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Single crystals growth and magneto-thermal properties of $Dy_3Ga_5O_{12}$ garnet

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Single crystals of $Dy_3Ga_5O_{12}$ garnet have been grown by the Czochralski method and the anisotropy of magnetic entropy evaluated for use as a magnetic material for a magnetic refrigeration in place of $Gd_3Ga_5O_{12}$ single crystals. As the size of the single crystal is large enough, and the anistropy is small, this crystal is suited to use for magnetic refrigeration in the temperature range of 1.8 to 15 K.

1. Introduction

In recent years, low temperature refrigeration techniques have progressed well. Particularly, magnetic refrigeration has been noted as a new refrigeration system, producing liquid helium or superfluid helium in a lower temperature range than 20 K, due to its high efficiency compared with gas refrigeration [1]. Magnetic materials for magnetic refrigeration must possess the following characteristics: a large magnetic entropy, a low magnetic phase transition temperature, a small heat capacity, a high thermal conductivity and a high electrical resistivity [1]. Some magnetic materials which satisfy these conditions could be single crystals of antiferromagnetic rare earth garnets such as $Gd_3Ga_5O_{12}$ (GGG), $Dy_3Al_5O_{12}$ (DAG), $Dy_3Ga_5O_{12}$ (DGG) and $Gd_3(Ga_{1-x}Al_x)_5O_{12}$ ($x = 0.1$ to 0.4) (GAGG) [1]. Until now, GGG single crystals have been used for magnetic materials in the temperature range of 1.8 to 15 K, as GGG has a large magnetic entropy due to its large total angular momentum, and moreover large size single crystals of high quality are produced as substrate materials for magnetic bubble memory devices [2–4]. However, the magnetic entropy change of GGG single crystals become so small above 15 K that it is difficult to raise the starting temperature of magnetic refrigeration. On the other hand the garnet single crystals including Dy still have a large magnetic entropy above 15 K. This is mainly caused by the large g-factor (spectroscopic splitting factor) different from the large total angular momentum for GGG, so the magnetic entropy change of Dy-garnet single crystals is still large above 15 K. Dy-garnet single crystals are, therefore, expected to be able to raise the starting temperature of magnetic refrigeration. As the magnetization of Dy-garnet single crystals is affected by an anisotropic crystal field, it is important to evaluate the anisotropy of the magnetic entropy as well as magnetization. The most important matter is to grow the large size single crystals suitable for magnetic refrigeration. Tomokiyo *et al.* have reported the entropy of $Dy_3Ga_5O_{12}$, one of the Dy-garnets [5]. They evaluate the entropy in magnetic fields less than 5 Tesla (T) using only the small size single crystal and take no account of the effect of the magnetization anisotropy caused by the anisotropic crystal field.

In the present work, we have grown the large size single crystals of $Dy_3Ga_5O_{12}$ garnet using the Czochralski method, and evaluate some characteristics necessary to magnetic refrigeration on the bases of the magnetization and the adiabatic demagnetization measurements.

2. Experimental procedure

2.1. Crystal growth

Single crystals of $Dy_3Ga_5O_{12}$ garnet (DGG) were grown by the Czochralski method in an iridium crucible of 47 mm in diameter and 48.5 mm in height, using RF power supply. The starting materials were Dy_2O_3 (Research Chemicals, USA) and Ga_2O_3 (Rhone Poulenc, France) powders, having 99.99% purity. The oxides were heated to eliminate moisture prior to mixing. The mixed powders, having 1 wt % higher Ga_2O_3 concentration than stoichiometry to compensate for gallium loss during the crystal growth, were pressed and sintered at 1473 K in air for 24 h. The sintered sample became stoichiometric $Dy_3Ga_5O_{12}$ garnet. A typical charge for a run was 430 g. The pulling rate was 4 mm h^{-1} and rotation rates were 20 and 40 r.p.m. In these rotation rates, the solid–liquid interface was almost convex toward the melt. All crystals were grown in a N_2 atmosphere containing 2% O_2. The gas flow rate was 700 ml min^{-1} to depress the evaporation of Ga_2O_3. The growing direction was $\langle 1\,1\,1\rangle$. The seed material was $Gd_3(Al_{0.2}Ga_{0.8})_5O_{12}$ single crystals [6]. The diameter of these crystals were controlled by a weighing method.

