JOURNAL OF MATERIALS SCIENCE 26 (1991) 3753–3757

Magnetic properties of $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$ garnet single crystals

H. KIMURA, T. NUMAZAWA, M. SATO, H. MAEDA
National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Ibaraki 305, Japan

Magnetic properties of $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$ (DGGG) garnet single crystals were calculated using the Weiss molecular field theory and also measured using the vibrating sample magnetometer in the temperature range 4.2–40 K in the effective magnetic field from 0–7 T. The magnetic properties of DGGG single crystals are distributed between those of $Dy_3Ga_5O_{12}$ (DGG) and $Gd_3Ga_5O_{12}$ (GGG) single crystals, but are considerably closer to those of DGG. Based on the magnetic properties, the magnetic entropy change, ΔS_M, was evaluated in the temperature range below 15 K. DGGG single crystals are a prospective material for magnetic refrigeration below 15 K.

1. Introduction

Single crystals of rare-earth gallium garnets were expected to be useful for cryogenic magnetic refrigeration [1–4]. A $Dy_3Ga_5O_{12}$ (DGG) single crystal is one promising material for the magnetic refrigeration to generate liquid He or super-fluid He from He gas below 15 K. However, it is very difficult to grow DGG single crystal because of spiral growth [4]. In order to reduce the spiral growth of DGG single crystal, the substitution of Gd for Dy is effective, such as $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$ (DGGG) solid solution single crystals [5]. Magnetic properties, especially magnetic entropy change, are the most important characteristics for the magnetic refrigeration [4]. However, no magnetic properties of DGGG single crystals have been reported.

In the present work, the magnetization of the DGGG single crystals was calculated and also measured using the Weiss molecular field theory, and then the magnetic entropy change was evaluated. The possibility of application of DGGG single crystal to magnetic refrigeration is discussed based on the magnetic entropy change and the adiabatic demagnetization measurements.

2. Weiss molecular field theory

DGGG single crystals are an antiferromagnetic material. Based on the Weiss molecular field theory, the magnetization, M, is described by the total angular moment, J, and the coefficient, α, related to the magnetic field, H, and temperature, T, as follows [6]

$$M(T, H) = Ng\mu_B J\left(\frac{2J+1}{2J}\coth\frac{2J+1}{2J}\alpha - \frac{1}{2J}\coth\frac{1}{2J}\alpha\right) \quad (1)$$

with

$$\alpha = g\mu_B J\frac{\lambda M + H}{kT} \quad (2)$$

and

$$\lambda = -\frac{2k}{Ng^2\mu_B^2 J(J+1)}T_N \quad (3)$$

where N is the atomic number in unit volume, μ_B is the Bohr magneton, g is the g-factor, k is the Boltzmann constant and T_N is the Nèel temperature.

The magnetic entropy change, ΔS_M, at a given temperature is calculated using the following equation,

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \quad (4)$$

For the calculation, we assume the values of J, g and T_N to be as shown in Table I, which are interpolated in proportion to the Gd content, x, between the values of DGG and GGG [4, 7, 8]. In this calculation, ΔS_M is rarely affected by T_N because the calculation is performed in the temperature range 4.2–40 K which is considerably higher than T_N.

Fig. 1 shows the relation between the magnetic entropy change, ΔS_M, and the temperature calculated from Equation 4 with $x = 0.25$, 0.5 and 0.75 in $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$. ΔS_M increases with increasing x in the temperature range below 17 K. Conversely, ΔS_M decreases above 17 K. In any case, the values of ΔS_M are distributed between those of DGG ($x = 0$) and GGG ($x = 1$). Such a Gd content, x, dependency of

TABLE I Assumed parameters for calculation of ΔS_M for $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$

x	J	g	T_N
0	0.50	13.00	0.3
0.25	1.30	10.25	0.3
0.5	2.0	7.50	0.3
0.75	2.80	4.75	0.3
1	3.50	2.00	0.3

