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Low-field magnetocaloric effect in $(Gd_{1-x}Dy_x)_3Al_2$ alloys

Zhida Han[a,b,c,*], Ping Zhang[a], Bin Qian[a,b], Xuefan Jiang[a,b], Dunhui Wang[c], Jie Chen[a], Jinfu Feng[a,b], Youwei Du[c]

[a] Department of Physics, Changshu Institute of Technology, Changshu 215500, People's Republic of China
[b] Jiangsu Laboratory of Advanced Functional Materials, Changshu Institute of Technology, Changshu 215500, People's Republic of China
[c] Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

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ABSTRACT

The effects of Dy substitution on the magnetic properties and magnetocaloric effect of $(Gd_{1-x}Dy_x)_3Al_2$ (x = 0–0.5) alloys have been investigated by X-ray diffraction and magnetization measurements. It was found that Dy substitution decreased the cell volume as well as the magnetic transition temperature. The maximum magnetic entropy change for a magnetic field change from 0 to 1 T almost keep constant with values of −2.2 to −2.5 J/kg K, while the refrigerant capacity (RC) decreases with Dy addition. The adjustable Curie temperature, moderate magnetic entropy change, and large RC make these alloys potential candidates as magnetic refrigerant.

1. Introduction

Magnetic refrigeration is based on the magnetocaloric effect (MCE), which is an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change of a magnetic material upon application of a magnetic field [1]. Since magnetic refrigeration is expected to be a future technology because of its energy efficiency and environment safety, the exploration of materials with large MCE is strongly desired. Generally, due to high magnetic moments, heavy rare earth elements and their compounds are considered as the best candidate materials for finding a large MCE. The highest MCE around room temperature involving a second-order transition (SOT) known so far is produced by the rare earth metal Gd [2]. In systems with first-order transition (FOT), such as $Gd_5Si_2Ge_2$ [3], giant peak values of ΔS_M originating from the abrupt change of magnetization have been observed. However, in FOT systems, thermal hysteresis, magnetic hysteresis, and narrow working temperature span inhibit their practical application. Up to now, Gd is the most popular magnetic refrigerant for the room temperature magnetic refrigerator [4].

Considering the various requirements for practical application, it is necessary to search for some magnetic refrigerants possessing qualities comparable to (or higher than) Gd but having different Curie temperature (T_C). Some Gd-based materials with different transition temperature, such as Gd-based solid solutions [1,5,6], $GdAl_2$ [7], and Gd-based amorphous alloys [8–10] have been studied. Among them, Gd_3Al_2 compound with Zr_3Al_2 tetragonal structure orders ferrimagnetically at T_C = 281 K in zero magnetic field, while in magnetic fields larger than 3 T a metamagnetic transition occurs between 40 and 50 K [11,12]. As a result, a singe peak in $\Delta S_M(T)$ near T_C is observed for low magnetic field change, and at high field variation $\Delta S_M(T)$ exhibits a structure with two peaks [12]. In this paper, we studied the influence of Dy substitution for Gd on the magnetic property and the low-field magnetocaloric effect in the $(Gd_{1-x}Dy_x)_3Al_2$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) alloys.

2. Experimental

$(Gd_{1-x}Dy_x)_3Al_2$ (x = 0, 0.1, 0.2, 0.3, 0.4, 0.5) alloys were prepared by arc melting the raw materials in argon atmosphere repeatedly. The ingots were annealed at 1173 K in an evacuated quartz tube for three days followed by water quenching. The structure of the samples was determined by X-ray diffraction (XRD). Their magnetic properties were measured by a vibrating sample magnetometer (7307, Lakeshore) under a magnetic field up to 1 T.

* Corresponding author at: Department of Physics, Changshu Institute of Technology, Changshu 215500, People's Republic of China. Tel.: +86 512 528991253; fax: +86 25 52252553.
E-mail addresses: zhida.han@gmail.com, zhidahan@hotmail.com (Z. D. Han).

