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Large refrigerant capacity of *R*Ga (*R* = Tb and Dy) compounds

X. Q. Zheng,[1] J. Chen,[2] J. Shen,[3] Hu Zhang,[1] Z. Y. Xu,[1] W. W. Gao,[1] J. F. Wu,[3] F. X. Hu,[1] J. R. Sun,[1] and B. G. Shen[1,a)]

[1]*State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

[2]*Beijing Institute of Aerospace Testing Technology, China Aerospace Science and Technology Corporation, Beijing 100074, People's Republic of China*

[3]*Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

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The magnetic properties and magnetocaloric effects (MCEs) of *R*Ga (*R* = Tb and Dy) compounds are investigated. The TbGa compound exhibits two successive magnetic transitions: spin-reorientation (SR) transition at $T_{SR} = 31$ K and second-order ferromagnetic (FM)–paramagnetic (PM) transition at Curie temperature $T_C = 154$ K, while the DyGa compound undergoes a SR transition with T_{SR}=25 K and a FM–PM transition with $T_C = 113$ K. It is noteworthy that a broad distribution of the magnetic entropy change peak is observed. The values of the refrigerant capacity (RC) for TbGa and DyGa are found to be 620.6 and 381.9 J/kg for a field change of 0–5 T, respectively. And for a field change of 0–7 T, the values are 900 and 584.2 J/kg, respectively. The large value of RC for TbGa and DyGa originates from the combined contribution from SR and FM–PM transitions, which enlarges the temperature span of large MCE. © *2012 American Institute of Physics*. [doi:10.1063/1.3672842]

I. INTRODUCTION

Excellent magnetocaloric properties have been observed in some magnetic materials with first-order phase transitions.[1–4] However, the first-order phase transition is usually accompanied by considerable thermal and magnetic hysteresis, thus reducing the RC of magnetic materials. It is of importance to explore magnetic refrigerant materials with large reversible MCEs as well as high RC values based on the second-order magnetic transition.

Binary *R*Ga (*R* = rare-earth) intermetallic compounds crystallize in the orthorhombic CrB type structure with the space group of *Cmcm*.[5] They are ferromagnets that undergo the second-order ferromagnetic (FM)–paramagnetic (PM) transitions at respective Curie temperature T_C.[6–8] A systematic investigation of the magnetic structure for *R*Ga (Pr-Er) was carried out by measuring the temperature dependencies of the hyperfine interactions and it was observed that the *R*Ga (*R* = Nd, Sm, Ho, and Er) compounds exhibit spin-reorientation (SR) transition below T_C.[8] Recently, the magnetic and magnetocaloric properties of *R*Ga (*R* = Gd, Ho, and Er) have been studied.[9–11] In this paper, we carefully investigate the magnetic properties and MCEs of *R*Ga (*R* = Tb and Dy).

II. EXPERIMENT

The *R*Ga (*R* = Tb and Dy) ingots were prepared in a purified Ar atmosphere by arc-melting of the stoichiometric amounts of the high purity (>99.9 wt. %) constituent elements on a water cooled copper hearth. To achieve compositional homogeneity, the obtained ingot was wrapped in a molybdenum foil, sealed in a high-vacuum quartz tube, annealed at 800 °C for 7 days and then quenched into liquid nitrogen. The phase structure and the crystal lattice parameters were examined by the Rietveld refinement of the room-temperature x-ray powder diffraction (XRD) data collected using the Cu $K\alpha$ radiation. Magnetization measurements were carried out as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer.

III. RESULTS AND DISCUSSION

The room-temperature XRD patterns of the *R*Ga (*R* = Tb and Dy) compounds and the Rietveld analysis results are shown in Fig. 1. The refinement result shows that the prepared compounds are of single phase, crystallizing in the orthorhombic CrB-type structure (space group *Cmcm*), as the previous reports.[5] The structure can be described as the stacking of triangular prims with rare-earth atoms at the corners and the gallium atoms nearly at the center.[12] *R* atoms and Ga atoms occupy two different 4c (0, y, 1/4) equivalent sites.[5] The lattice parameters of *R*Ga (*R* = Tb and Dy) are listed in Table I, together with those of the samples with *R* = Gd, Ho, and Er for comparison.[9–11] It is clearly observed that the lattice parameters decrease continuously with the *R* atom sweeping from Gd to Er due to the lanthanide contraction.

