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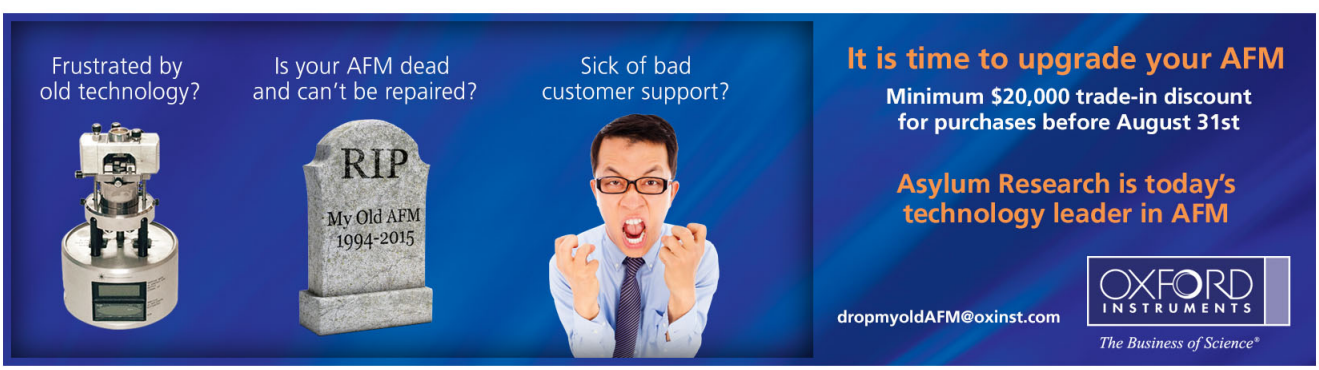

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Enhancement of magnetocaloric effect in the Gd_2Al phase by Co alloying

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To understand the effect of Co doping on the magnetic entropy changes in Gd_2Al phase, a series of Gd_2AlCo_x alloys with $0 \le x \le 0.6$ were synthesized by arc-melting and the crystal structure was analyzed by XRD. The magnetic properties were investigated, and the entropy changes were calculated for a magnetic field change of 50 kOe. All the as-cast alloys doped with Co exhibited greater magnetic entropy changes than the original binary Gd_2Al phase. The main reasons attributed to this are the increase of ferromagnetic interaction indicated by the disappearance of cusp and sharp drop in magnetization and the reduction of the critical field required to trigger the field-induced transition below 50 K in Gd_2Al phase after Co alloying. © *2014 AIP Publishing LLC*.
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I. INTRODUCTION

Many rare earth (R)-based intermetallic compounds have attracted significant interest over the past two decades due to their large magnetocaloric effect (MCE) from ultra-low temperature to room temperature.[1–7] The ternary Gd-Co-Al system has been intensively studied due to the interesting magnetic properties and potential applications as magnetic refrigerants working near liquid nitrogen temperature in both glassy and crystalline states.[8,9] Gd-Co-Al system exhibits table-like MCE suitable for the ideal Ericsson cycle which has been obtained in $Gd_{53}Co_{19}Al_{28}$ and $Gd_{52.5}Co_{16}Al_{31}$ compositions.[10] In Ref. 10, we reported that the alloys' magnetic entropy change ($-\Delta S_M$) curves fit the experimental data very well above 65 K. However, the calculated $-\Delta S_M$ values are always lower than the experimental data when the temperature is lower than 65 K. It was speculated that it may be due to dissolution of Co in the Gd_2Al phase or by the magnetic interaction among the component phases.