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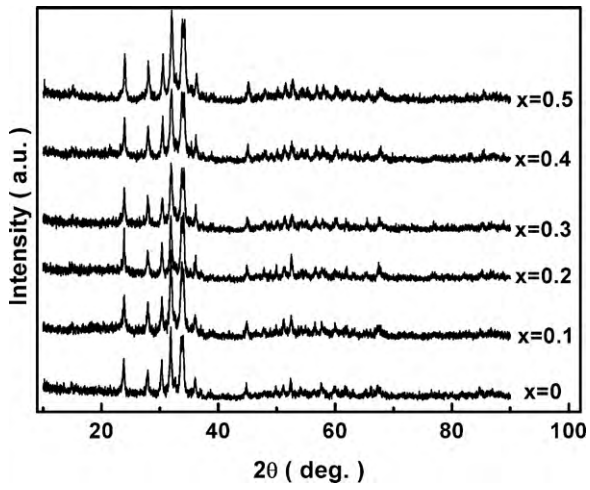

Fig. 1. The XRD patterns of $(Gd_{1-x}Dy_x)_3Al_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys at room temperature.

3. Results and discussion

The powder XRD patterns taken at room temperature are shown in Fig. 1, which indicates that all samples crystallize in Zr_3Al_2-type structure with space group $P4_2nm$. The lattice constants a and c are calculated from the XRD data by a software named checkcell. Fig. 2 shows the lattice constants (a and c) and cell volume (v) as functions of Dy concentration. Due to the smaller radius of Dy than Gd, a, c and v decrease with increasing Dy concentration.

Fig. 3 shows the temperature dependence of magnetization for $(Gd_{1-x}Dy_x)_3Al_2$ in a magnetic field of 0.1 T. The values of T_C, which are defined as the temperature where |dM/dT| is maximum, are listed in Table 1. From the plot (Fig. 3, inset), we can observe that the values of T_C decrease almost linearly with increasing Dy content. T_C is expected to further decrease by increase of Dy concentration up to 76 K in Dy_3Al_2 [13]. In addition, the magnetization reduction with Dy addition in 0.1 T field could be attributed to the increase of anisotropy. Since Gd ion is an S-state ion and has negligible field anisotropy in Gd-rich alloys, the substitution of Gd by Dy should result in the increase of anisotropy.

Isothermal magnetization $M(H)$ curves for these alloys were measured around T_C. Fig. 4(a) shows $M(H)$ curves for Gd_3Al_2 alloy. It has been realized that hysteresis in magnetization as a function of temperature and magnetic field would lower the efficiency

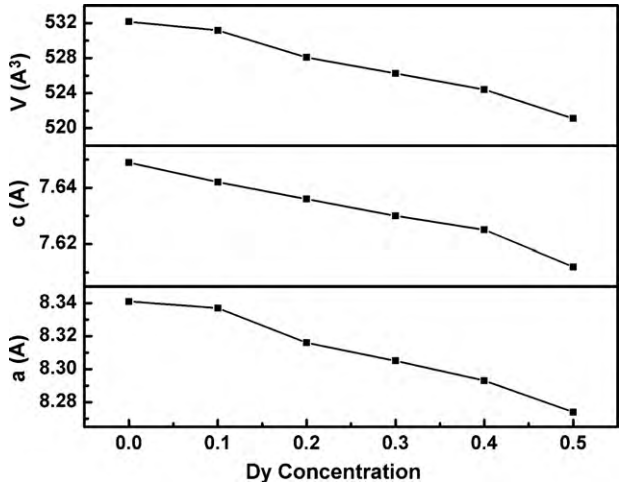

Fig. 2. The lattice constants and cell volume as functions of Dy concentrantion.