Figure 2 shows the temperature dependencies of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations for *R*Ga (*R* = Tb and Dy) under a magnetic field of 1 T. It is found that the TbGa compound exhibits two successive magnetic transitions: spin-reorientation transition at $T_{SR} = 31$ K

a)Author to whom correspondence should be addressed. Electronic mail: shenbg@aphy.iphy.ac.cn.

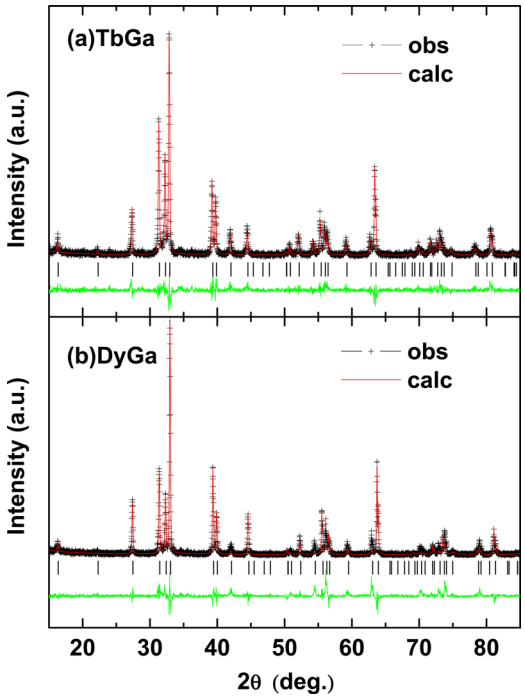

FIG. 1. (Color online) Rietveld refined powder x-ray diffraction patterns of *R*Ga [*R*=Tb (a) and Dy (b)] at room temperature. The observed data are indicated by crosses and the calculated profile is the continuous line overlaying them. The short vertical lines indicate the angular positions of the Bragg peaks of TbGa and DyGa, respectively. The lower curve is the difference between the observed and calculated intensity.

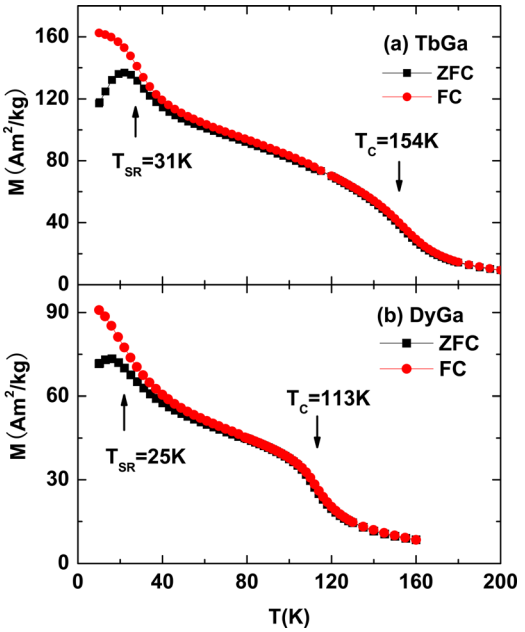

FIG. 2. (Color online) Temperature dependencies of zero-field-cooling and field-cooling magnetizations for *R*Ga [*R* = Tb (a) and Dy (b)] under a magnetic field of 1 T.

and second-order FM–PM transition at $T_C = 154$ K, and the DyGa compound undergoes a SR transition with $T_{SR} = 25$ K and a second-order FM–PM transition with $T_C = 113$ K. The T_C values observed here are in good agreement with the previous results.[7,8] No thermal hysteresis is observed in the ZFC and FC curves above T_C. However, it is noted that the ZFC and FC magnetization data show thermomagnetic irreversibility below T_C as observed in Ref. 11 and it is likely due to a domain wall pinning effect.

