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Giant magnetocaloric effect in Ho$_{12}$Co$_7$ compound

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Magnetic properties and magnetocaloric effects of Ho$_{12}$Co$_7$ compound are investigated by magnetization and heat capacity measurement. The Ho$_{12}$Co$_7$ compound undergoes antiferromagnetic (AFM)-AFM transition at $T_1 = 9$ K, AFM-ferromagnetic (FM) transition at $T_2 = 17$ K, and FM-paramagnetic transition at $T_C = 30$ K, with temperature increasing. There are two peaks on the magnetic entropy change ($\Delta S_M$) versus temperature curves and the maximal value of $-\Delta S_M$ is found to be 19.2 J/kg K with the refrigerant capacity value of 554.4 J/kg under a field change from 0 to 5 T. The shape of the $\Delta S_M$-$T$ curves obtained from heat capacity measurement is in accordance with that from magnetization measurement. The excellent magnetocaloric performance indicates the applicability of Ho$_{12}$Co$_7$ as an appropriate candidate for magnetic refrigerant in low temperature ranges. © 2013 American Institute of Physics. [http://dx.doi.org/10.1063/1.4788706]

Magnetic refrigeration based on magnetocaloric effect (MCE) is a kind of technology used for cooling and it has several advantages such as environment friendliness and high efficiency compared with gas compression-expansion refrigeration.¹⁻⁴ Many magnetic materials with first-order phase transition have been found to exhibit large MCEs, such as Gd$_2$Si$_2$Ge$_2$, La(Fe,Si)$_3$, MnAs$_1$–xSb$_x$, MnFeP$_{1-x}$As$_x$, and NiMnGa.⁵⁻¹⁰ Much attention has also been paid to the rare earth ($R$)-based intermetallic compounds with a giant MCE and low-temperature phase transition for the purpose of magnetic refrigerant application.¹¹⁻¹³ Especially, the materials with two or more transitions exhibit considerable value of refrigerant capacity (RC), because all the transitions contribute to the magnetic entropy change ($\Delta S_M$).¹⁴⁻¹⁷

It was reported that there are eight intermetallic compounds existing in the Co–Ho system, and Ho$_{12}$Co$_7$ is among them.¹⁸ Although R$_{12}$Co$_7$ ($R$ = Gd, Tb, Dy, Ho, Er) compounds have identical monoclinic structures, they exhibit different magnetic properties.¹⁹ Both of Gd$_{12}$Co$_7$ and Tb$_{12}$Co$_7$ compounds undergo one ferromagnetic (FM)-paramagnetic (PM) transition and the maximal values of magnetic entropy change ($-\Delta S_M$) are observed to be 4.6 and 3.08 J/kg K for a field change of 0–2 T, respectively.¹⁹⁻²¹ However, a spin reorientation behavior, with no contribution to MCE, is observed below Curie temperature ($T_C$) for the Gd$_{12}$Co$_7$ compound.²²

In the present paper, the magnetic properties and MCEs of Ho$_{12}$Co$_7$ compound are investigated by magnetization and heat capacity measurement. Two peaks close to each other are observed on the curves of $\Delta S_M$ versus temperature. The maximal $-\Delta S_M$ and RC values are found to be 9.2 J/kg K and 206.2 J/kg for a field change of 0–2 T. And as for a field change of 0–5 T, the maximal $-\Delta S_M$ and RC values are found to be 19.2 J/kg K and 554.4 J/kg, respectively.

Polycrystalline Ho$_{12}$Co$_7$ was prepared by arc melting starting materials in a high-purity argon atmosphere. The purities of starting materials were better than 99.9%. The sample was turned over and remelted several times to ensure its homogeneity. Ingot obtained by arc melting was subsequently wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1023 K for 7 days, and then quenched to room temperature. The crystal structure of the samples was characterized using x-ray powder diffraction (XRD) using Cu K$_\alpha$ radiation. Magnetizations were measured as functions of both temperature and magnetic field by using a vibrating sample magnetometer with quantum design (SQUID-VSM). Heat capacity measurements were carried out by employing Physical Properties Measurement System (PPMS).

The temperature ($T$) dependence of magnetization ($M$) was measured in both zero field- cooled (ZFC) and field-cooled (FC) processes in order to determine the thermal hysteresis and the magnetic transition temperature. Figure 2(a) shows the thermomagnetic $M$-$T$ curves of Ho$_{12}$Co$_7$ measured under an external magnetic field of 0.01 T. According to the $M$ versus $T$ characteristics, it is suggested that the Ho$_{12}$Co$_7$ compound undergoes three magnetic transitions in sequence with decreasing temperature. The transition at the highest temperature corresponds to a change from PM-to-FM state at $T_C = 30$ K. The rest two phase transitions are FM-antiferromagnetic (AFM) transition at $T_2 = 17$ K and AFM-AFM transition at $T_1 = 9$ K, which will be confirmed by the isothermal magnetization curves.

