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Large magnetic refrigerant capacity of $HoFe_{1-x}Co_xAl$ ($x = 0, 0.3$) compounds

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Abstract Magnetic and magnetocaloric properties of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) were investigated. Both HoFeAl and $HoFe_{0.7}Co_{0.3}Al$ undergo a second-order ferromagnetic (FIM) to paramagnetic (PM) transition at Curie temperatures (T_C) of 87 and 82 K, respectively. The magnetocaloric effect is improved by the introduction of Co in HoFeAl compound. For a field change from 0 to 5 T, the maximum values of magnetic entropy change ($-\Delta S_M$) are 7.0 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ for HoFeAl and 8.6 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ for $HoFe_{0.7}Co_{0.3}Al$. In addition, the refrigerant capacity (RC) is enhanced largely from 416.2 $J{\cdot}kg^{-1}$ for HoFeAl to 561.9 $J{\cdot}kg^{-1}$ for $HoFe_{0.7}Co_{0.3}Al$. This large RC is attributed to the large ΔS_M and the wide temperature span of ΔS_M peak in $HoFe_{0.7}Co_{0.3}Al$ compound. The physical mechanism of improvement in magnetocaloric effect by Co substitution in HoFeAl was also discussed in detail.

Keywords RTX compound; Intermetallic compound; Magnetocaloric effect; Refrigerant capacity

1 Introduction

Magnetic refrigeration, based on magnetocaloric effect (MCE), is considered to be one of the promising cooling technologies, due to its energy-saving and environmentally friendly properties in comparison with the conventional gas compression method. In the past decades, great effort has been devoted to researching magnetic refrigerant materials. Up to now, giant MCEs have been found in materials with a first-order magnetic transition (FOMT), such as $Gd_5Si_2Ge_2$ [1], $La(Fe, Si)_{13}$ [2], MnAs [3, 4], $MnFeP_{1-x}As_x$ [5] and Ni–Mn–X Heusler alloys [6–8]. However, FOMT is usually accompanied by considerable thermal and magnetic hysteresis, therefore reducing the effective refrigerant capacity (RC). At the same time, the materials with second-order magnetic transition (SOMT) attract much attention for the excellent magnetic reversibility and large RC, which signify that these materials are more reliable for the practical application of magnetic refrigeration.

Owing to the variation of crystalline structure of many RTX-type (R = rare earths, T = 3d transition metals and X = p-block elements) compounds, the magnetic and magnetocaloric properties were deeply explored [9]. RFeAl (R = heavy rare earths, except Yb) compounds crystallize in a hexagonal $MgZn_2$-type structure [10] and undergo a ferrimagnetic (FIM) to paramagnetic (PM) transition at their respective Curie temperatures (T_C) [11–13]. The results of Mican et al. [14] indicate that $HoFe_{2-x}Al_x$ crystallizes in hexagonal $MgZn_2$ structure and remains in ferrimagnetic ground state when Al content is tuned from 0.750 to 1.125. Dong et al. [15], Li et al. [16], Zhang et al. [17] and Kaštil et al. [18] successively reported the magnetocaloric properties of RFeAl compounds. Among all the RFeAl series, the magnetic entropy change ($-\Delta S_M$) of HoFeAl is the largest, i.e., 7.5 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ at $T_C = 80$ K with the field change of 0–5 T [17]. On the other hand, HoCoAl also exhibits the largest MCE in the series of RCoAl compounds, i.e., $|\Delta S_M| = 21.5$ $J{\cdot}kg^{-1}{\cdot}K^{-1}$ at $T_C = 10$ K for a field change of 0–5 T [19]. Therefore, it is expected that MCE of HoFeAl could be improved by substituting Fe with Co. In order to confirm the speculation and further understand MCE of

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$HoFe_{1-x}Co_xAl$ compounds, in this paper, the magnetic and magnetocaloric properties of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) were investigated systematically.

2 Experimental

Polycrystalline compounds of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) were prepared by arc melting appropriate quantity of high-purity elements in argon atmosphere. The ingots were turned over and remelted several times in order to ensure homogeneity. Then, the as-cast alloys were annealed in vacuum quartz tube at 1023 K for 10 days. The phase structure was examined by X-ray diffraction (XRD, Bruker Phaser) with Cu Kα radiation. The magnetic measurements were taken using vibrating sample magnetometer (VSM, Quantum Design SQUID).

