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Magnetic properties and magnetocaloric effects of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds

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We carefully studied the magnetic properties and magnetocaloric effect of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds. The $Gd_xEr_{1-x}Ga$ compounds undergo two magnetic transitions with temperature increasing: spin-reorientation or antiferromagnetic-to-ferromagnetic (FM) transition and FM-to-paramagnetic transition. As the content of Gd increases from 0 to 1, the transition temperature in low temperature region changes from 15 K to 66 K and the Curie temperature increases obviously from 30 K to 181.9 K. Although the maximum value of magnetic entropy change (ΔS_M) for $Gd_xEr_{1-x}Ga$ decreases with the increase of x, the refrigerant capacity (RC) improves remarkably compared with that of ErGa compound. Table-like ΔS_M curves are observed for the compounds with $x = 0.1$, 0.2, 0.3, and 0.4, which are very useful for real cooling applications. And $Gd_{0.2}Er_{0.8}Ga$ and $Gd_{0.3}Er_{0.7}Ga$ compounds show better magnetocaloric features than others in this series under considerations of both ΔS_M and RC. The results of this series of compounds show us a possible way to design and improve the magnetic refrigerant materials by making some substitutions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4854875]

I. INTRODUCTION

Magnetic refrigeration is a new technology for cooling or gas liquefaction, and it is based on magnetocaloric effect (MCE). Magnetic refrigeration has great advantage over conventional refrigeration, which is based on gas compression-expansion, for its high efficiency and environmental friendliness.[1–4] Many magnetic materials have been found to exhibit large MCEs near room temperature, such as $Gd_5Si_2Ge_2$, La(Fe, M)$_{13}$(M = Si, Al), $MnAs_{1-x}Sb_x$, $MnFeP_{1-x}As_x$, and NiMnGa.[5–9] The magnetic materials which show large MCEs in low and middle temperature ranges have also attracted much attention, for they can be used for gas liquefaction.[10–13] Especially, the materials with several magnetic transitions have shown excellent performances in low temperature zone in recent years.[12,13]

Binary alloys between rare earth and gallium show interesting magnetic properties in low and middle temperature ranges, and the spin-reorientation (SR) in RGa (R = Pr, Nd, Sm, Gd, Tb, Dy, Ho, and Er) compounds has been confirmed by Mossbauer measurements.[14] It was found that most of the RGa compounds undergo two transitions with temperature increasing: SR transition and ferromagnetic (FM) to paramagnetic (PM) transition. The MCEs have been studied for most of this series, and both SR transition and FM-to-PM transition contribute to MCE.[12,15,16] We make substitution of Gd for Er in the ErGa compound. The magnetic properties and MCEs of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds are studied in detail. And we expect to obtain the magnetic refrigerant materials with excellent performance of MCE by adjusting the content of Gd.

II. EXPERIMENTAL DETAILS

The polycrystalline $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds are prepared by arc melting Gd, Er, and Ga in argon atmosphere. And the purity of the starting elements is more than 99.9%. In order to make the ingots homogenous, they are turned over and melted several times. Then, the samples are wrapped in molybdenum foils, sealed in a high-vacuum quartz tube, and annealed at 800 °C for 7 days. After annealing, they are quenched into liquid Nitrogen. To confirm purity and crystal structure of the samples, we carry out powder X-ray diffraction (XRD) experiments with Cu $K\alpha$ radiation. The temperature dependence of magnetization and the field dependence of magnetization are measured by using Quantum-Designed Vibrating Sample Magnetometer (SQUID-VSM). Though the MCE of GdGa has been studied by Zhang *et al.*,[17] the magnetic property and MCE below 100 K were not given in that work. Here, we make samples and carry out measurements and calculations newly for GdGa compound. The data of ErGa are cited from Ref. 12 completely. The cited results have been marked out in Table I.