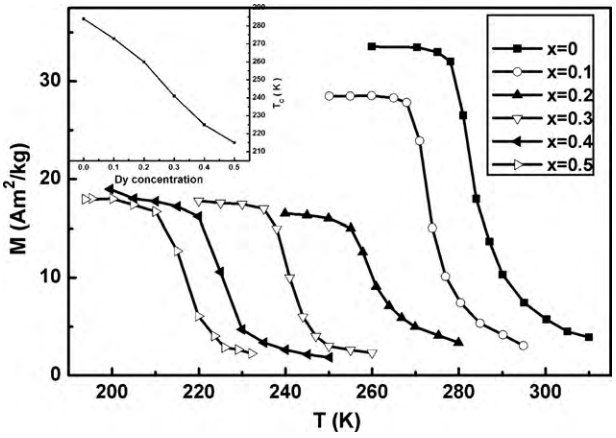

Fig. 3. The temperature dependence of magnetization for $(Gd_{1-x}Dy_x)_3Al_2$ in the magnetic field of 0.1 T.

of the magnetic refrigeration. Many investigations in FOT systems have focused on depression of hysteresis without much loss of MCE. On the other hand, the SOT systems have the inherent advantage of small hysteresis near T_C. In $(Gd_{1-x}Dy_x)_3Al_2$ alloys, no thermal hysteresis were observed between heating and cooling process. To investigate the magnetic hysteresis, we select three typical $M(H)$ curves of Gd_3Al_2, as shown in Fig. 4(b). Obviously each isotherm shows a reversible behavior between the field increase and decrease. It is known that Arrott plot is a useful tool to identify the metamagnetic behavior [14]. As shown in Fig. 4(c), neither inflection nor a negative slope in the Arrott plot can be observed around T_C, confirming the second-order nature of the transition.

The ΔS_M as a function of temperature for a magnetic field change from 0 to 1 T for $(Gd_{1-x}Dy_x)_3Al_2$ alloys was calculated from isothermal magnetization curves using Maxwell relation

$$\Delta S_M(T, H_0) = \int_0^{H_0} \left[\frac{\partial M(T,H)}{\partial T}\right]_H dH \quad (1)$$

For magnetization measurements carried out at constant temperature and discrete H intervals, it can be approximated by

$$\Delta S_M(T, H_0) \approx \frac{1}{\Delta T}\left[\int_0^{H_0} M(T+\Delta T, H)dH - \int_0^{H_0} M(T,H)dH\right] \quad (2)$$

The temperature dependence of ΔS_M for a magnetic field change from 0 to 1 T for $(Gd_{1-x}Dy_x)_3Al_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys are shown in Fig. 5. All samples show negative peaks around T_C. The maximum values of ΔS_M are −2.3, −2.5, −2.2, −2.4, −2.3, and −2.3 J/kg K, for alloys with $x = 0$, 1, 2, 3, 4, 5, and 6, respectively. These values are comparable to some SOT systems, such as $Gd_{1-x}In_x$ (2.1–2.8 J/kg K for $\Delta H = 1$ T) [6], FeCoCrZrB (1–1.4 J/kg K for $\Delta H = 1$ T) [15], but are much smaller than some FOT systems, such as $GdSi_2Ge_2$ (19 J/kg K for $\Delta H = 5$ T) [3], $MnAs_{1-x}Sb_x$ (30–40 J/kg K for $\Delta H = 5$ T) [16], $Ni_{43}Mn_{46}Sn_{11}$ (10.4 J/kg K for $\Delta H = 1$ T) [17].