The magnetic properties and MCE of R_2Al (R = Nd, Gd, Tb, Dy, Ho, Er) compounds have been widely studied, especially for the Gd_2Al phase.[11,12] However, the authors are not aware of any reports on the effect of alloying on the structure and magnetic properties of these alloys. In this work, our aim is to clarify the reason accounting for the presence of table-like MCE that is reported previously by studying the effect of alloying Co in the Gd_2Al phase. Gd_2AlCo_x (x = 0, 0.05, 0.1, 0.2, 0.4, and 0.6) alloys are synthesized, and their structure and the magnetic properties are reported. The results show that the increase of ferromagnetic interaction and the reduction of the critical field of metamagnetic transition by Co alloying result in the improvement of the MCE of Gd_2Al phase.

II. EXPERIMENTAL

The Gd-Co-Al ternary alloy was prepared from 99.9% Gd, 99.9% Al, and 99.99% Co by arc-melting in a Ti-gettered argon atmosphere in an arc furnace (purity is presented by weight percent). The arc-melted ingot was flipped over and remelted four times to ensure homogeneity. Weight loss was negligible during arc melting. The phase purity of the alloys was verified by powder x-ray diffraction (XRD) using a PANatytical X'pert Pro diffractometer with Co $K\alpha$ radiation. The generator voltage and tube current were 45 kV and 40 mA, respectively. Continuous scanning with step size of 0.008356° and count time of 200.66 s/step were employed in order to obtain data with good signal-to-noise ratio. The magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer, MPMS XL-7 from Quantum Design, Inc.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the as-cast alloys with compositions of Gd_2AlCo_x (x = 0.05, 0.1, 0.2, 0.4, and 0.6) for phase identification. It can be seen that within the resolution of XRD, three samples, $Gd_2AlCo_{0.05}$, $Gd_2AlCo_{0.1}$, and $Gd_2AlCo_{0.2}$, have the Gd_2Al main phase and Gd_3Al_2 minor phase. Gd_2Al and Gd_3Al_2 crystallize in the Co_2Si-type structure with the space group of pnma and Gd_3Al_2-type phase with the space group of $P4_2nm$, respectively. Some peaks of Gd_3Al_2 minor phase separated from Gd_2Al phase within the range of 2θ less than 50 degrees are indicated by downward arrows. According to the Gd-Al binary diagram,[13] Gd_2Al can be formed by a peritectic reaction of the liquid and the Gd_3Al_2 phase. So, the presence of some minor Gd_3Al_2 in the Gd_2Al alloy is reasonable. With the increase in Co content, some Bragg peaks indicated by blue asterisks within the ranges of 2θ less than 50° belonging to $Gd_{57.5}Co_{20}Al_{22.5}$ phase are present in the XRD patterns of $Gd_2AlCo_{0.4}$ and $Gd_2AlCo_{0.6}$. The $Gd_{57.5}Co_{20}Al_{22.5}$ phase crystallizes

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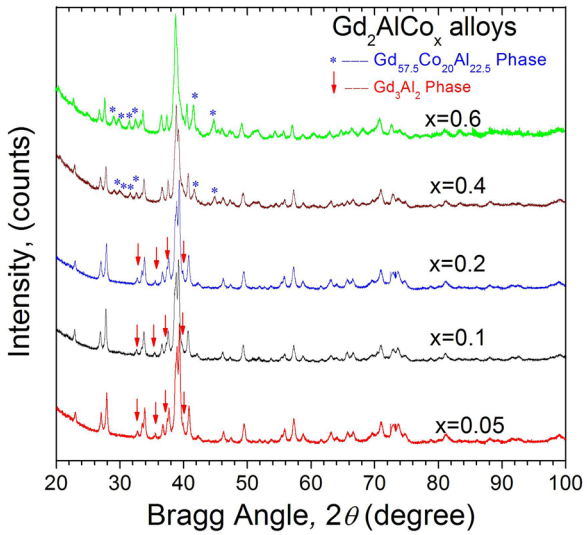

FIG. 1. XRD patterns of the Gd_2AlCo_x (x = 0.05, 0.1, 0.2, 0.4, and 0.6) alloys.

in the orthorhombic crystal system with the space group of Pbam.[14]

