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Large magnetocaloric effect with a wide working temperature span in the R_2CoGa_3 (R = Gd, Dy, and Ho) compounds

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We investigate magnetic properties and magnetocaloric effects of R_2CoGa_3 (R = Gd, Dy, and Ho) compounds. It is found that all the compounds are ferromagnetic with the Curie temperatures of $T_C = 50$, 17, and 10 K for R = Gd, Dy, and Ho, respectively. The R_2CoGa_3 have large magnetic entropy change (ΔS) that arise from the second-order ferromagnetic-to-paramagnetic phase transition. The maximum values of ΔS are found to be -12.6, -10.8, and -13.8 J/kg K with corresponding refrigerant capacity values of 382, 252, and 287 J/kg for a magnetic field change of 0–50 kOe, respectively. The large ΔS values with little or no hysteresis losses as well as wide working temperature spans imply that the R_2CoGa_3 compounds may serve as promising candidates for magnetic refrigeration. *© 2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4884233]

I. INTRODUCTION

The rare-earth transition metal intermetallic compounds have attracted much attention due to their interesting magnetic properties and practical applications in a wide spectrum of industries. Magnetocaloric effect (MCE) technology is well known for its practical applications to obtain ultra-low temperature and potential application at room temperature. When a magnetic field is applied to a magnetic material, a change in the material's polarization will be induced. The consequent changes in the entropy and temperature of the material are named as MCE.[1–9] Nowadays, the MCE technology has become a hot point in current research due to its merits of high energy-efficiency and eco-friendly characters,[1–4] especially since the discovery of $Gd_5Si_2Ge_2$.[5] Subsequently, $La(Fe,Si)_{13}$,[6] $MnAs_{1-x}Sb_x$,[7] $MnFeP_{1-x}As_x$,[8] and Mn-based heusler alloys[9] have sprung up one after another. However, these materials with first-order phase transition have narrow working temperature spans. On the contrary, materials with second-order phase transition or multiple transitions are reported to have wide working temperature spans, in which ErGa,[10] Eu_4PdMg,[11] and some composite materials[12,13] are extensively studied in recent years. In this paper, we focus on the magnetic and magnetocaloric properties of R_2CoGa_3 compounds. We find these materials have large magnetic entropy changes (ΔS), little or no hysteresis losses, and wide working temperature spans as well. These advantages make R_2CoGa_3 compounds potential magnetic refrigerants.

II. EXPERIMENTAL DETAILS

The R_2CoGa_3 ingots were prepared with stoichiometric mixture of high purity starting materials (Gd, Dy, Ho, Co, and Ga) by arc melting method under the protection of high-purity argon atmosphere. The purities of all the constituent elements were better than 99.9 wt. %. The 3 wt. % excess of the R element was added to make up the weight loss due to the evaporation of the R element in the melting process. The samples were turned over and re-melted several times during preparation to ensure each of them a better homogeneity. The as-cast ingots were sealed in a quartz tube filled with high-purity argon atmosphere and then annealed at 1173 K as reported in Ref. 14, for two weeks which was one week longer than that in the previous report, expecting each of the obtained samples to have a better homogeneity. Commercial D2 powder X-ray diffractometer from Bruker, Inc., by using Cu Kα radiation was used to analyze the phase compositions of the samples. The DC magnetization measurements were performed by a commercial superconducting quantum interference device magnetometer (SQUID, Quantum Design).

III. RESULTS AND DISCUSSION

Standard θ–2θ powder X-ray diffraction (XRD) patterns for R_2CoGa_3 samples are measured and the results are shown

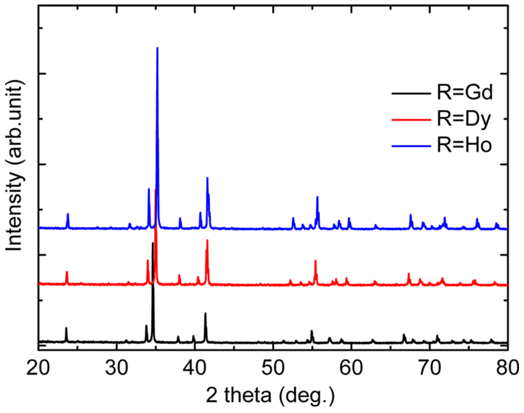

FIG. 1. XRD patterns for R_2CoGa_3 compounds.