III. RESULTS AND DISCUSSION

The XRD patterns of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds are obtained. Almost all of the peaks can correspond to the Bragg positions of the orthorhombic CrB-type structure (space group *Cmcm*) except a few small peaks near

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TABLE I. The transition temperatures and magnetocaloric parameters of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds.

			0–2 T				0–5 T				
	T_{SR} or T_t K	T_C K	ΔS_{SR} J/kgK	ΔS_C J/kgK	T_{width} K	RC J/kg	ΔS_{SR} J/kgK	ΔS_C J/kgK	T_{width} K	RC J/kg	Refs.
x = 0	15[a]	30[a]	7.6[a]	10.9[a]	22.6[a]	166[a]	16.5[a]	21.3[a]	30.9[a]	492.6[a]	12
x = 0.1	20.6	49	4.6	4.8	48.6	184.7	10.4	11.4	56.2	535.2	Thiswork
x = 0.2	21.4	76.4	4.9	3.7	74.4	244.8	10.9	8.4	80.9	659.4	
x = 0.3	22.9	98.7	1.9	3.2	95.9	222.7	7.3	6.9	108.3	685.3	
x = 0.4	21	115.8	1.4	2.6	94.1	170.4	5.7	5.5	129.3	629.9	
x = 0.6	26.7	146.8	3.2	2.6	153.6	250.4	6.5	5.4	162.8	707.2	
x = 0.8	28.8	167.7	1.5	2.7	168.3	254	3.9	5.6	185.5	715.3	
x = 1	66	181.9	1.1	2.7	99.8	182.6	3.0	5.3	159.4	616.1	
x = 1[a]	100[a]	183[a]	1.1[a]	2.3[a]	86.5[a]	136.8[a]	3.3[a]	4.8[a]	117.4[a]	438.2[a]	17

[a]The results are cited or estimated from the relevant references.

34.3°and 36.7°. That is to say, the $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds are uniformly crystallized in the form of Cr-B type structure and are all approximately single phase.

The thermomagnetization curves of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds are measured. The temperature dependence of the magnetization is shown in Fig. 1 in an applied field of 0.01 T. Sharp decrease is observed on each *M–T* curve with temperature increasing, which is corresponding to FM-to-PM transition at T_C. Another anomaly is observed in low temperature range for all of the thermomagnetization curves. In compounds with a low content of Gd, such as $Gd_{0.1}Er_{0.9}Ga$ and $Gd_{0.2}Er_{0.8}Ga$, the magnetic properties are similar to ErGa compound. And when the content of Gd is large, such as $Gd_{0.6}Er_{0.4}Ga$ and $Gd_{0.8}Er_{0.2}Ga$, the magnetic properties show similar feature to GdGa compound. According to previous reports,[12,14,17] the transition in low temperature range is *SR* transition for most $Gd_xEr_{1-x}Ga$ compounds and we marked that transition temperature as T_{SR}. For $Gd_{0.3}Er_{0.7}Ga$ and $Gd_{0.4}Er_{0.6}Ga$ compounds, the transition in low temperature range is an antiferromagnetic (AFM) to FM transition, as discussion in Fig. 2. And we mark that transition temperature as T_t in this case. In fact, the *SR* transition of ErGa and GdGa has been studied carefully by Mössbauer spectrum.[14] The magnetic moments point to different directions at different temperatures, which are the result of competition between exchange interaction and crystal field interaction.