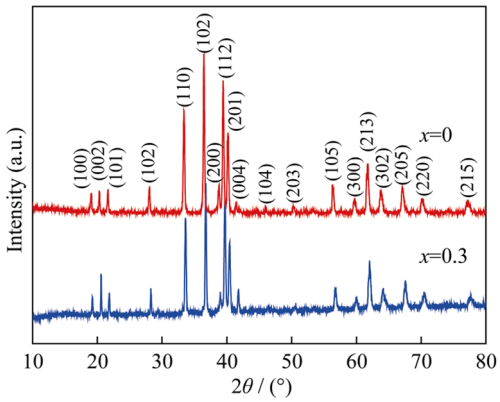

Fig. 1 XRD patterns of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) compounds

3 Results and discussion

Figure 1 shows room-temperature XRD patterns of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) compounds. It reveals that all the peaks can be indexed according to the previous work [10], and the samples are determined to crystallize in a clean-phase hexagonal $MgZn_2$-type structure (space group: $P6_3/mmc$, No. 194) as reported before [9, 10]. In addition, the Bragg peak position deviation between the two patterns suggests that the lattice constant decreases when partial Fe atoms were replaced by smaller Co.

Thermomagnetic measurements were taken in order to investigate the phase transition of $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) compounds. Figure 2a, b displays the temperature dependencies of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations (M) under a field of 0.01 T for HoFeAl and $HoFe_{0.7}Co_{0.3}Al$, respectively. A phase transition from FIM to PM state takes place at T_C, which is defined as the local minimum of dM/dT curve (insets in Fig. 2). The T_C of HoFeAl is 87 K, which is roughly close to the value reported earlier [11]. The obtained T_C of $HoFe_{0.7}Co_{0.3}Al$ is 82 K, which is slightly lower than that of HoFeAl. Isostructure HoTAl (T = Fe and Co) compounds have different T_C because of their different magnetic coupling strengths due to atom distances. It is estimated that the T_C of $HoFe_{0.7}Co_{0.3}Al$ should be 67.4 K if the T_C decreases linearly from HoFeAl ($T_C = 92$ K from Ref. [9]) to HoCoAl ($T_C = 10$ K from Ref. [9]). However, the measured value is not in accordance with this speculation, implying the nonlinear function between the transition temperature and x in $HoFe_{1-x}Co_xAl$ compounds. A small quantity of Co in RTX compounds does not show magnetic moment [9, 20], but Fe still has small moment [15]. Thus, it