2.2. Magnetization and adiabatic demagnetization measurement

Samples for the magnetization measurements were prepared from grown single crystals. The shape was spherical and the diameter was ~ 2 mm. The magnetization measurements along the three crystal directions of $\langle 1\,1\,1\rangle$, $\langle 1\,1\,0\rangle$ and $\langle 1\,0\,0\rangle$, were performed for the temperature range from 4.2 to 40 K and for the applied magnetic field range from 0 to 7 T using a vibrating sample magnetometer. The magnetic

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susceptibility was deduced from the magnetization measurement in a weak applied field less than 1 T. The temperature of the sample was measured using an Ag–Au + 0.07% Fe thermocouple contacting with it.

Furthermore, from the magnetization values M, the magnetic entropy changes ΔS_M were obtained by Equation 1:

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \mathrm{d}H \quad (1)$$

where T is temperature and H is an effective magnetic field.

For the adiabatic demagnetization measurement, a sample of cylindrical shape was prepared, weighing ~ 30 g. The measurement was performed for the temperature range from 7 to 30 K and for the applied field range from 0 to 6 T. The temperature of the sample was adjusted by supplying the heat power through a manganine wire wound noninductively around the sample side, then the adiabatic temperature drop was measured when the applied field was removed. The temperature was measured using a carbon glass resistance temperature sensor (CGR) inserting a hole of sample centre which was drilled subsonically.

3. Results and discussion

3.1. Crystal growth

Fig. 1 shows one of the grown $Dy_3Ga_5O_{12}$ (DGG) garnet single crystals. The crystal is yellow and transparent, and its size is about 20 mm in diameter and 30 mm in length. The X-ray powder diffraction shows that the crystal has single phase of garnet and its lattice parameter is 1.2321 nm.

According to a cross-polarized light image for a wafer of DGG single crystal cut parallel to the ⟨1 1 1⟩ growth direction, it can be observed that the change of the solid–liquid interface shapes from convex to concave toward the melt. The interface shape transition occurs when the rotation rate is 40 r.p.m. and the diameter is 19 mm. This condition is in agreement with that of $Gd_3Ga_5O_{12}$ (GGG) single crystals [7]. Similar interface transition has been reported for GGG, $Y_3Al_5O_{12}$ (YAG) and $Dy_3Al_5O_{12}$ (DAG) [7–10]. In DGG single crystals, the weak convex of the interface can be observed before the transition in the same manner as DAG single crystals [10], and the strong concave after the transition. Therefore, the DGG single crystals generally grow without facet in the convex grown region. However, the faceting growth is occasionally observed when the rotation rate is 20 r.p.m. The weak convex may be a special characteristic of Dy-garnet single crystals. In the convex grown region, the single crystals tend to grow spirally as shown in Fig. 1, so it is difficult to keep a shape of constant diameter. Some causes of this spiral growth are suggested [11], but are still uncertain. In this case, the weight fraction of solid is only 0.23 before the spiral growth. The strong concave of the interface shape after its transition and the spiral growth, enhance the difficulty of growing large size DGG single crystals more than 20 mm in diameter and 30 mm in length, even when the automatic diameter control system is used.

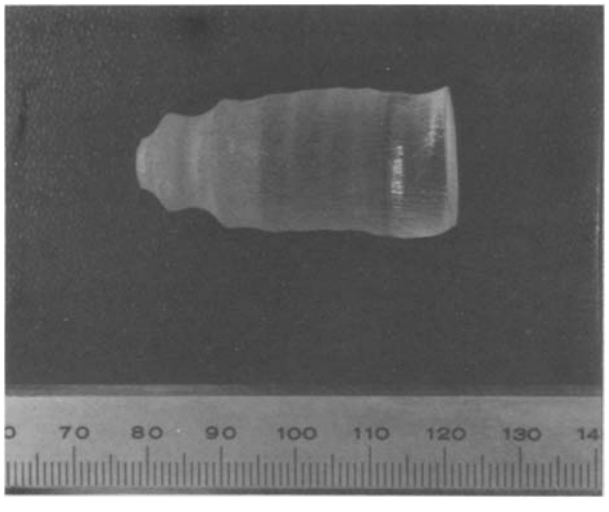

Figure 1 A grown crystal of $Dy_3Ga_5O_{12}$ garnet.