Isothermal magnetization curves up to 5 T at 5 K for $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds and isothermal magnetization curves for $Gd_{0.3}Er_{0.7}Ga$ in whole temperature range are shown in Fig. 2. The magnetization goes up and comes to its saturation value quickly with magnetic field increasing for $Gd_xEr_{1-x}Ga$ (x = 0, 0.1, 0.2, 0.6, 0.8, and 1.0) compounds, which is the typical characteristic of the FM ground state. For $Gd_{0.3}Er_{0.7}Ga$ and $Gd_{0.4}Er_{0.6}Ga$ compounds, it is possible that the magnetic exchange interaction is not large enough to counterbalance the crystal field interaction below T_t, and Er and Gd magnetic moment each points to the favorite directions on their own. That is to say, the AFM ground state exists below T_t in $Gd_{0.3}Er_{0.7}Ga$ and $Gd_{0.4}Er_{0.6}Ga$ compounds. As a result, the magnetization at 5 K increases linearly with increasing magnetic field in low field ranges (see Fig. 2). Besides, it is found that the magnetization exhibits a sharp increase when the applied field exceeds a certain value,

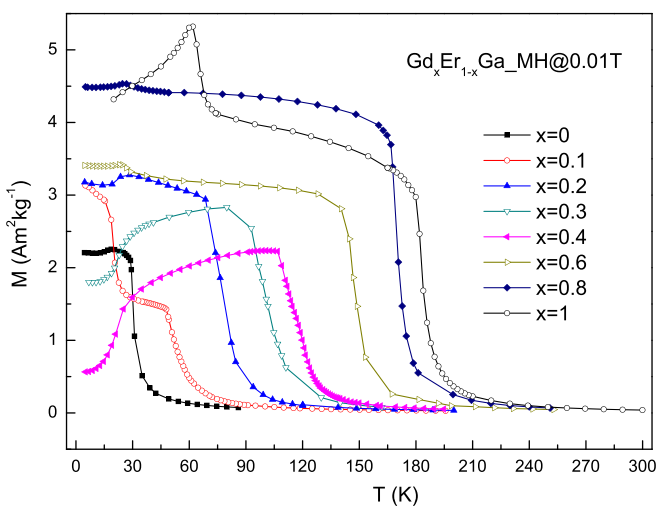

FIG. 1. Temperature dependences of the magnetization with the applied field of 0.01 T for $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds.

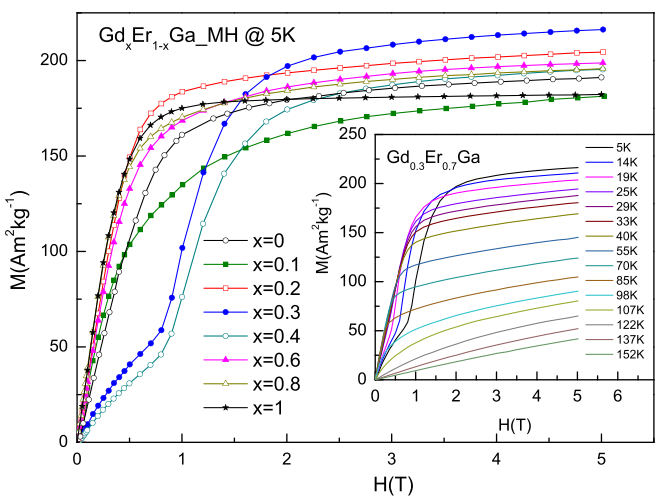

FIG. 2. Isothermal magnetization curves of $Gd_xEr_{1-x}Ga$ ($0 \le x \le 1$) compounds up to 5 T at 5 K. The inset is the isothermal magnetization curves of $Gd_{0.3}Er_{0.7}Ga$ compound.