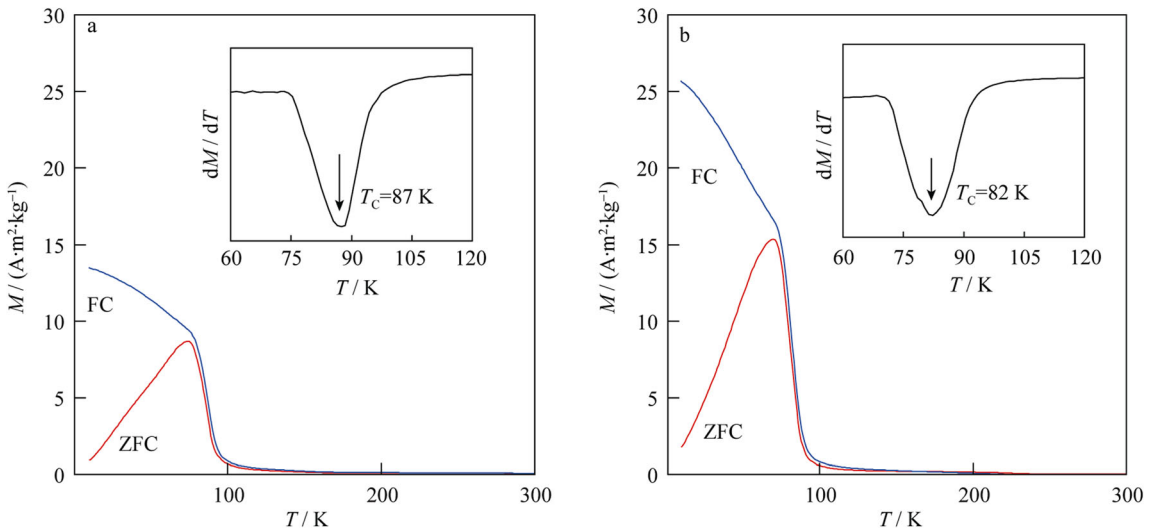

Fig. 2 Temperature (T) dependences of magnetization (M) of $HoFe_{1-x}Co_xAl$ for **a** $x = 0$ and **b** $x = 0.3$ under 0.01 T. Insets the first derivatives of magnetization vs. temperature