0022–2461/91 $03.00 + .12

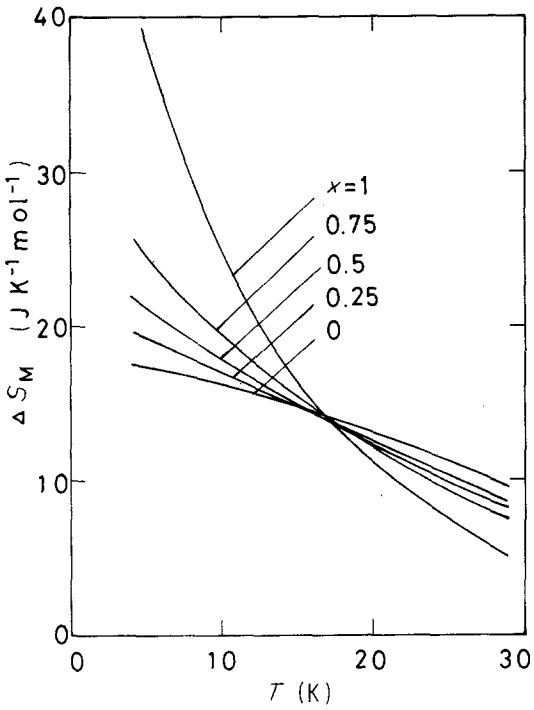

Figure 1 Relation between magnetic entropy change, ΔS_M, and temperature, T, in various magnetic fields for $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$, calculated from Equations 1–4.

ΔS_M is attributed to how ΔS_M is affected by J or g; the larger the g-factor, the greater the ΔS_M in the higher temperature region, and the larger the J, the greater the ΔS_M in the lower temperature region.

3. Experimental procedure

For the magnetization measurements, spherical samples with a diameter of about 2 mm were prepared from the grown single crystals with $x = 0.25$, 0.5 and 0.75. The magnetization measurements were performed along the $\langle 1\,1\,1 \rangle$ crystal direction in the effective magnetic field from 0–7 T in the temperature range between 4.2 and 40 K using a vibrating sample magnetometer. An effective magnetic field was obtained using the demagnetizing factor of the spherical shape of the sample. Although the Dy ion has an anisotropic magnetization, the ΔS_M of DGG rarely depends on the crystal direction [4]. The magnetic susceptibility was deduced from the magnetization measurement in a weak effective magnetic field below 1 T. The temperature of the sample was measured using an Ag–Au + 0.07 % Fe thermocouple in contact with it.

From the magnetization–field curves measured at various temperatures, the magnetic entropy change, ΔS_M, of the sample was also obtained using Equation 4.

For the adiabatic demagnetization measurement, a cylindrical-shaped sample was prepared, weighing about 30 g. The sample was first held at a given temperature of 7–30 K in an applied magnetic field of 0–6 T, and then demagnetized adiabatically. The initial temperature of the sample before demagnetization was adjusted by supplying the heat power through a manganine wire wound noninductively around the sample, and then the temperature drop was measured immediately after the heater power and the applied magnetic field were removed. The temperature was measured using a carbon glass resistance temperature sensor (CGR) inserted into a hole at the sample centre which was drilled subsonically.

4. Results and discussion

Fig. 2 shows the relation between the magnetization, M, and the effective magnetic field, H, for the crystal with $x = 0.5$. Similar curves are measured for other different Gd content single crystals. For DGG, the magnetization tends to saturate at temperatures below 10 K in effective magnetic fields above 5 T [4]. On the other hand, saturation is not observed for DGGG. This is due to the effect of substitution of Gd for Dy. Fig. 3 shows the relation between the magnetization and the effective magnetic field for the crystals with $x = 0.25$, 0.5 and 0.75 at 4.2 K. The value of the saturation magnetization with $x = 0.75$ is the largest of the three, and tends to decrease with decreasing x.