3.2. Magnetization and adiabatic demagnetization measurement

Fig. 2 shows the relation between the magnetization, M and the effective field, H along the ⟨1 1 1⟩ direction. Similar relations are obtained along the ⟨1 1 0⟩ and ⟨1 0 0⟩ directions. The anisotropy of magnetization is very weak: the maximum difference in those magnetizations is only about 5% at 4.2 K and 7 T. In the temperature range below 10 K, the magnetization tends to saturate above 5 T. This tendency is not observed in Gd-garnet single crystals [1].

Fig. 3 shows the dependence of the product of the magnetic susceptibility and temperature $\chi_m T$ on temperature T. In the temperature range below 10 K, the values of $\chi_m T$ decrease linearly with decreasing temperature in accordance with the Curie–Weiss law. However, the values tend to deviate from the Curie–Weiss law above 10 K, affected by the excited state doublet near 30 K [10]. Table I shows magnetic

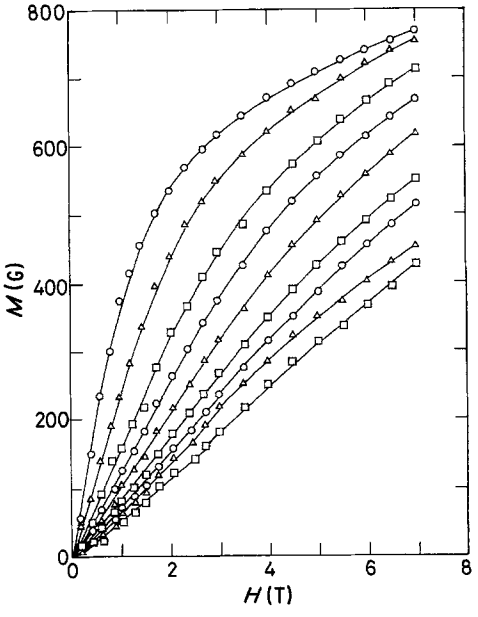

Figure 2 Relation between magnetization, M and effective magnetic field, H of $Dy_3Ga_5O_{12}$ garnet. Temperature T = 4.2, 1.1, 12.8, 16.6, 21.0, 27.0, 30.2, 35.1 and 40.6 (K, reading from top to bottom).

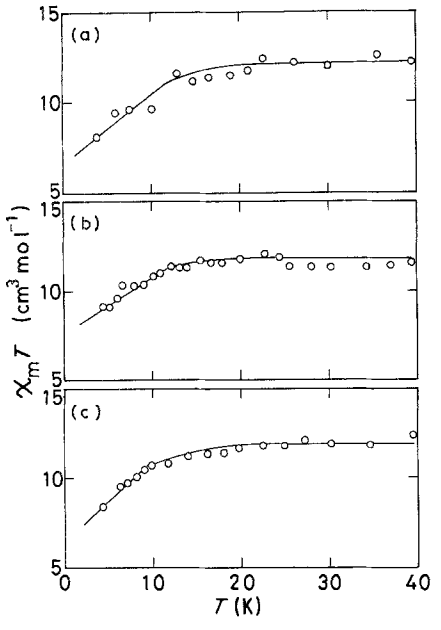

Figure 3 Relation between the product of magnetic molar susceptibility and temperature $\chi_m T$, and temperature T in the three crystalline axes for $Dy_3Ga_5O_{12}$ garnet. (a) ⟨1 1 1⟩, (b) ⟨1 1 0⟩, (c) ⟨1 0 0⟩.