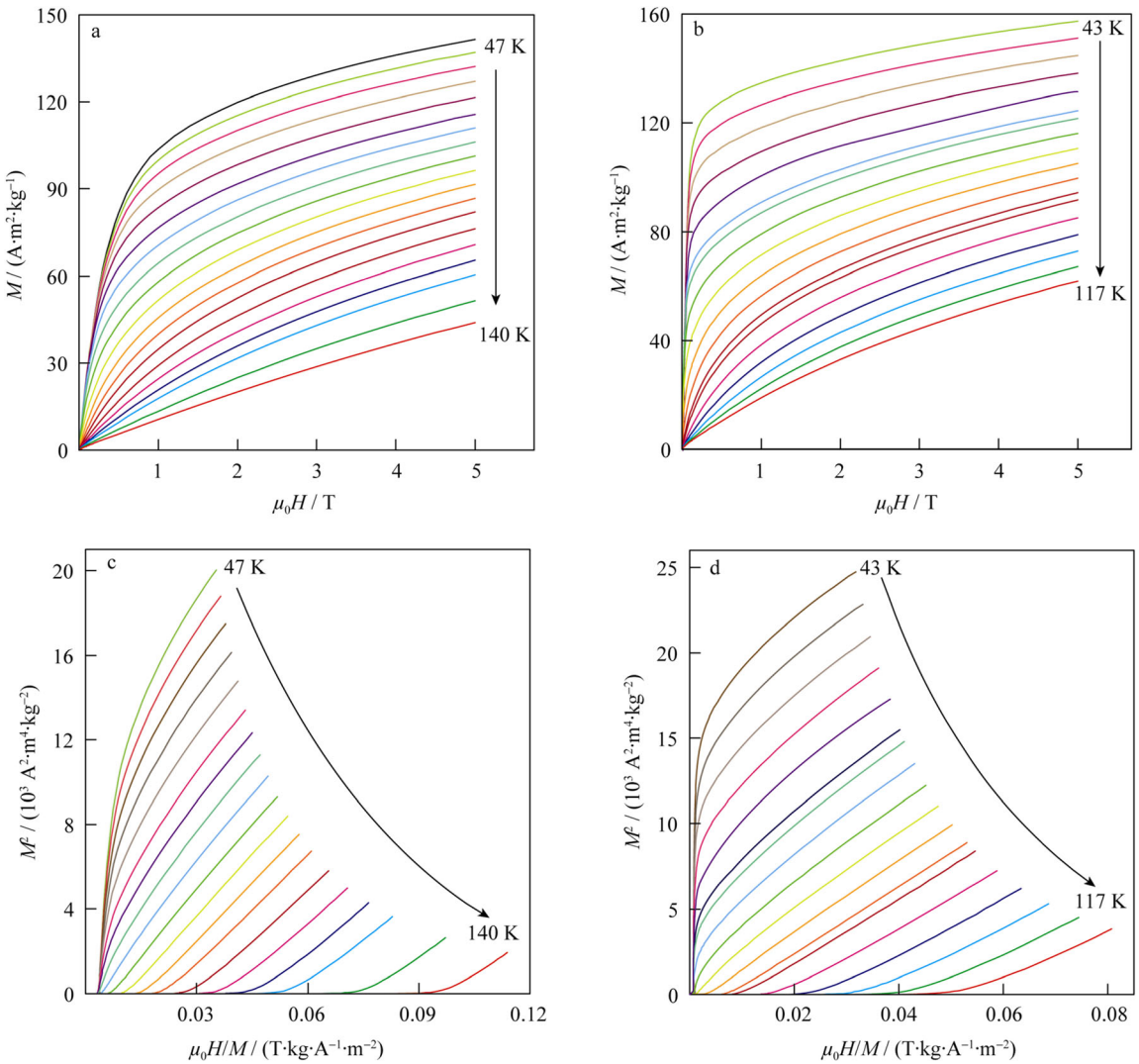

Fig. 3 Magnetization isotherms of $HoFe_{1-x}Co_xAl$ under magnetic fields up to 5 T for **a** $x = 0$ and **b** $x = 0.3$; Arrott plots of $HoFe_{1-x}Co_xAl$ in a wide temperature range for **c** $x = 0$ and **d** $x = 0.3$

is speculated that the dilution and substitution of Fe by Co in $HoFe_{1-x}Co_xAl$ may weaken the antiferromagnetic coupling between Ho and Fe sublattices and then increase the total magnetization shown in thermomagnetic curves (Fig. 2). It is observed that the ZFC and FC curves are nearly reversible in the vicinity of T_C, which is a typical characteristic of SOMT. However, thermomagnetic irreversibility between the two branches is observed at lower temperatures, which is usually explained as the ZFC frozen narrow domain-wall-pinning effect, competing magnetic interactions and the strong magnetic anisotropy [9, 21].

The isothermal magnetization relation (M–H curves) of HoFeAl and $HoFe_{0.7}Co_{0.3}Al$ was measured to evaluate their magnetocaloric properties under different fields up to 5 T. The temperature step is 4 K in the vicinity of T_C, while larger temperature step is chosen in the regions far away from T_C. Figure 3a, b shows M–H curves of HoFeAl and $HoFe_{0.7}Co_{0.3}Al$, respectively. Below their T_C, the magnetization increases rapidly at low fields and tends to saturate with the increase of field. However, the saturation magnetization (M_S at 5 T) of $HoFe_{0.7}Co_{0.3}Al$ at 47 K (150.6 $A{\cdot}m^2{\cdot}kg^{-1}$) is 6.5% larger than that of HoFeAl at 48 K (141.4 $A{\cdot}m^2{\cdot}g^{-1}$), and furthermore, the magnetic field required to reach saturation magnetization of $HoFe_{0.7}Co_{0.3}Al$ is lower than that of HoFeAl. The increase of saturation magnetization and lowered saturation field might be related to the weakened antiferromagnetic coupling between Ho and Fe, or the change of domain wall structure. Figure 3c, d displays Arrott–Belov plots of HoFeAl and $HoFe_{0.7}Co_{0.3}Al$, respectively. It is found that these plots do not show either inflection point or negative slope, proving the characteristic of second-order FIM-PM transition [22]. This is consistent with the fact of absence of thermal hysteresis in Fig. 2.