Fig. 2 shows the temperature (T) dependence of magnetization (M) of the Gd_2AlCo_x (x = 0.05, 0.1, 0.2, 0.4, and 0.6) alloys in the presence of 0.1 kOe magnetic field. It is worth noting that all the Co doped samples in this figure were measured under cooling. To illustrate the influence of Co on the magnetic properties of Gd_2Al, the M-T cooling curve of a binary Gd_2Al alloy with applied field of 1 kOe is also shown in the inset. XRD measurement on Gd_2Al (not shown) suggests that it adopts single phase structure within the resolution. For the Gd_2Al alloy, magnetization has a cusp at around 48 K, which is related to a paramagnetic to antiferromagnetic transition. These results are consistent with Li *et al.*[15] Furthermore, Gd_2Al sample undergoes a ferromagnetic transition at 270 K. This higher temperature ferromagnetic transition in Gd_2Al phase was reported in previous works.[11–15] Gd_3Al_2 phase undergoes a ferromagnetic

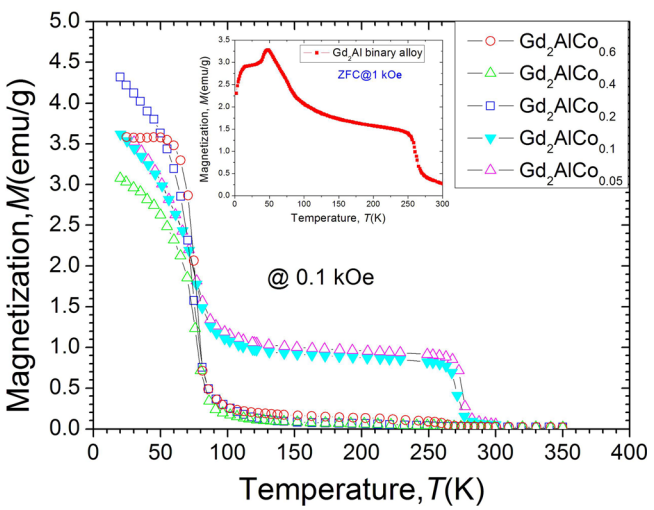

FIG. 2. Temperature (T) dependence of magnetization (M) of the Gd_2AlCo_x (x = 0.05, 0.1, 0.2, 0.4, and 0.6) alloys. The inset shows M-T plot of a binary Gd_2Al alloy.

transition near 270 K.[16] The ferromagnetic transition in the Gd_2Al sample can be attributed to the transition of minor Gd_3Al_2 phase, whose quantity is so small that it can not be detected by XRD. Magnetic measurement is more sensitive for the ferromagnetic phase. So, the minor Gd_3Al_2 phase can be detected in the M-T plot.

For all the Co doped alloys, the magnetization decreases with increasing temperature below 80 K. No cusp in the magnetization can be found in these alloys. For the $Gd_2AlCo_{0.6}$ alloy, a characteristic of the saturation in magnetization can be observed when temperature is lower than 50 K. In addition, a sharp drop in magnetization for all compositions can be found near 70 K. The sharp drop in magnetization near 70 K is the transition between paramagnetic to ferromagnetic phase. Disappearance of features of cusp and the presence of sharp drop in magnetization suggest that ferromagnetic interaction increases in the Co doped samples with increasing Co content. In addition, for the $Gd_2AlCo_{0.05}$ and $Gd_2AlCo_{0.1}$ alloys, a ferromagnetic transition can also be observed near 270 K, which comes from the Gd_3Al_2 phase as shown in the inset of Fig. 2. Further increasing the Co content, the ferromagnetic transition becomes weak in $Gd_2AlCo_{0.2}$, $Gd_2AlCo_{0.4}$, and $Gd_2AlCo_{0.6}$ samples near 270 K. Therefore, Fig. 2 illustrates that Co doping in Gd_2Al phase acts to weaken the ferromagnetic interaction of Gd_3Al_2 phase whose transition temperature is near 270 K and strengthen the ferromagnetic interaction when the temperature is lower than 70 K.

