.5$ and $x=5$ magnetization curves have a ferromagnetic character suggestive of long range magnetic order, but the lower Fe concentrations, ($x=1.75$ and $x=1$) have magnetization curves with gentle curvature suggestive of superparamagnetic behavior. However, the data do not fall on a single line when plotted vs H/T, presumably because of temperature dependence of the superparamagnetic moments. The curvature of the $x=1$ magnetization curve is even more evident at 6 K. The magnetization curve of the $x=0$ material (GGG) is very nearly linear, even at 6 K.

Values of ΔS_m were calculated using Eq. (3) by numerical differentiation and integration of the magnetization data. The results are displayed in Fig. 1. The increased values of ΔS_m for increasing Fe concentration are in qualitative agreement with the theoretical results, under the assumption that higher Fe concentrations correspond to larger cluster sizes. The samples with higher Fe concentration have greater values of ΔS_m than GGG at the high temperatures; by extrapolation of ΔS_m vs T to lower temperatures, samples with lower Fe concentration would have higher values of ΔS_m at temperatures below 6 K.

Measurements of ΔS_m for $Gd_3Ga_{5-x}Fe_xO_{12}$ with $x=0$, $x=1$, and $x=1.75$ were also made using a commercial SQUID magnetometer equipped with a superconducting magnet. The measured values of ΔS_m for a 5 T applied field are shown in Fig. 3. The enhancement in ΔS_m which re-

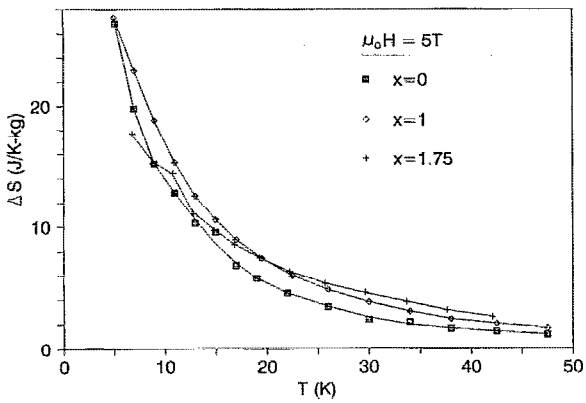

FIG. 3. Measured values of ΔS_m in $Gd_3Ga_{5-x}Fe_xO_{12}$ for $x=0$, 1.0, and 1.75 for a maximum applied field of $\mu_0 H=5$ T.

sults from the addition of Fe is not as dramatic as at 0.9 T applied field, but the enhancements are still significant for $T>8$ K. In addition, the intersections of the $x\neq 0$ $\Delta S_m(T)$ curves with the $x=0$ curve occur at higher temperatures as the Fe concentration (and the cluster moment) is increased, in agreement with the calculations.[13]

Electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) measurements were made at room temperature on materials where $x=0$, 1, 1.75, and 2.5. The large linewidth of GGG is mostly due to dipolar broadening, and because the Fe ions sit at points between the Gd ions, the resonance of the Fe ions would be expected to show an even greater dipolar broadening than the Gd ions alone in the absence of any exchange interaction. The EPR linewidth reduces smoothly with increasing iron concentration, as shown in Fig. 4. These results are consistent with exchange narrowing due to exchange interactions between Gd and Fe moments.

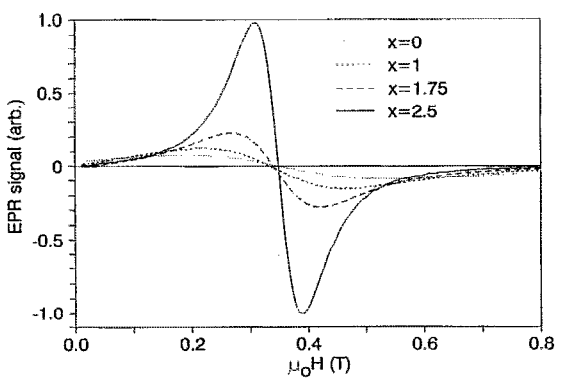

FIG. 4. X-band EPR signals for $Gd_3Ga_{5-x}Fe_xO_{12}$ at room temperature, normalized by second integral of the signal. The linewidth decreases with increasing Fe concentration, consistent with increased exchange interaction between Gd spins.