Fig. 4 shows the temperature dependence of the product of magnetic susceptibility and temperature, $\chi_m T$ for the crystals with $x = 0.25$, 0.5 and 0.75. The values of χ_m are obtained from the linear part of the curves below 1 T in Fig. 2. In the temperature range below 10 K, the values of $\chi_m T$ linearly decrease with decreasing temperature in accordance with the Curie–Weiss law. However, the values tend to deviate from the Curie–Weiss law above 10 K, being affected by the excited state doublet of the Dy ion, which appeared near 30 K for DGG. The various parameters

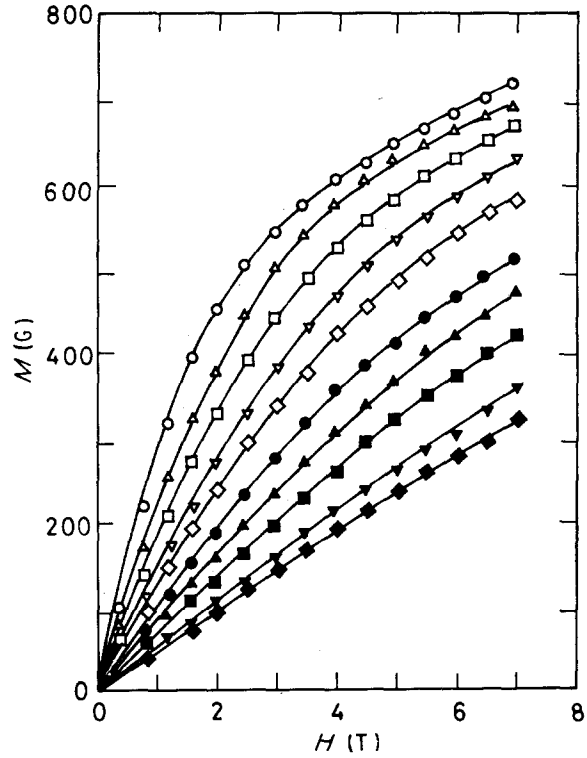

Figure 2 Relation between magnetization, M, and effective magnetic field, H, at various temperatures with $x = 0.5$. Temperature = (○) 4.2, (△) 6.9, (□) 9.0, (▽) 11.9, (◇) 14.0, (●) 18.1, (▲) 22.6, (■) 28.3, (▼) 35.6 and (◆) 40.4 K.

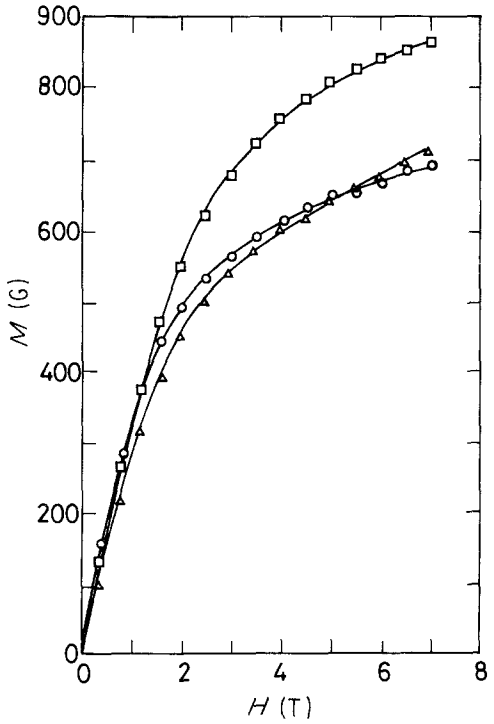

Figure 3 Relation between magnetization, M, and effective magnetic field, H, with $x = (\bigcirc)$ 0.25, $(\triangle)$ 0.5 and $(\square)$ 0.75 at 4.2 K.