In addition to the peak value of ΔS_M, the refrigerant capacity is another important parameter to evaluate the magnetic refrigerant. The refrigerant capacity, which is defined as:

$$q = \int_{T_{cold}}^{T_{hot}} \Delta S(T, H_0)_{H_0} dT \quad (3)$$

(here T_{cold} and T_{hot} are the temperature of the cold and hot sinks, respectively) is a measure of how much heat can be transferred between the cold and hot sinks in one ideal refrigeration cycle. We calculated refrigerant capacity (q) of $(Gd_{1-x}Dy_x)_3Al_2$ alloys in the temperature range between 20 K below and above their T_C. The results are listed in Table 1. It can be seen that RC decreases with the increase of Dy concentration. These values are comparable to those

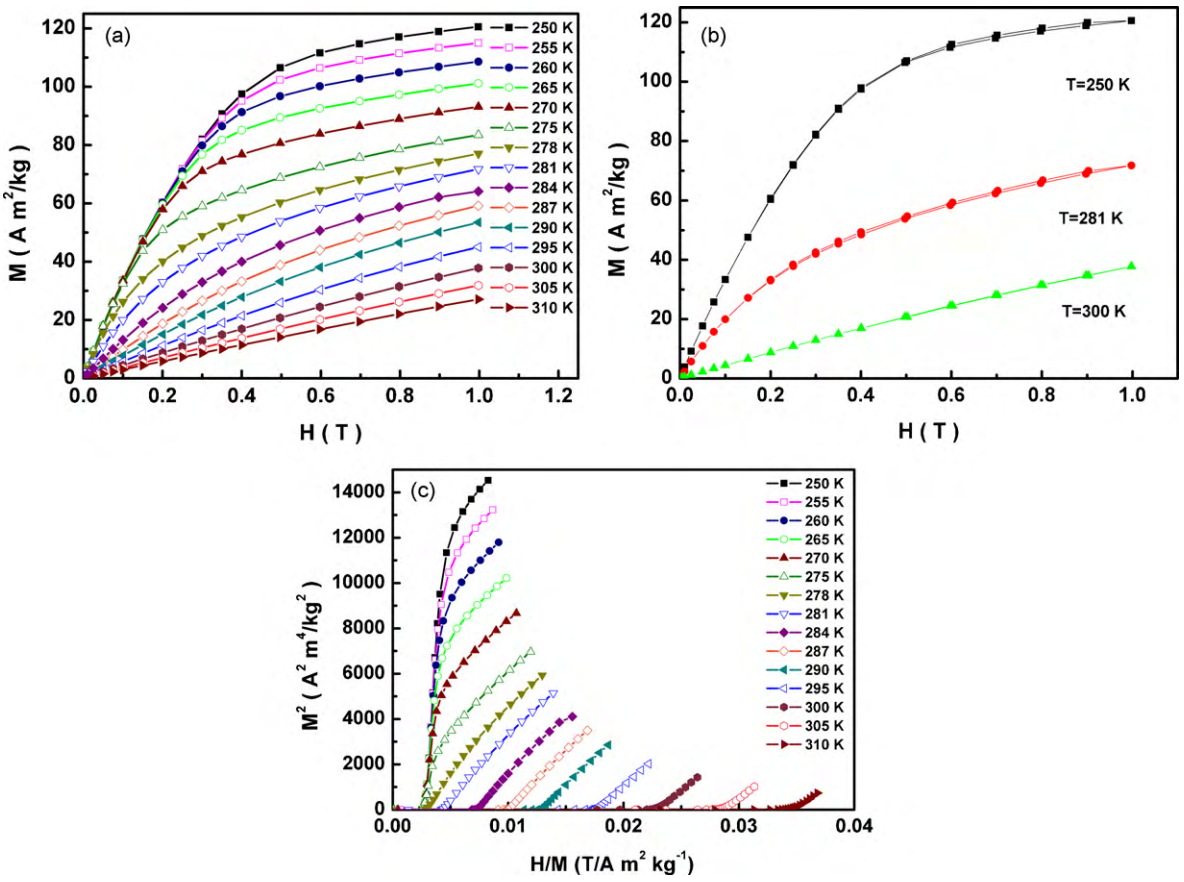

Fig. 4. (a) The isothermal magnetization curves near the transition temperature for Gd_3Al_2 alloy. (b) The isothermal magnetization curves on field increase and decrease for Gd_3Al_2 alloy at three typical temperatures. (c) Arrott plots of Gd_3Al_2.

of some magnetic refrigerants with similar working temperature, such as Gd (63.4 J/kg in the field of 1 T) [6], FeCoCrZrB (32–54 J/kg in the field of 1 T) [15], $Ni_{43}Mn_{46}Sn_{11}$ (50 J/kg in the field of 1 T, calculated from the $\Delta S_M - T$ data of Ref. [17]).