The magnetization isotherms of Gd_2Al, $Gd_2AlCo_{0.1}$, $Gd_2AlCo_{0.2}$, and $Gd_2AlCo_{0.6}$ alloys at different temperatures with applied magnetic field between 0 and 50 kOe are shown in Fig. 3. It can be seen that all the four samples undergo a metamagnetic transition induced by external magnetic field when temperature is lower than 40 K. This field-induced transition in Gd_2Al phase was first reported by Oesterreicher.[17] For Gd_2Al, the magnetization increases linearly with increasing field above 60 K. For $Gd_2AlCo_{0.1}$, the magnetization process below 10 kOe shows features of initial saturation for all measured temperatures that are from the ferromagnetic secondary phases of Gd_3Al_2 whose transition temperature is about 270 K. However, for $Gd_2AlCo_{0.2}$ and $Gd_2AlCo_{0.6}$, the magnetization increases linearly with the increase in field when temperatures are higher than 90 K, which confirms the weakening of higher temperature ferromagnetic interaction in the samples; the magnetization process below 10 kOe at temperatures lower than 80 K also shows the features of initial saturation, which can be ascribed to the ferromagnetic interaction induced by Co doping.

The critical field, H_T, which induces the metamagnetic transition at a given temperature, is defined as the magnetic field at the maxima of $\frac{dM}{dH}$ vs. H.[18] All the H_T data of the Gd_2AlCo_x samples derived from the magnetization process at 40 K are depicted in Table I. It can be seen that H_T for all the Co alloyed samples is lower than that of the un-doped Gd_2Al.

The magnetic entropy changes ($-\Delta S_M$) with an applied field change from 0 to 50 kOe calculated by using the M-H data in Fig. 3 are shown in Fig. 4. The maximum of $-\Delta S_M$

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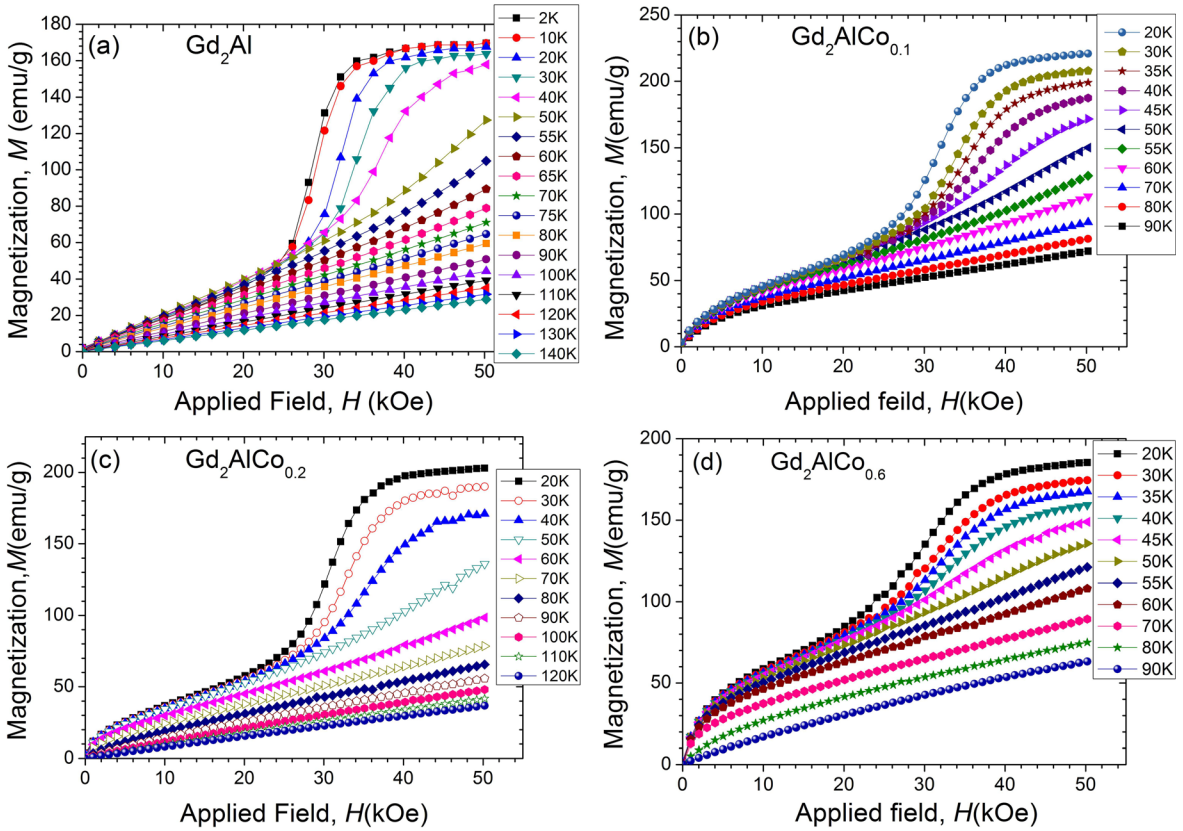