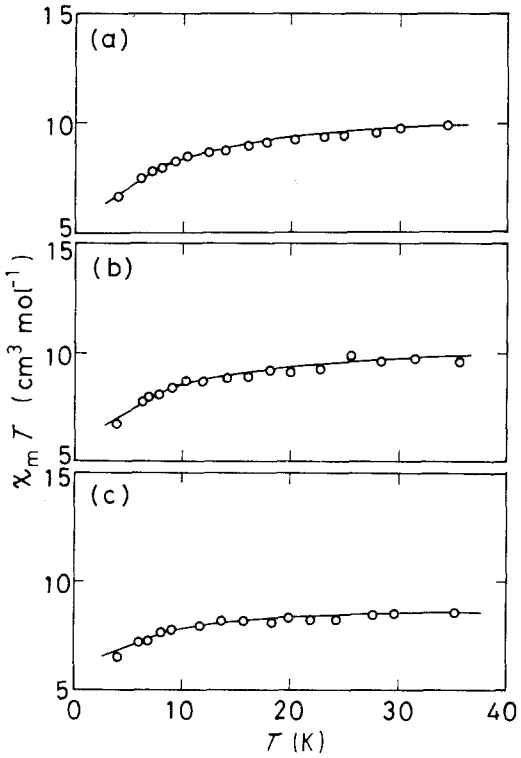

Figure 4 Temperature dependence of the product of magnetic susceptibility and temperature, $\chi_m T$, obtained from the linear part below 1 T in Fig. 2. (a) $x = 0.25$, (b) $x = 0.5$, (c) $x = 0.75$.

were determined from the $\chi_m T$–T curves below 10 K, fitted to Equation 5

$$\chi_m = \frac{C_m}{T + \theta_p} + \alpha' \qquad (5)$$

Table II shows the magnetic parameters of $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$ single crystals, namely the Curie–Weiss constant, C_m, the paramagnetic Curie temperature, θ_p, the Van Vleck contribution α', the magnetic moment p and the g-factor on the ground state doublet. The values of GGG are taken from the results of Wolf *et al.* [7]. Present analysis shows that the magnetic properties of DGGG are distributed between those of DGG and GGG, but are especially closer to those of DGG.

Fig. 5 shows the relation between the magnetic entropy change, ΔS_M, and temperature, T, in various initial effective magnetic fields before demagnetization with $x = 0.5$, obtained using Equation 4 from the data in Fig. 2. ΔS_M decreases with decreasing initial effective magnetic field.

Fig. 6 shows the temperature dependence of ΔS_M for various Gd contents DGGG single crystals when the initial effective magnetic field is 7 T. As x increases, ΔS_M decreases in the temperature above 15 K, and contrary, ΔS_M increases below 15 K. The ΔS_M–T relation obtained from the magnetic measurements shows a similar tendency to that calculated from the Weiss molecular field theory. Fig. 7 shows a comparison between the calculated and experimental ΔS_M in an effective magnetic field of 7 T with $x = 0.5$. The experimental values are larger than the calculated ones

TABLE II Magnetic properties of $(Dy_{1-x}Gd_x)_3Ga_5O_{12}$ single crystal, namely the Curie–Weiss constant, C_m, the paramagnetic Curie temperature, θ_p, the Van-Vleck contribution, α', the magnetic moment, p, and the g-factor on the ground state doublet

x	C_m (Kcm^3 mol^{-1})	θ_p(K)	α'(cm^3 mol^{-1})	p/μ_B
0	6.05	0.33	0.42	7.00
0.25	6.49	0.02	0.16	7.21
0.5	6.29	0.05	0.25	7.09
0.75	6.54	0.21	0.16	7.23
1	7.82	2.3	—	7.91

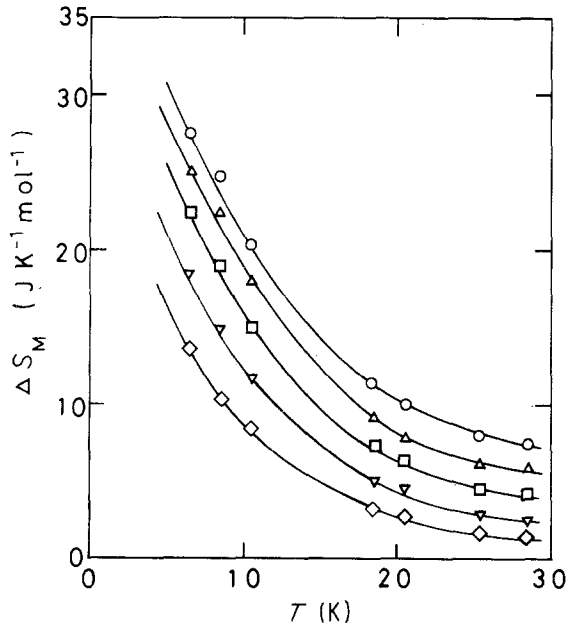

Figure 5 Relation between magnetic entropy change, ΔS_M, and temperature, T, with $x = 0.5$ in various effective magnetic fields of $(\bigcirc)$ 7, $(\triangle)$ 6, $(\square)$ 5, $(\triangledown)$ 4 and $(\diamond)$ 3 T.