The $M$-$T$ curves under different external magnetic field are shown in Fig. 2(b). One can find that $T_1$ increases

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monotonically with magnetic field increasing from 0.01 to 0.3 T. However, almost no change is observed for $T_2$ and $T_C$ with magnetic field change. It indicates that a field-induced metamagnetic transition from AFM to FM state occurs below $T_2$, and $T_1$ is pushed towards higher temperature with the applied magnetic field increasing. Similar phenomenon has been observed in PrGa compound.23

The temperature dependences of the heat capacity in different magnetic fields are shown in Fig. 2(c). The peaks around 30 K, which are obvious for $H = 0$ T and 0.5 T, are corresponding to $T_C$. It is found that there are obvious differences of heat capacity below $T_2$ for different magnetic field. The reason why the applied magnetic field affects heat capacity so greatly is that a magnetic transition from the weak AFM ground state to the FM state occurs. There is no obvious peak related to AFM-AFM transition temperature for zero-field heat capacity curve, but a clear peak around 13 K appears on the heat capacity curve for an applied field of 0.5 T. As is illustrated in the $M$-$T$ curves, the peak is corresponding to AFM-AFM transition and it has been pushed by the applied field from $T_1$ (= 9 K) to higher temperature (~13 K). In the temperature range between $T_2$ and $T_C$, the differences of heat capacity for different magnetic field are not as clear as those in lower temperature range. That is because Ho$_{12}$Co$_7$ compound is FM state in this range, and the influence of applied field on heat capacity is small. The heat capacity data demonstrate that the statement of magnetic transition on the basis of $M$-$T$ curves is reasonable.

It is also found from Fig. 2(a) that the heating and cooling $M$-$T$ curves show a reversible behavior near $T_C$ and it is accompanied without thermal hysteresis, indicating a nature of the second-order phase transition. The inset of Fig. 2(a) shows the reciprocal magnetic susceptibility $\chi$ versus temperature. It is found that the magnetic susceptibility of the Ho$_{12}$Co$_7$ compound can be fitted to the Curie–Weiss law above ~40 K. The effective magnetic moment $\mu_{\text{eff}}$ per Ho ion for Ho$_{12}$Co$_7$, obtained from the linear temperature dependence of $\chi^{-1}$, is 11.3 $\mu_B$, which is close to the value expected for a free Ho$^{3+}$ ion ($\mu_{\text{eff}} = 10.6 \mu_B$). Considering

![Graph](image_url)
that the sample is almost a single phase and free from impurities, the small difference may result from a small moment on Co as observed in Tb₈Co₁₆₇Si₃₂₄.

Figure 3(a) shows the isothermal magnetization curves of Ho₁₂Co₇ in a temperature range of 3–50 K under the magnetic fields up to 7 T. The isothermal magnetization curves in some selected temperature ranges at low magnetic fields are shown in Figs. 3(b)–3(d), respectively. One can find that the isothermal magnetization curves between T₂ = 17 K and Tₐ = 30 K show FM characters (Fig. 3(d)). The magnetization remains a linear dependence of the magnetic field at low field range below T₂ = 17 K (Figs. 3(b) and 3(c)), indicating the existence of AFM ground state. Now we can confirm the transition around T₂ is corresponding to FM-AFM transition, and the one around T₁ is corresponding to AFM-AFM transition. The magnetization curves deviate from the linear relationship, when the applied field exceeds a certain value, showing a field-induced metamagnetic transition from AFM to FM state. The critical field determined from the maximum of dM/dH for Ho₁₂Co₇ is found to be 0.12 T at 6 K and 0.28 T at 16 K. The result indicates that the Ho₁₂Co₇ compound is a weak antiferromagnet below T₂, and a small magnetic field can destroy the AFM structure. One can also find from Fig. 3(a) that the isothermal magnetization curves obtained well above Tₐ show strong curvatures at low fields. Similar results have been observed in some other intermetallic compounds. It may result from the existence of short-range ferromagnetic correlations in the PM state. The Arrott plot of Ho₁₂Co₇ is shown in Fig. 4. In the Landau free energy theory, an S-shaped curve is expected when there is a
negative contribution of some higher order term, such as a negative $M^2$-term, in the Landau free energy expansion. And the appearance of S-shaped Arrott plots can be used to affirm the occurrence of metamagnetism transition. The S-shaped Arrott plots below $T_C$ confirm the existence of the field-induced first-order AFM-FM transition. The positive slope of the Arrott plot above $T_C$ indicates a characteristic of a second-order PM-FM transition.