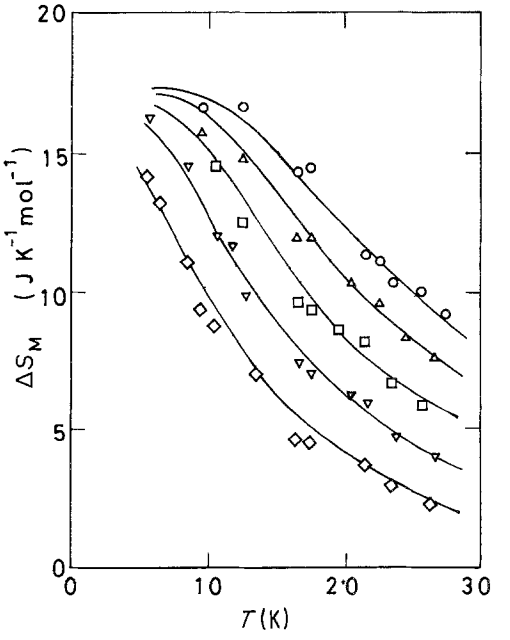

Figure 4 Relation between magnetic entropy change ΔS_M and temperature T in various effective magnetic fields H obtained from the M–H curves in Fig. 2. Solid curves show the calculation using the Weiss molecular field theory. ◇, 3 T; ▽, 4 T; □, 5 T; △, 6 T; ○, 7 T.

properties such as Curie–Weiss constant C_m, paramagnetic Curie temperature θ_p, Van–Vleck contribution α, magnetic moment p and g-factor along the three crystalline axes on the ground state doublet. These values are determined from the $\chi_m T$–T curves below 10 K in Fig. 3, according to Equation 2:

$$\chi_m = \frac{C_m}{T + \theta_p} + \alpha \quad (2)$$

In these values, a small anisotropy can be obtained as pointed out by Fillipi *et al.* [12]. The maximum value of g-factor is 8.5 at ⟨1 1 0⟩ direction and the minimum value is 8.0 at ⟨1 1 1⟩ direction. The difference of g-factor is about 6%, which is smaller than 40% of DAG single crystals [13].

Fig. 4 shows the relation between the magnetic entropy change ΔS_M and temperature T in various effective magnetic fields along the ⟨1 1 1⟩ direction. These values are obtained using the data in Fig. 2 and Equation 1. The same relations are also obtained along the ⟨1 1 0⟩ and ⟨1 0 0⟩ directions. These results mean that the effect of the crystal field can be negligible in the DGG single crystal. Namely, when the DGG single crystal is used for the magnetic material of magnetic refrigeration, its refrigeration efficiency can be the same with respect to the crystal direction. In Fig. 4, the solid curves show the result of calculations using the Weiss molecular field theory when the g-factor is 13 and the total angular momentum is 0.5 [1]. This large g-factor is affected by the excited state doublet. The measured values are in good agreement with the calculated ones.

Fig. 5 shows the relation between the total entropy S and temperature T. The total entropy S is represented by Equation 3

$$S = S_M + S_L \quad (3)$$

where S_M is the magnetic entropy and S_L is the lattice entropy. Furthermore, S_M can be separated into two entropies such as S_{M_0} and ΔS_M, as shown in Equation 4:

$$S_M = S_{M_0} + \Delta S_M \quad (4)$$

where S_{M_0} is the magnetic entropy in zero magnetic field and ΔS_M is the change of S_M when the magnetic field is applied. The sum of S_{M_0} and S_L can be calculated from the specific heat in zero magnetic field C_0. In Fig. 5, the total entropy curve at 0 T is obtained from the data of the specific heat Tomokiyo *et al.* [5] using Equation 5

$$S_{M_0} + S_L = \int_0^T \frac{C_0}{T}\,dT \quad (5)$$

The total entropy S, when a magnetic field is applied, is determined by the subtraction of the magnetic entropy change ΔS_M from the S–T curve at 0 T. These entropy curves are in agreement with the data of Tomokiyo *et al.* [5] in a magnetic field less than 5 T.