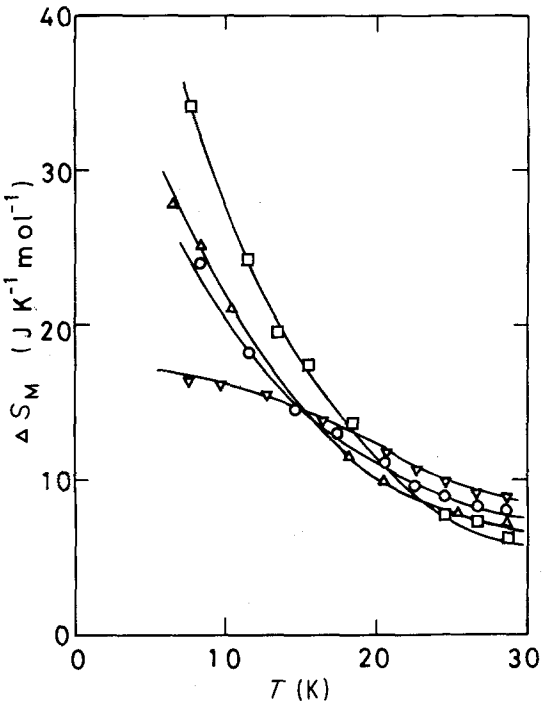

Figure 6 Relation between experimental magnetic entropy change, ΔS_M and temperature, T, with x = (▽) 0, (○) 0.25, (△) 0.5 and (□) 0.75.

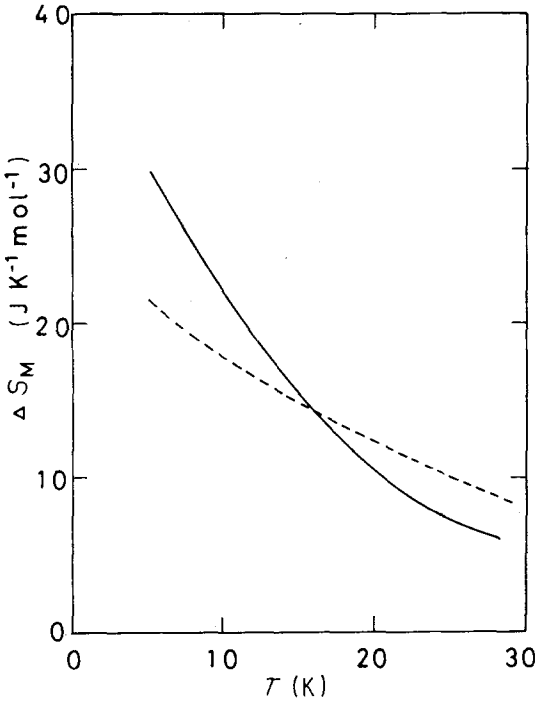

Figure 7 Comparison between temperature dependence of calculated and experimental ΔS_M in an effective magnetic field of 7 T with x = 0.5. (——) experimental results, (– – –) calculated results.

below 15 K and smaller above 15 K. Generally, for ferromagnetic materials, the experimental ΔS_M value tends to be larger than the calculated one in the higher temperature range above the magnetic transition temperature [9]. In the case of the antiferromagnetic material, DGGG, the same tendency is seen below 15 K. On the other hand, the smaller values above 15 K are mainly due to the excited state doublet in Dy compounds. Strictly speaking, it may decrease accuracy to use the one molecular field theory for substitution-type solid solutions, because microscopic randomness of magnetic interaction between local spins increases with increasing substitution content. However, the average one molecular field theory cannot give the main difference between the calculation and the experiment for DGGG. Of course, the difference cannot be caused by the concentration deviation in the crystal, because the deviation is small, by chemical analysis [5]. However, the Weiss molecular field theory is useful to evaluate the magnetic entropy for rare-earth garnet solid solutions, such as DGGG single crystals.