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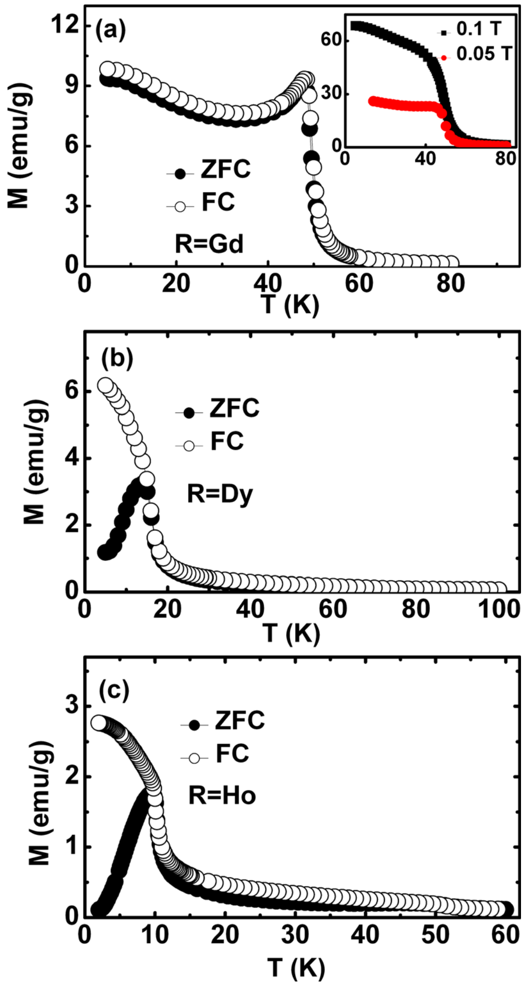

FIG. 2. Temperature dependences of magnetization measured in ZFC and FC models for the R_2CoGa_3 compounds: (a) $R = Gd$, (b) $R = Dy$, (c) $R = Ho$.

in Fig. 1. One could easily find the similarity among the patterns. The refinement indicates that all samples crystallized into a clean hexagonal R_2RhSi_3-type structure as mentioned in the previous reports.[14,15] Fig. 2 shows the temperature dependences of magnetization (M-T) curves collected in zero-field cooling (ZFC) and field-cooling (FC) modes. Figs. 2(a)–2(c) show the M-T curves for samples with $R = Gd$, Dy, and Ho, respectively. All the FC curves are typical for ferromagnetic materials. The Curie temperatures (T_C) determined by the minimum of dM/dT are 50, 17, and 10 K, respectively, coinciding with the results published before.[14,15] The consistence of the transition temperature between the previous results and ours confirms the purities of the samples in our case, which are in accordance with the XRD results. On the other hand, the M-T curves in Fig. 2(a) are substantially different from those of other two samples by the appearance of peaks and disappearance of irreversibility between the ZFC curve and the FC curve. In previous studies, Routsi *et al.*[14] ascribed the irreversibility in $R = Dy$ and Ho samples to the magnetic anisotropy, with consideration of the isotropic behavior of Gd^{3+} ion and the unique M-T curves for Gd_2CoGa_3 in the three samples. The irreversibility was finally ascribed to the intrinsic domain wall pinning effect by the A. C. susceptibility measurements.[14] But shown in Ref. 14 are only the M-T curves measured at 1 kOe for Gd_2CoGa_3, in which no peaks are found. In our case, the peaks appear in

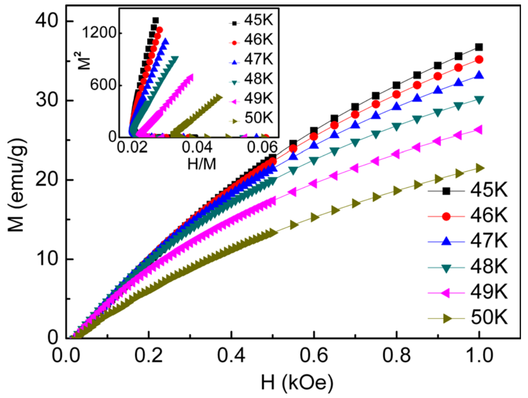

FIG. 3. Initial magnetization curves up to magnetic field of 1 kOe with the inset showing the corresponding Arrott-plots for Gd_2CoGa_3 compound.