FIG. 3. Isothermal magnetization measured at different temperatures under applied field from 0 to 50 kOe. (a) Gd_2Al; (b) $Gd_2AlCo_{0.1}$; (c) $Gd_2AlCo_{0.2}$; (d) $Gd_2AlCo_{0.6}$.

$(-\Delta S_{Mmax})$ for all samples are depicted in Table I. It is worth noting that the isothermal magnetization and demagnetization of the Gd_2Al alloy were measured and the results (not shown) suggested that when the temperature is below 20 K, the hysteresis for the Gd_2Al metamagnetic transition is small but detectable. However, when the temperature is above 20 K, the hysteresis is so small that it can be neglected. So, the effect of hysteresis of metamagnetism on the net magnetic entropy changes is ignored because many of the magnetization isotherms are measured above 20 K (see Fig. 3). It can be seen from Table I that all the $-\Delta S_{Mmax}$ of the samples with Co doping are greater than that of Gd_2Al alloy. For $Gd_2AlCo_{0.2}$ alloy, the maximum of magnetic entropy changes is 7.9 J/kgK near 47.5 K, which is about 20% larger than that of binary Gd_2Al, 6.5 J/kgK. The reason can be attributed to the decreasing of critical magnetic field H_T after alloying. The decreasing of H_T can enhance the area between two magnetization curves, which favors the improvement of magnetic entropy changes. Furthermore, for the Co doped alloys, $-\Delta S_{Mmax}$ increases and reaches the maximum of 7.9 J/kgK for $Gd_2AlCo_{0.2}$ and then decreases. From the structure analysis and magnetic measurements, it is known that there is minor Gd_3Al_2 phase or $Gd_{57.5}Co_{20}Al_{22.5}$ phase in the Gd_2AlCo_x samples. The maximum magnetic entropy changes of Gd_3Al_2 and $Gd_{57.5}Co_{20}Al_{22.5}$ under 0 to 50 kOe field is only 3.5 J/kgK (Ref. 16) and 5.5 J/kgK,[14] respectively. So, their presence in the samples has no contribution to the increase of magnetic entropy changes. The further

TABLE I. Structure within the XRD resolution, Critical field (H_T) at 40 K, maximum magnetic entropy change ($-\Delta S_{Mmax}$) for $\Delta H = 50$ kOe of Gd_2AlCo_x (x = 0, 0.05, 0.1, 0.2, 0.4, and 0.6) alloys.