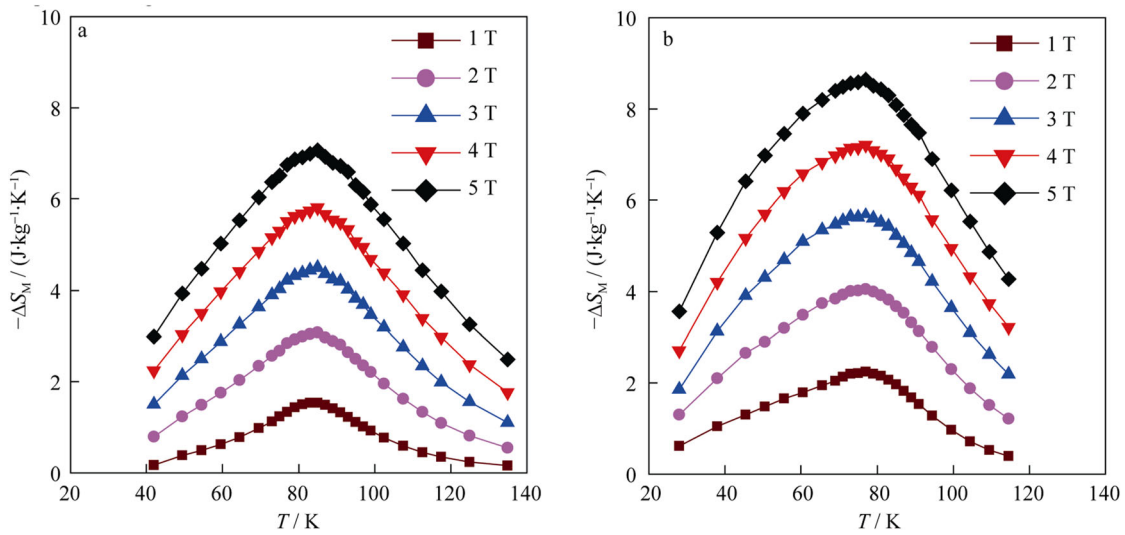

Fig. 4 Temperature dependence of magnetic entropy change ($-\Delta S_M$) of $HoFe_{1-x}Co_xAl$ for **a** $x = 0$ and **b** $x = 0.3$

The ΔS_M in the vicinity of T_C is calculated by using the following integration [1]:

$$\Delta S_M = \int_0^H (\partial M/\partial T)_H dH \quad (1)$$

where H is magnetic field. The temperature dependences of ΔS_M under different magnetic field for HoFeAl and $HoFe_{0.7}Co_{0.3}Al$ are presented in Fig. 4a, b, respectively. For a field change of 0–5 T, the maximum values of $-\Delta S_M$ reach 7.0 J·kg^{-1}·K^{-1} at 85 K for HoFeAl and 8.6 J·kg^{-1}·K^{-1} at 77 K for $HoFe_{0.7}Co_{0.3}Al$. The entropy changes of these two compounds can be comparable to or even larger than those of some FOMT materials in the same temperature range, such as $Er(Co_{0.9}Mn_{0.1})_2$, $Mn_{2.95}Co_{0.05}GaC$ and Ce_2Fe_{17} [23]. In addition, the value of RC is calculated by:

$$RC = \int_{T_1}^{T_2} |\Delta S_M| dT \quad (2)$$

where T_1 and T_2 are the temperatures at half-maximum of the $|\Delta S_M|$ peak [1], and they are 46 and 122 K for HoFeAl, and 32 and 114 K for $HoFe_{0.7}Co_{0.3}Al$, respectively. For $\mu_0\Delta H = 5$ T(μ_0 is the permeability in vacuum, and ΔH is the field change), the RC values are obtained to be 416 J·kg^{-1} for HoFeAl and 562 J·kg^{-1} for $HoFe_{0.7}Co_{0.3}Al$. It is clearly noted that the RC value increases remarkably by 35% after the substitution of Fe by Co, which is attributed to the larger ΔS_M of $HoFe_{0.7}Co_{0.3}Al$ in a wider temperature span. This large value of RC for $HoFe_{0.7}Co_{0.3}Al$ is comparable to that of DyGa (382 J·kg^{-1}) [24] and HoGa (455 J·kg^{-1}) [25] in the same temperature range, making $HoFe_{0.7}Co_{0.3}Al$ alloy a good candidate for magnetic refrigerants operating on an Ericsson cycle over a wide temperature range.

4 Conclusion

In summary, $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) alloys crystallize in $MgZn_2$-type structure. A second-order FIM-PM transition is observed at their respective T_C of 87 and 82 K. For a field change of 0–5 T, the maximum values of $-\Delta S_M$ are 7.0 J·kg^{-1}·K^{-1} for HoFeAl and 8.6 J·kg^{-1}·K^{-1} for $HoFe_{0.7}Co_{0.3}Al$. The corresponding values of RC are 416.2 and 561.9 J·kg^{-1}. The substitution of Fe by Co in $HoFe_{1-x}Co_xAl$ ($x = 0$, 0.3) weakens the antiferromagnetic coupling and leads to the enhancement of magnetization and MCE. The result may give some clues for improving the performance of magnetic refrigeration materials.

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