Magnetization isotherms of *R*Ga (*R* = Tb and Dy) were measured in a wide temperature range under increasing and decreasing fields up to 7 T (Fig. 3). Both TbGa and DyGa are found to exhibit similar *M*-*H* curves. The magnetization increases rapidly at low fields and shows a tendency to saturate with an increase of the field, exhibiting typical FM nature. For both TbGa and DyGa, the magnetization curves under increasing and decreasing fields are completely reversible in a wide temperature range around T_C and no magnetic hysteresis is observed. From M-H curves, we can also get the M^2 versus H/M curves, i.e., Arrott plots of *R*Ga (*R* = Tb and Dy) around T_C. Neither inflection nor negative slope in the Arrott plots is observed, indicating that the *R*Ga (*R* = Tb and Dy) compounds exhibit second-order FM–PM transition. The second-order phase transition usually means thermal and magnetic reversibility, which has been confirmed in Figs. 2 and 3. And this is favorable to practical applications of the magnetic refrigeration materials.

The ΔS_M of *R*Ga (*R* = Tb and Dy) was calculated based on isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. The ΔS_M as a function of temperature is shown in Fig. 4. For TbGa, there are two sharp peaks in the ΔS_M-T curves around T_{SR} and T_C, respectively, corresponding to the two transitions detected in the *M*-*T* curves. The maximal values of $-\Delta S_M$ are 10.8 and 8.1 J/kg K at T_{SR} and T_C for a field change of 0–7 T, respectively. Similar results are observed in HoGa,[10] ErGa,[11] $HoAl_2$,[13] and Gd_4Co_3.[14] It can be seen from Fig. 4(a) that the two peaks partly overlaps between T_{SR} and T_C, which enlarges greatly the temperature range of MCE. For DyGa, its maximal values of $-\Delta S_M$ are 5.8

TABLE I. The crystallographic, magnetic, and magnetocaloric data for the *R*Ga (*R* = Gd-Er) compounds.

Compounds	a (Å)	b (Å)	c (Å)	T_{SR} (K)	T_C (K)	ΔS_M at T_{SR} (J/kg K)	ΔS_M at T_C (J/kg K)	RC (J/kg)	Refs.
GdGa	4.3388(2)	11.0104(3)	4.1058(2)	~100	183	~3.3[a]	4.8[a]	~438[*a]	9
TbGa	4.317(8)	10.929(1)	4.084(1)	31	154	8.3[a]/10.8[b]	5.9[a]/8.1[b]	620.6[a]/900[b]	this work
DyGa	4.297(4)	10.856(5)	4.062(4)	25	113	4.3[a]/5.8[b]	5.8[a]/8.1[b]	381.9[a]/584.2[b]	this work
HoGa	4.280(9)	10.781(9)	4.042(4)	20	69	7.8[a]	17.1[a]	455[a]	10
ErGa	4.263(0)	10.728(8)	4.030(6)	15	30	16.5[a]	21.3[a]	494[a]	11

[*]The result is estimated from the temperature dependence of ΔS_M in Ref. 9.
[a]The values are obtained for a field change of 0−5 T.
[b]The values are obtained for a field change of 0−7 T.