Alloys	Structure	H_T (kOe)	$-\Delta S_{Mmax}$ (J/kgK)
Gd_2Al	Gd_2Al	38.2	6.5
$Gd_2AlCo_{0.05}$	$Gd_2Al + Gd_3Al_2$	35.0	7.5
$Gd_2AlCo_{0.1}$	$Gd_2Al + Gd_3Al_2$	36.1	7.8
$Gd_2AlCo_{0.2}$	$Gd_2Al + Gd_3Al_2$	35.1	7.9
$Gd_2AlCo_{0.4}$	$Gd_2Al + Gd_{57.5}Co_{20}Al_{22.5}$	35.0	7.5
$Gd_2AlCo_{0.6}$	$Gd_2Al + Gd_{57.5}Co_{20}Al_{22.5}$	32.5	7.4

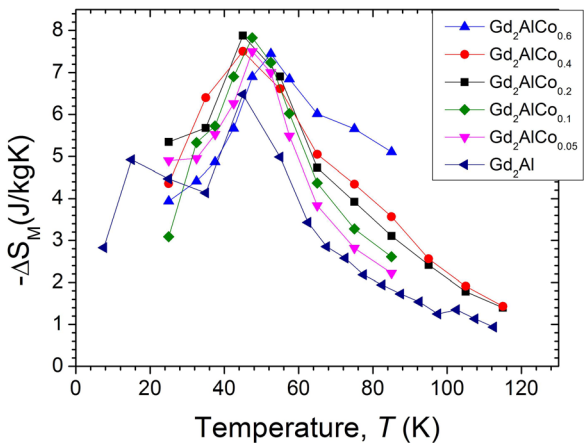

FIG. 4. The magnetic entropy changes under 0–50 kOe magnetic field changes for Gd_2AlCo_x (x = 0, 0.05, 0.1, 0.2, 0.4, and 0.6) alloys calculated from magnetization isotherms.

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decreasing of $-\Delta S_{Mmax}$ when Co composition is increased is due to the presence of $Gd_{57.5}Co_{20}Al_{22.5}$ secondary impurity (see Fig. 1).

In our previous work,[10] $Gd_{52.5}Co_{16.5}Al_{31}$ and $Gd_{53}Co_{19}Al_{28}$ alloys were found to exhibit a table-like platform in their magnetic entropy changes with the magnitude of about 7.0 J/kgK in the region from 47.5 K to 77.5 K. However, near 47 K, the magnetic entropy changes for the component phases Gd_2Al, Gd_2Co_2Al, and Gd $Co_{0.74}Al_{1.26}$ are about 6.5, 5.4, and 5.9 J/kgK, respectively,[10] which are lower than 7.0 J/kgK. It suggests that materials which consist of the above three phases cannot have the magnetic entropy change larger than 7.0 J/kgK. Transition temperature of Gd_2Al phase occurs near 50 K. So, the reason for the presence of the table-like magnetic entropy changes over 7.0 J/kgK was assumed to be attributed to the improvement of the MCE in Gd_2Al phase due to the dissolution of Co.[10] In this work, all the ternary Gd_2AlCo_x alloys with x less than 0.6 possess greater magnetic entropy changes near their individual magnetic transitions than that of the binary Gd_2Al alloy. These results confirm that the presence of table-like magnetic entropy changes near 50 K can be attributed to the contribution from the Gd_2Al phase with Co alloying.

IV. CONCLUSIONS

In summary, Co alloying can increase the ferromagnetic interaction near the antiferromagnetic transition about 48 K and reduce the critical field of the field-induced transition in the Gd_2Al phase. It is responsible for the enhancement of magnetic entropy change from 6.5 to 7.9 J/kgK near 48 K for Gd_2Al phase with $\Delta H = 50$ kOe. This improvement in magnetic entropy change can be said to account for the presence of "table-like" MCE in the $Gd_{52.5}Co_{16.5}Al_{31}$ and $Gd_{53}Co_{19}Al_{28}$ composites with magnitude of 7.0 J/kgK below 65 K.

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