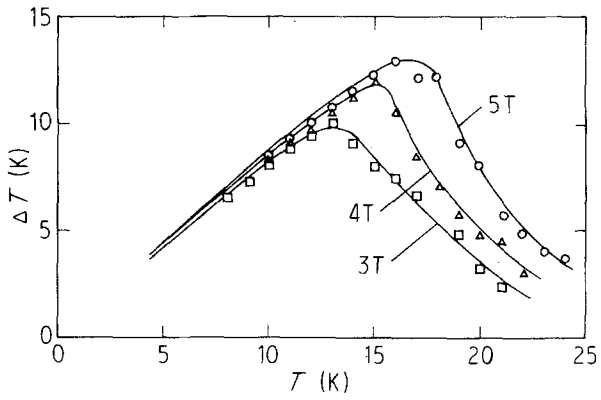

Figure 8 Relation between temperature drop, ΔT, measured by adiabatic demagnetization experiment, and starting temperature, T, in various effective magnetic fields, H, with x = 0.25.

From the point of view of application to magnetic refrigeration, these materials are useful in that they have a large magnetic entropy change, ΔS_M, which can be controlled by the amount of substitution of Gd for Dy. Fig. 8 shows the relation between the temperature drop, ΔT, which is measured by the adiabatic demagnetization experiment from various magnetic fields, and the starting temperature, T, with x = 0.5. Similar relations are obtained with x = 0.25 and 0.75. These curves show that the DGGG single crystals have a large magneto-thermal effect. Therefore, DGGG single crystals are the promising magnetic material for magnetic refrigeration below 15 K.

In order to draw the exact entropy–temperature curves, which are necessary to design the magnetic refrigeration cycle, the magnetic entropy must be determined in zero magnetic field which is evaluated from measurement of a specific heat capacity [4]. In the near future, the specific heat capacity for DGGG single crystals will be measured.

5. Conclusions

The magnetic properties of DGGG single crystals are distributed between those of DGG and GGG, being considerably closer to those of DGG. For the magnetic entropy change, ΔS_M, both the calculated values using the Weiss molecular field theory and the experimental ones, show a similar tendency, but the absolute values are larger in the experiment than in the calculation in the temperature range below 15 K, and smaller above 15 K.

Based on the magnetic properties, DGGG single crystals are a prospective material for magnetic refrigeration, to generate liquid He or superfluid He from the He gas at a temperature below 15 K.

Acknowledgement

The authors thank Mr M. Sakamoto for helpful discussions and experimental support.

References

1. J. A. BARCLAY, O. MOZE and P. PATERSON, *J. Appl. Phys.* **50** (1979) 5870.
2. Y. HAKURAKU and H. OGATA, *Jpn J. Appl. Phys.* **25** (1986) 140.
3. A. TOMOKIYO, H. YAYAMA, T. HASHIMOTO, T. AOMINE, M. NISHIDA and S. SAKAGUCHI, *Cryogenics* **25** (1985) 271.
4. H. KIMURA, H. MAEDA and M. SATO, *J. Mater. Sci.* **23** (1988) 809.
5. H. KIMURA, T. NUMAZAWA, M. SATO and H. MAEDA, *J. Crystal Growth* **87** (1988) 523.
6. T. HASHIMOTO, T. NUMAZAWA, M. SHINO and T. OKADA, *Cryogenics* **21** (1981) 647.
7. W. P. WOLF, M. BALL, M. T. HUTCHINGS, M. J. M. LEASK and A. F. G. WAYATT, *J. Phys. Soc. Jpn* **17** Suppl. B-1 (1962) 443.
8. D. G. ONN, H. MEYER and J. P. REMEIKA, *Phys. Rev.* **156** (1967) 663.
9. H. MAEDA, M. SATO and M. UEHARA, *J. Jpn Inst. Metals* **47** (1983) 687 (in Japanese).

Received 2 January
and accepted 19 November 1990