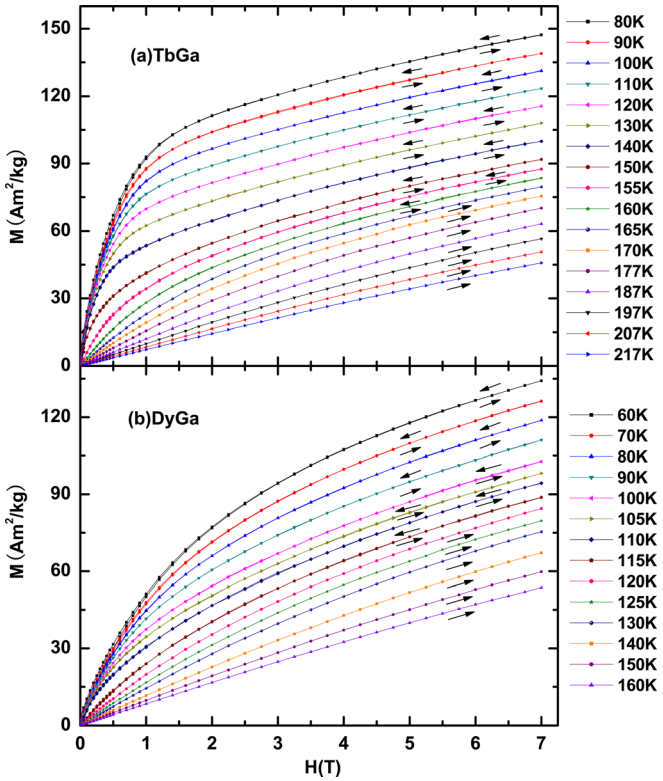

FIG. 3. (Color online) Isothermal magnetization curves for *R*Ga [*R* = Tb (a) and Dy (b)] in a wide temperature range under increasing and decreasing fields up to 7 T.

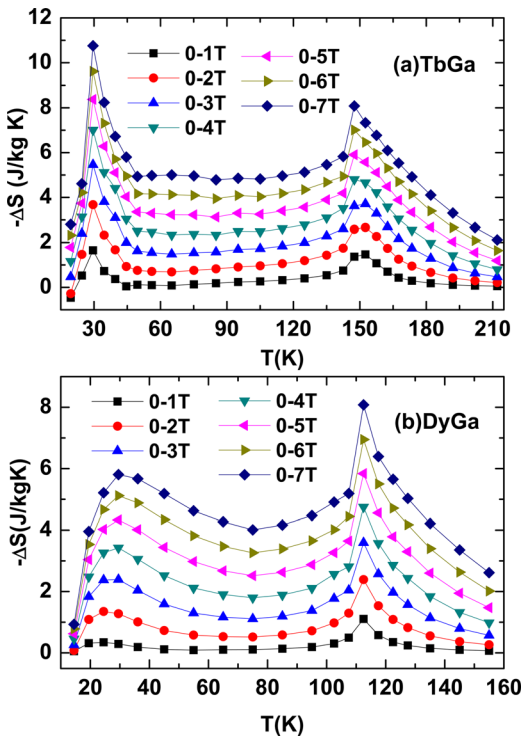

FIG. 4. (Color online) Magnetic entropy change ΔS_M as a function of temperature for *R*Ga [*R* = Tb (a) and Dy (b)] under field changes of 1, 2, 3, 4, 5, 6, and 7 T.

and 8.1 J/kg K at T_{SR} and T_C, respectively, for a field change of 0–7 T.

As another important criterion to evaluate the magnetocaloric properties of magnetic refrigerant materials, the RC of *R*Ga (*R* = Tb and Dy) compounds were estimated based on the ΔS_M–*T* curves by using the approach suggested by Gschneidner *et al.*[15] The RC value is defined as $RC = \int_{T1}^{T2} |\Delta SM| dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak, respectively. It is noteworthy that a broad distribution of the ΔS_M peak is observed. The value of RC for TbGa is found to be 900 J/kg with $T_1 = 22.7$ K (temperature of the cold end) and $T_2 = 183$ K (temperature of the hot end) for a field change of 0–7 T. For the DyGa compound, the RC value is 584.2 J/kg with $T_1 = 19.6$ K and $T_2 = 136.9$ K. The magnetic and magnetocaloric data for the *R*Ga compounds with *R* = Gd-Er are also listed in Table I. Although the TbGa compound has a moderate ΔS_M, its RC value is much larger than those of other magnetic refrigerant materials in a wide temperature range. The large RC of TbGa originates from the combined contribution from SR and FM–PM transitions, which enlarges the temperature span of the MCE. It is noted that the value of ΔS_M for *R*Ga increases monotonically with the decrease of T_C as the *R* atomic number increases. The results indicate that the working temperature and temperature span of the MCE could be tuned by the substitution between different *R* elements. Therefore, the *R*Ga compounds are expected to be good candidates for the magnetic refrigeration.

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