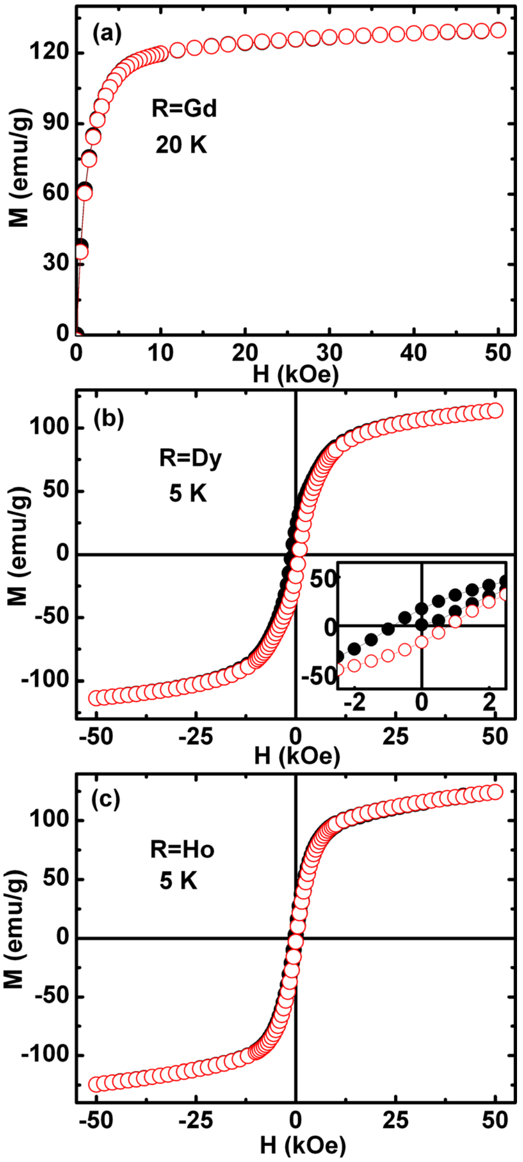

FIG. 4. Curves of magnetization versus magnetic field at typical temperatures for (a) $R = Gd$, (b) $R = Dy$, (c) $R = Ho$, respectively. The inset of Fig. 2(b) shows the coercive field of Dy_2CoGa_3.

the *M*-*T* curves measured at 0.1 kOe but these peaks disappear in the *M*-*T* curves measured under the fields of 0.5 kOe and 1 kOe as shown in the inset of Fig. 2(a), which coincides with the results in Ref. 14. In general, the peaks existing in the *M*-*T* curves are ascribed to the antiferromagnetic (AFM) ordering or the Hopkinson effect. Taking into consideration of the disappearance of the peaks in the *M*-*T* curves under a low field of 0.5 kOe, the signs of AFM ordering, such as the slope change in the *M*-*H* curves and negative slope in the Arrott plot, should be detected below 0.5 kOe if they are really existent. To identify whether the AFM ordering exist in Gd_2CoGa_3, the initial magnetization curves up to 1 kOe in the vicinity of T_C are measured, and the results are presented in Fig. 3 where the inset shows the corresponding Arrott plots. No signs of metamagnetic transition related to AFM ordering are found. So the peaks in the *M*-*T* curves might be attributed to the Hopkinson effect.

Figs. 4(a)–4(c) show the curves of magnetization versus magnetic field at typical temperature. No hysteresis effect is found in samples with $R=$ Gd and Ho as shown in Figs. 4(a) and 4(c), which accord well with the results in Ref. 14. However, a coercive field of 1 kOe and hysteresis effect are detected in sample with $R=$ Dy, which are clearly seen in the inset of Fig. 4(b). The hysteresis effect can induce the loss of the refrigeration capacity and is harmful to the practical application. The influence of the hysteresis effect on the MCE characteristics of the samples will be discussed later.

Figs. 5(a)–5(f) show the isothermals and the corresponding Arrott-plots (M^2 vs H/M) for R_2CoGa_3 compounds measured at various temperatures in the vicinity of their respective transition temperatures. The curvature behavior below the T_C indicates the ordering state in the sample. It should be noted that the magnetizations are not saturated even under the high field of 50 kOe except that of Gd_2CoGa_3. The unsaturated magnetizations are ubiquitous for samples with anisotropy. In our case, taking into account of the unique behavior Gd_2CoGa_3 observed in Fig. 2(a) and the hexagonal structure of the samples, the unsaturated magnetizations in samples with $R=$ Dy and Ho could be attributed to the magnetocrystalline anisotropy. Meanwhile, the positive slope in the Arrott plot confirms the occurrence of second-order magnetic phase transition for all the three samples according to the Banerjee's criterion.[16]