Fig. 6 shows the ideal Carnot cycles in a magnetic field of 6 T when DGG and GGG [13] single crystals are used for magnetic materials. Dotted lines show the cycle operated for the temperature range from 4.2 to

TABLE I Curie constant C_m, Van–Vleck contribution α, paramagnetic Curie temperature θ_p, magnetic moment p and g-factor of $Dy_3Ga_5O_{12}$ single crystal in various crystal directions

	C_m(K cm^3 mol^{-1})	θ_p(K)	α (cm^3 mol^{-1})	p (μ_B)	g
⟨1 1 1⟩	6.05	0.33	0.42	7.0	8.0
⟨1 1 0⟩	6.79	0.23	0.37	7.4	8.5
⟨1 0 0⟩	6.66	0.21	0.40	7.3	8.4

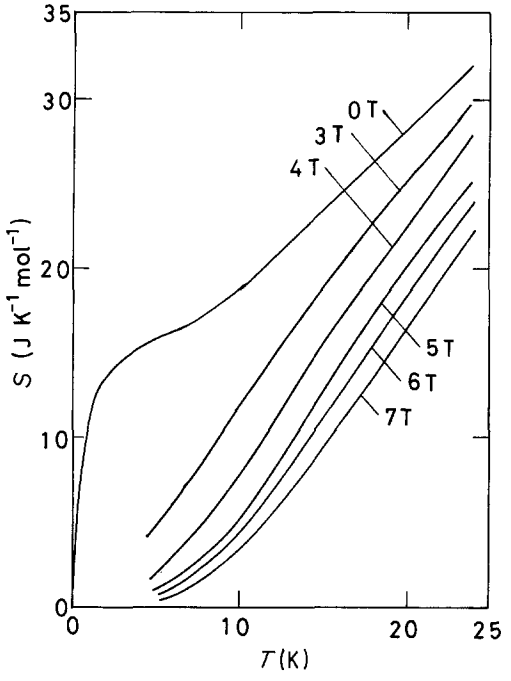

Figure 5 Relation between entropy, S and temperature, T in various effective magnetic fields, H obtained from the values of ΔS_M in Fig. 4.

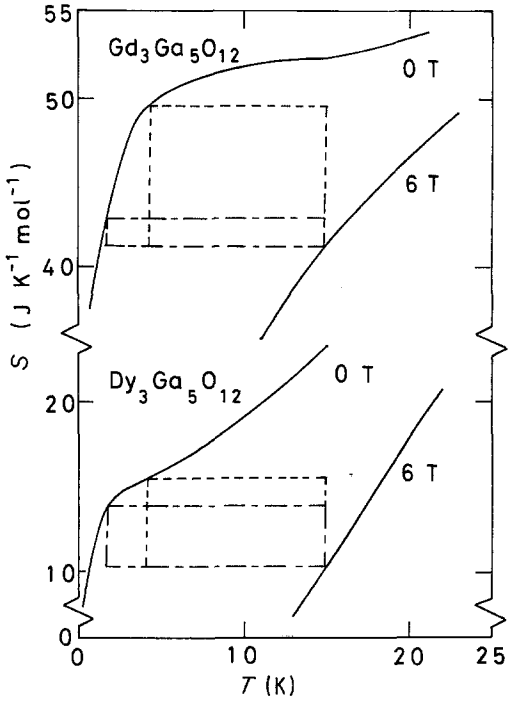

Figure 6 The Carnot cycles of $Dy_3Ga_5O_{12}$ and $Gd_3Ga_5O_{12}$ garnet single crystals when the magnetic field is 6 T. The dotted line is the 4.2 to 15 K temperature region and the dashed line is the 1.8 to 15 K temperature region.

15 K, and dashed lines from 1.8 to 15 K. In the temperature range of 4.2 to 15 K, the DGG single crystal is inferior to the GGG single crystal because the work of the Carnot cycle is small. In the temperature range of 1.8 to 15 K, on the other hand, the DGG single crystal is slightly superior to the GGG single crystal. Therefore, the DGG single crystal is better than the GGG crystal for magnetic refrigeration, producing superfluid helium from 15 K.