The large RC in $(Gd_{1-x}Dy_x)_3Al_2$ should be attributed to the large value of magnetization change (ΔM) across the magnetic transition. From Eq. (1) and Eq. (2), the RC in the field of H_0 between T_{cold} and T_{hot} can be expressed as:

$$q = \int_0^{H_0} [M(H, T_{hot}) - M(H, T_{cold})]dH \quad (4)$$

It can be seen that RC is mainly determined by ΔM across the transition instead of $\partial M/\partial T$. This is different from the value of ΔS_M, which is strongly dependent on $\partial M/\partial T$ and the type of phase transition. Furthermore, hysteresis loss in FOT systems should be subtracted from RC, which lowers the effective RC in FOT systems [18]. Based on above discussion, large RC can be obtained in SOT systems with large ΔM.

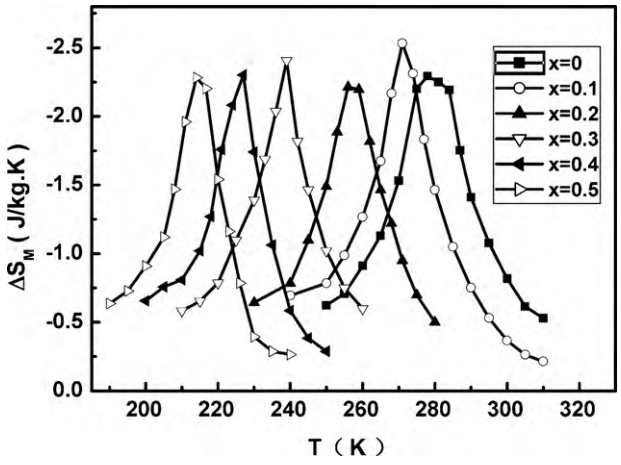

Fig. 5. The temperature dependence of ΔS_M for a magnetic field change from 0 to 1 T for $(Gd_{1-x}Dy_x)_3Al_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.

Table 1
The values of lattice constants (a and c), cell volume (v), Curie temperature (T_C), magnetic entropy change (ΔS_M) in the magnetic field of 1 T, and refrigerant capacity (RC) for $(Gd_{1-x}Dy_x)_3Al_2$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) alloys.

x	a (Å)	c (Å)	v (Å)	T_C (K)	ΔS_M (J/kg K)	RC (J/kg)
0	8.341	7.649	532.2	284	−2.3	63.1
0.1	8.337	7.642	531.2	273	−2.5	59.5
0.2	8.316	7.636	528.1	260	−2.2	53.5
0.3	8.305	7.630	526.3	241	−2.4	53.1
0.4	8.293	7.625	524.4	225	−2.3	48.7
0.5	8.274	7.612	521.1	215	−2.3	47.9

4. Conclusion

In summary, we have investigated the effects of substitution of Gd by Dy on the magnetic and MCE properties of $(Gd_{1-x}Dy_x)_3Al_2$ alloys. It was found that the Dy substitution decreases lattice constants and magnetic transition temperature. Moderate values of ΔS_M (−2.2 to −2.5 J/kg K) as well as large RC were obtained in the temperature range between 215 and 284 K. The adjustable T_C and the favorable properties of MCE make $(Gd_{1-x}Dy_x)_3Al_2$ alloys potential candidates for magnetic refrigeration.

Acknowledgements

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