In an ideal refrigeration cycle for practical application, the working material must absorb entropy from the load that needs to be cooled, while it is in thermal contact with the load (isothermal entropy change ΔS). On the other hand, the heat per kilogram could take in is used for quantifying the refrigerant capacity (RC). Thus, for characterizing the MCE properties of material, the magnitudes of the Δ*S* and RC are two key parameters that are generally used. In our case, the Δ*S* is calculated by Maxwell's relationship $\Delta S=\int_0^H(\partial M/\partial T)_H dH$, and RC is determined by integrating the area below the Δ*S*-*T* curve, with the temperatures at half maximum of Δ*S* used as boundaries. The variation of Δ*S* with temperature for different magnetic field changes is shown in Fig. 6. The maximum values of Δ*S* are found to be −12.6, −10.8, and −13.8 J/kg K with RC values of 382, 252, and 287 J/kg for $R=$ Gd, Dy, and Ho under a field change of 0–50 kOe, respectively. It is evident that the peak values of Δ*S* are comparable to those of some of potential magnetic refrigerant materials exemplified by $PrNi$,[17] $NdCo_2B_2$,[18] $DyNi_2$,[19] Er_3Ni_2,[20] $Tb_6Co_2Si_3$,[21]

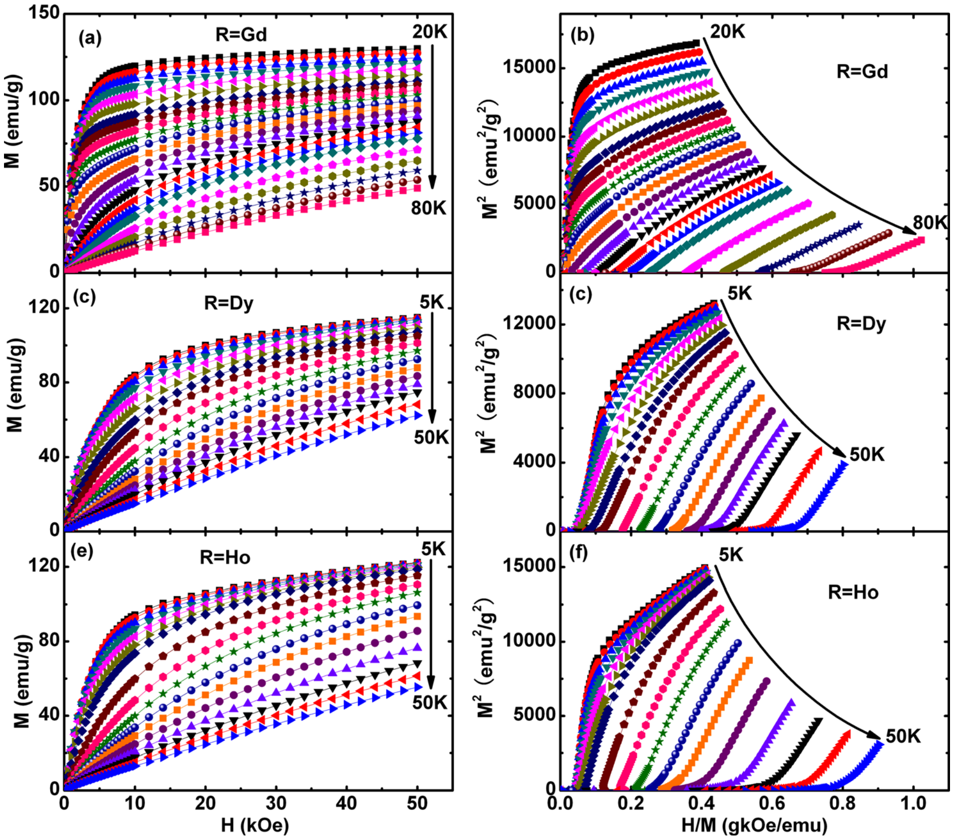

FIG. 5. Magnetic isothermals and Arrott-plots of the R_2CoGa_3 compounds measured during field increasing mode.