Fig. 7 shows the relation between the temperature drop ΔT, measured by the adiabatic demagnetization experiment, and starting temperature T in various effective magnetic fields. Solid curves are calculated from the S–T curves as shown in Fig. 5. The measured values are in good agreement with the calculated curves.

4. Conclusion

$Dy_3Ga_5O_{12}$ garnet single crystals can be grown by the Czochralski method. These crystals tend to grow spirally, however their sizes are large enough to use for magnetic refrigeration. From the results of the magnetization along the ⟨1 1 1⟩, ⟨1 1 0⟩ and ⟨1 0 0⟩ crystal directions, a small anisotropy in magnetization caused by the crystal field is observed. However, there is no problem in using the magnetic materials for magnetic refrigeration. From the results of the S–T curves. $Dy_3Ga_5O_{12}$ single crystal is suited for magnetic refrigeration in the temperature range from 1.8 to 15 K.

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References

1. H. MAEDA, H. KIMURA and M. SATO, *Cryogen. Engng* **20** (1985) 269 (in Japanese).
2. W. A. STEYERT, *J. Appl. Phys.* **49** (1978) 1227.

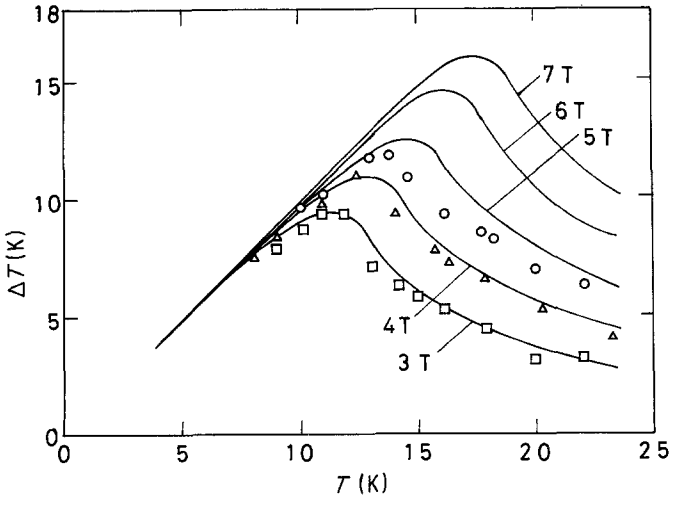

Figure 7 Relation between temperature change, ΔT, and initial temperature, T, in various magnetic fields, H. Solid curves are calculated from S is shown in Fig. 5.

3. J. A. BARCLAY, O. MOZE and PATERSON, *ibid.* **50** (1979) 5870.
4. Y. HAKURAKU and H. OGATA, *Jpn. J. Appl. Phys.* **25** (1986) 140.
5. A. TOMOKIYO, H. YAYAMA, T. HASHIMOTO, T. AOMINE, M. NISHIDA and S. SAKAGUCHI, *Cryogenics* **25** (1985) 271.
6. H. KIMURA, H. MAEDA and M. SATO, *J. Crystal Growth* **74** (1986) 187.
7. J. R. CARRUTHERS, *ibid.* **36** (1976) 212.
8. B. COCKAYNE, M. CHESSWAS and D. B. GASSON, *J. Mater. Sci.* **4** (1969) 450.
9. B. COCKAYNE, B. LENT and J. M. ROSLINGTON, *ibid.* **11** (1976) 259.
10. Y. MIYAZAWA, M. MORI and S. HONMA, *J. Crystal Growth* **43** (1978) 541.
11. F. J. BRUNI, "Crystals for Magnetic Application" (Springer-Verlag, Berlin, 1978) p. 59.
12. J. FILIPPI, F. TCHEOU and J. ROSSAT-MIGNOD, *Solid State Commun.* **33** (1980) 827.
13. T. HASHIMOTO, *Cryogen. Engng* **20** (1985) 262 (in Japanese).

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