CONCLUSIONS

The magnetic properties and derived thermodynamic properties of the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials are consistent with superparamagnetic behavior at low Fe concentrations. Conceptually, the replacement of Ga atoms with Fe atoms in the material creates an indirect exchange interaction between neighboring Gd magnetic moments. Evidence for this interaction is found in the exchange narrowing of the EPR spectrum of the materials as Fe concentration is increased. At low temperatures, the exchange interaction between Gd spins is found to lead to the formation of magnetically ordered clusters. Evidence for the formation of such clusters is found in the nonlinearity of the magnetization curves at 10 K which is characteristic of superparamagnetic behavior.

The magnetocaloric properties of the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials are in qualitative agreement with calculations of ΔS_m for superparamagnetic materials, specifically in the enhancement of ΔS_m with increasing Fe concentration (cluster size) and in the crossover from small cluster moments giving the highest ΔS_m at low temperatures to large cluster moments giving the greatest ΔS_m at higher temperatures. Application of the $Gd_3Ga_{5-x}Fe_xO_{12}$ materials to magnetic refrigeration seems very promising. The magnitude of ΔS_m for the $x=1.75$ sample exceeds ΔS_m for GGG by a large margin for temperatures from 10 to 80 K. This implies that $Gd_3Ga_{5-x}Fe_xO_{12}$ materials may allow operation of a magnetic refrigerator at temperatures well in excess of the present maximum of 20 K.

ACKNOWLEDGMENT

The authors would like to acknowledge H. J. Brown for assistance in magnetization measurements.

[1] N. Kurti and F. Simon, Proc. R. Soc. A **149**, 152 (1935).
[2] C. G. B. Garrett, *Magnetic Cooling* (Harvard University Press, Wiley, New York, 1954).
[3] R. P. Hudson, *Principles and Applications of Magnetic Cooling* (North Holland, Amsterdam, 1972).
[4] O. V. Lounasmaa, *Experimental Principles and Methods Below 1K* (Academic, New York, 1974).
[5] J. A. Barclay, S. R. Jaeger, and F. C. Prenger, Adv. Cryog. Eng. **35B**, 1097, (1990).
[6] T. Hashimoto, T. Yazawa, R. Li, T. Kuzuhara, K. Matsumoto, H. Nakagome, M. Takahashi, M. Sahashi, K. Inomata, A. Tomokiyo, and H. Yayama, Adv. Cryog. Eng. Mats. **33**, 733 (1988).
[7] F. C. Prenger, D. D. Hill, J. Trueblood, T. Servais, J. Laatsch, and J. A. Barclay, Adv. Cryog. Eng. **35B**, 1105 (1990).
[8] R. Li, T. Numazawa, T. Hashimoto, A. Tomoyiko, T. Goto, and S. Todo, Adv. Cryog. Eng. **32**, 287 (1986).
[9] G. F. Dionne, J. Appl. Phys. **41**, 4874 (1970).
[10] G. F. Dionne, Mater. Res. Bull. **6**, 805 (1971).
[11] R. D. Shull, L. J. Swartzendruber, and L. H. Bennett, Proceedings of the 6th International Cryocoolers Conference, edited by G. Green and M. Knox, David Taylor Research Center Publ. No. DTRC-91/002, Annapolis, MD, 231 (1991).
[12] L. H. Bennett, R. D. McMichael, L. J. Swartzendruber, R. D. Shull, and R. E. Watson, J. Magn. Magn. Matls. **104-107**, 1094 (1992).
[13] R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. Bennett, and R. E. Watson, J. Magn. Magn. Matls. **111**, 29 (1992).