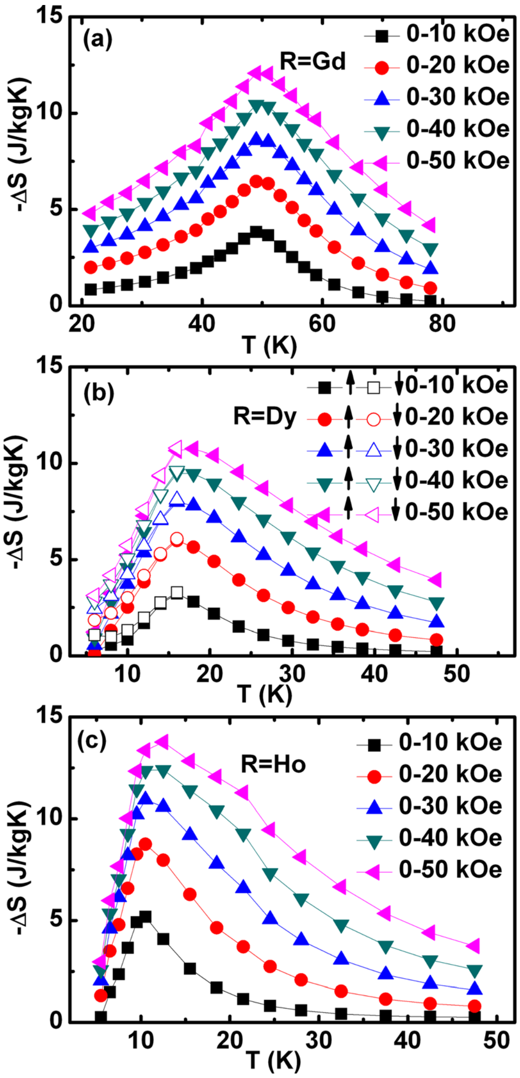

FIG. 6. Temperature dependences of magnetic entropy change for the R_2CoGa_3 compounds for different magnetic field changes.

TABLE I. Transition temperatures and values of ΔS and RC under a field change of 0–50 kOe for different giant magnetocaloric materials including R_2CoGa_3 compounds.

Sample	Magnetic ground state	T_C (K)	$-\Delta S$ (J/kg K) (0–50 kOe)	Working span	RC (J/kg) (0–50 kOe)
Gd_2CoGa_3	FM	50	12.6	27–70 K	382
Dy_2CoGa_3	FM	17	10.8	10–40 K	252
Ho_2CoGa_3	FM	10	13.8	7–32 K	287
$EuFe_2As_2$ (Ref. 24)	AFM	19	14.6	…	336
$DyNi_2$ (Ref. 25)	FM	21.5	13.5	…	209
$ErMn_2Si_2$ (Ref. 26)	FM	4.5	25.2	…	365
ErRuSi (Ref. 27)	FM	8	21.2	…	416
TmCuAl (Ref. 28)	FM	4	24.3	…	373
HoPdIn (Ref. 29)	FM	23	14.6	…	496
Eu_4PdMg (Ref. 11)	FM	150	5.5	…	605
CeSi (Ref. 30)	AFM	6	13.7	…	110
GdCoAl (Ref. 31)			7	47.5–77.5	…

Gd_2Co_2Ge,[22] etc. Though the maximum values of ΔS are not as large as those of the materials with giant ΔS such as EuSe[23] and so on, large RC could be obtained due to the wide working temperature span. On the other hand, the hysteresis loss mentioned above is shown as the discrepancy between the ΔS measured in a field increasing and decreasing modes as exhibited in Fig. 6(b). The small discrepancy can induce little harm to the RC. For all the R_2CoGa_3 compounds, we list their values of T_C, ΔS together with working temperature span and RC in Table I. For a comparison with the other MCE materials reported recently, these materials are also plotted in Table I. The large ΔS values with little or no hysteresis losses as well as wide working temperature spans make R_2CoGa_3 compounds attractive candidates serving as magnetic refrigerants.

IV. CONCLUSIONS

In this paper, we investigate the magnetic and magnetocaloric properties of the R_2CoGa_3 ($R = $ Gd, Dy, and Ho) compounds. These compounds each are crystallized into an R_2RhSi_3-type structure, and their T_C are determined to be 50, 17, and 10 K, respectively. Second-order phase transition generates large ΔS, and the maximum values of ΔS are -12.6, -10.8, and -13.8 J/kg K with RC values of 382, 252, and 287 J/kg for $R = $ Gd, Dy, and Ho under a field change of 0–50 kOe, respectively. The large RC arises from the wide working temperature span. The excellent performances make R_2CoGa_3 compounds attractive candidates for magnetic refrigeration.

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