The $\Delta S_M$ of Ho$_{12}$Co$_7$ was calculated from isothermal magnetization data by using the Maxwell relation $\Delta S_M = \int \frac{\partial M}{\partial T}dT \mu dH$ and from heat capacity data through the expression $\Delta S_M = \int \left[ C(T,H) - C(T,0) \right]dT$ as well. Figure 5(a) shows the $\Delta S_M$ as a function of temperature for different magnetic field changes. The curves obtained using magnetization data are not in good agreement with the corresponding curves obtained using heat capacity. Considering that the actual combined relative error in the $\Delta S_M$ calculated from magnetization data can reach $\sim 20\%$ and that from heat capacity data can be $\sim 4\%$, the deviations between the value of $\Delta S_M$ calculated from the two methods are in the error range with the maximal error being $\sim 17\%$ and $\sim 11\%$, for the field change of 0-2 T and 0-5 T, respectively. Although there are differences between the curves obtained from the two methods, the shape of the curves matches well with each other. It is clear that there are two peaks on the $\Delta S_M$-T curves, which indicates that both AFM-FM and PM-FM transitions contribute to MCE. Figure 5(b) shows that when the field change is small, for example, 0-0.2 T, the value of $\Delta S_M$ is positive in certain temperature range, and as the field change increasing, the value of $\Delta S_M$ changes into negative. That results from the occurrence of metamagnetism transition, because the positive or negative value of $\Delta S_M$ is related to AFM or FM state. Besides, with the field change increasing, the first peak corresponding to AFM-FM transition moves towards higher temperatures, while the second peak related to PM-FM transition almost centers at $\sim 30$ K, which is in accordance with the results of $M$-T and $Cp$-$T$ measurement.

When the field change is high enough, for example, 0-2 T and 0-5 T, the first peak is so close to the second one that they almost change into a larger peak. On the basis of magnetization measurement, the maximal value of $-\Delta S_M$ for Ho$_{12}$Co$_7$ is found to be 19.2 J/kg K around $T_C$ for a field change 0-5 T. Compared with the refrigerant materials in a similar temperature range, the value of Ho$_{12}$Co$_7$ compound is smaller than that of ErGa (21.3 J/kg K at 30 K), DyCuAl (20.4 J/kg K at 28 K), and ErCo$_2$ (33 J/kg K at 36 K) compounds, but it is larger than that of DyNiAl (19 J/kg K at 32 K), TbCoC$_2$ (15.3 J/kg K at 30 K), and GdNi$_5$ (11.5 J/kg K at 32 K). One can also see from Fig. 5(a) that both the peak value and peak width of $\Delta S_M$-$T$ curves depend on the magnetic field change. When the field change is 0-0.5 T, the maximum value of the two peaks is small and they are far apart from each other. However, when the applied field increases to 2 T and 5 T, the two peaks become one larger peak. That is to say, both of the maximal value and the width of the peak have an obvious increase. The peak shape is very helpful to improvement of the value of RC in Ho$_{12}$Co$_7$ compound. The RC value of Ho$_{12}$Co$_7$ compound was also calculated by using the approach suggested by Gschneidner et al. The RC is defined as $RC = \int dT \Delta S_M$, where $T_1$ and $T_2$ are the temperatures corresponding to both sides of the half-maximum value of $\Delta S_M$ peak, respectively. The RC value of Ho$_{12}$Co$_7$ is estimated to be 206.2 J/kg with $T_1 = 10.4$ K (temperature of the cold reservoir) and $T_2 = 39.8$ K (temperature of the hot reservoir) for a field changing from 0 to 2 T. And the RC value is estimated to be 554.9 J/kg with $T_1 = 12.3$ K and $T_2 = 49.8$ K for a field changing from 0 to 5 T. As a result, Ho$_{12}$Co$_7$ compound has an outstanding refrigerant capacity among the magneto-caloric materials in a similar temperature range, such as ErGa (RC = 494 J/kg with $T_1 = 14.3$ K and $T_2 = 45.2$ K), DyCuAl (RC = 427 J/kg with $T_1 = 17$ K and $T_2 = 45$ K), ErCo$_2$ (RC = 273 J/kg with $T_1 = 33$ K and $T_2 = 43$ K), DyNiAl (RC = 492 J/kg with $T_1 = 19$ K and $T_2 = 53$ K), TbCoC$_2$ (RC = 354 J/kg with $T_1 = 23.5$ K and $T_2 = 50$ K), and GdNi$_5$ (RC = 198 J/kg with $T_1 = 21$ K and $T_2 = 45$ K), although ErGa, DyCuAl, and ErCo$_2$ exhibit larger $\Delta S_M$ values. Here, the RC values of some compounds are estimated from the temperature dependence of $\Delta S_M$ in the literatures, respectively. The large value of $\Delta S_M$ and RC suggests that Ho$_{12}$Co$_7$ can be an appropriate candidate for magnetic refrigerant in low temperature ranges.

In summary, the Ho$_{12}$Co$_7$ compound undergoes a PM-FM transition at $T_1 = 30$ K, accompanied with a FM-AFM transition at $T_2 = 17$ K and an AFM-AFM transition at $T_1 = 9$ K. A field-induced metamagnetic transition from AFM to FM state occurs below $T_2$. With the magnetic field increasing, $T_1$ moves towards higher temperatures, but $T_2$ and $T_C$ almost keep the same value. There are two peaks on the $\Delta S_M$-$T$ curves and they become one larger peak when the
field change is 0–2 T and 0–5 T. The maximal values of \( -\Delta S_M \) and RC are determined to be 19.2 J/kg K and 554.9 J/kg for a field change of 0–5 T, respectively. The large value of \( D_{SM} \) and RC suggests that Ho12Co7 can be an appropriate candidate for magnetic refrigerant in low temperature ranges.

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