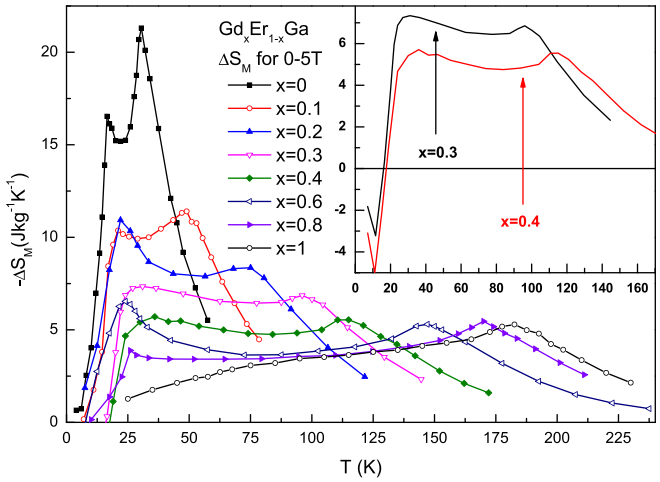

FIG. 3. Magnetic entropy change ΔS_M as a function of temperature for $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds under field change of 0–5 T. The under part below $\Delta S_M = 0$ has been cut off. The inset is the whole and enlarged view of $Gd_{0.3}Er_{0.7}Ga$ and $Gd_{0.4}Er_{0.6}Ga$.

indicating that the field-induced metamagnetic transition from AFM to FM state occurs.

The transition temperatures of $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds, which are determined from derivative of M-T curves, are all listed in Table I. Certain results of GdGa compound, we obtained newly are different from those in Ref. 17 and we will adopt the new results in the following discussion. From Table I, we can see that T_C increases from 30 K to 181.9 K as the content of Gd increases from 0 to 1. The reason is that the average value of spin quantum number (S) increases with the content of Gd, and T_C increases with S increasing. The T_{SR} and T_t are listed in the same column, and results show that the change of T_{SR} or T_t is not as large as T_C. The lowest and highest values of T_{SR} are 15 K and 66 K, respectively, for the $Gd_xEr_{1-x}Ga$ compounds.

The ΔS_M of the $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds is calculated from *M-H* data according to Maxwell relation: $\Delta S_M = \int_0^H (\partial M/\partial T)_H dH$. Figure 3 shows the ΔS_M curves of all the $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds for a field change of 0–5 T. It indicates that both *SR* transition and PM-to-FM transition contribute to MCE. As the content of Gd increases, the position of the peak near T_{SR} or T_t changes not much, but the peak near T_C moves to higher temperature obviously. As the content of Gd increases, the value of $|\Delta S_M|$ near T_{SR} or T_t decreases from 16.5 J kg^{-1}K^{-1} to 3.0 J kg^{-1}K^{-1} and the value of $|\Delta S_M|$ near T_C decreases from 21.3 J kg^{-1}K^{-1} to 5.3 J kg^{-1}K^{-1}. For $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds, the value of J decreases and the value of T_C increases with the content of Gd increasing, so the $|\Delta S_M|$ near T_C shows downtrend according to Oesterreicher and Parker.[18] For $Gd_{0.3}Er_{0.7}Ga$ and $Gd_{0.4}Er_{0.6}Ga$, the value of ΔS_M is positive below T_t (Inset of Fig. 3), and it is due to the disordered magnetic sublattice antiparallel to the applied magnetic field.[19,20]

The RC is also an important parameter to evaluate magnetic refrigerant materials. And the value of RC can be calculated by the following formula:[21] $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the two ends of the half-maximum width of the ΔS_M curves. All the magnetic parameters and MCE results of $Gd_xEr_{1-x}Ga$ $(0 \le x \le 1)$ compounds are all listed in Table I. We can see that though the maximum value of $|\Delta S_M|$ decreases with the content of Gd increasing, the value of RC is greatly improved compared with ErGa. Also we find that the T_{width} greatly extends as the content of Gd increases. And the extending of T_{width} plays an important role in improving the value of RC according to the calculation method. The exact value of RC fluctuates with the content of Gd increasing, but $Gd_{0.2}Er_{0.8}Ga$ and $Gd_{0.3}Er_{0.7}Ga$ compounds show better performances than others in this series by considering both ΔS_M and RC. Another important result is that table-like ΔS_M curves are observed for certain compounds, such as those in the case of $x = 0.1$, 0.2, 0.3, and 0.4. This kind of ΔS_M curves has been observed several times[22,23] and such a feature of ΔS_M curves is very useful for practical applications of refrigeration.

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