Magnetic properties and magnetocaloric effects in HoPd intermetallic*

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A large reversible magnetocaloric effect accompanied by a second order magnetic phase transition from PM to FM is observed in the HoPd compound. Under the magnetic field change of 0–5 T, the magnetic entropy change $-\Delta S_{\rm M}^{\rm max}$ and the refrigerant capacity *RC* for the compound are evaluated to be 20 J/(kg·K) and 342 J/kg, respectively. In particular, large $-\Delta S_{\rm M}^{\rm max}$ (11.3 J/(kg·K)) and *RC* (142 J/kg) are achieved under a low magnetic field change of 0–2 T with no thermal hysteresis and magnetic hysteresis loss. The large reversible magnetocaloric effect (both the large $-\Delta S_{\rm M}$ and the high *RC*) indicates that HoPd is a promising material for magnetic refrigeration at low temperature.

Keywords: magnetocaloric effect, magnetic entropy change, magnetic phase transformation

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1. Introduction

The magnetic refrigerator is based on the magnetocaloric effect (MCE), which plays an important role in the refrigeration area for its higher energy efficiency and lower environmental hazard, especially, compared with the conventional gas compression refrigeration.[1–4] The advanced magnetic materials are crucial for the magnetic refrigerant application, so it is necessary to go on exploring the advanced magnetic refrigerant materials with a large isothermal magnetic entropy change ($\Delta S_{\rm M}$) and/or a large adiabatic temperature change ($\Delta T_{\rm ad}$).[5] Up to now, many magnetic materials with large $-\Delta S_{\rm M}$ have been found, such as $LaFe_{13-x}Si_x$,[6–8] $MnFeP_{0.45}As_{0.55}$,[9–11] and $Gd_5Si_2Ge_2$.[12–14] The MCE materials working at room temperature can reduce the emission of green house gases. So much attention has been paid to search for magnetic refrigerants near room temperature.[15] On the other hand, the materials working at the low temperature regime are important for their potential applications in special technological areas, such as space science, liquefaction of hydrogen in the fuel industry, and liquefaction of helium, and can also help the facility to reach millikelvin.[16]

Until now, only the paramagnetic salts such as $Gd_3Gd_5O_{12}$, $GdLiF_4$, and GdF_3[17,18] have been commercially used. However the paramagnetic salts exhibit small MCE and strongly depend on the temperature. The rare earth-transition metal intermetallic compounds with ferromagnetic (FM) to paramagnetic (PM) transition or antiferromagnetic (AFM) to FM metamagnetic transition are believed to possess large MCE, and a series of materials have been reported, such as $ErMn_2Si_2$,[19] $ErCr_2Si_2$,[20] $ErRu_2Si_2$,[21] HoCuSi,[22] TmGa,[23] and TmCuAl.[24] They can be expected to have effective commercial applications in the technology of magnetic refrigeration at low temperature. In this paper, we report a study on the magnetic and magnetocaloric properties of the HoPd compound. The reversible $-\Delta S_{\rm M}^{\rm max}$ is 11.3 J/(kg·K) and 6.4 J/(kg·K) receptively with zero thermal hysteresis and magnetic hysteresis for low magnetic field changes of 2 T and 1 T. The *RC* value of the HoPd compound is increased with increasing field changes and reaches to 124 J/kg and 342 J/kg for the field changes of 2 T and 5 T, respectively. The results imply that the HoPd compound may have effective applications in low temperature magnetic refrigeration.

2. Experiments

The polycrystalline sample of HoPd was synthesized by arc melting of stoichiometric amounts of the elements with purity better than 99.9 at.% in argon atmosphere on a water-cooled copper hearth using a titanium zirconium alloy as the getter (the content of Ho was 3 at.% more than the theoretical value). The ingot was melted three times with the button being turned over after each melting to ensure the homogeneity. The sample was annealed at 1123 K for 7 days, and a subsequent quenching to room temperature was performed to obtain the crystalline sample. Powder X-ray diffraction (XRD) measure-

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ments with Cu $K\alpha$ radiation were performed at room temperature to identify the crystal structure and the lattice parameters. Magnetizations were measured by employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc.

3. Results and disscussion

Figure 1 shows the typical temperature dependence of the magnetization $M(T)$ for the HoPd compound under an applied magnetic field of $H = 0.01$ T. The compound exhibits a magnetic transition from FM to PM, and the Curie temperature (T_C) is determined to be 10 K, defined at the maximum slope of the M–T curve. It can be seen that there is almost no thermal hysteresis between the ZFC and FC curves as observed usually in SOPT when the temperature increases above T_C. However, a significant thermal irreversibility is clearly observed below T_C. The thermomagnetic irreversibility can be observed in many cases, such as spin-glass systems, materials with competing magnetic interactions, and materials with high anisotropy and low ordering temperature,[25] where the domain wall width could be comparable to the lattice spacing, thus resulting in a large pinning effect.[26] Considering the magnetic anisotropy due to the large orbital angular momentum in Ho atoms (or ions) and low T_C for HoPd, the thermomagnetic irreversibility is likely arising from the narrow domain wall pinning effect. With increasing magnetic field, the thermomagnetic irreversibility becomes smaller as shown in Fig. 1(b), and vanishes completely under a higher field. This indicates that the higher magnetic field would provide more energy for the domain walls to conquer the barriers of the pinning effect, thus reducing the irreversibility. The inset of Fig. 1(b) shows the reciprocal magnetic susceptibility χ_m^{-1} versus temperature for HoPd. The magnetic susceptibility of the HoPd compound at temperatures above 15 K follows the Curie-Weiss law $\chi_m^{-1} = (T - \theta_p)/C_m$. Here θ_p is the PM Curie temperature and C_m is the Curie–Weiss constant. The θ_p for HoPd is 10 K, which is equal to T_C from the M–T curve. The effective magnetic moment $\mu_{eff} = 10.68\mu_B$ is obtained based on the value of C_m, which is close to the theoretical value $10.6\mu_B$ for the Ho^{3+} ion.

Figure 2 shows the isothermal magnetization curves as a function of the magnetic field, which was measured in applied fields up to 5 T in a wide temperature range. It can be seen from Fig. 2 that there is a considerable difference among the M–H curves for the HoPd compound in different temperature ranges. In the 20–47 K temperature range, the field dependence of the magnetization shows a linear relation, whereas the isothermal curves for $T_C < T < 20$ K show an appreciable nonlinearity. The curvatures in the M–H curves above T_C probably indicate the existence of short-range FM correlations in the PM state. Additionally, it should be noticed that although the isothermal magnetization curves are gradually saturated with increasing magnetic field at considerably lower fields below T_C, the complete saturation is not realized at 5 T. The magnetic moment per Ho atom reaches about $7.2\mu_B$ at 2 K and 5 T, which is much smaller than the theoretical ordered state magnetic moment of $10.6\mu_B$ for the Ho atom. The lack of complete saturation in the HoPd compound is likely due to the crystalline electric field. Additionally, the magnetization isotherms of HoPd measured on increasing (solid) and decreasing (open) fields around T_C exhibit no magnetic hysteresis loss.

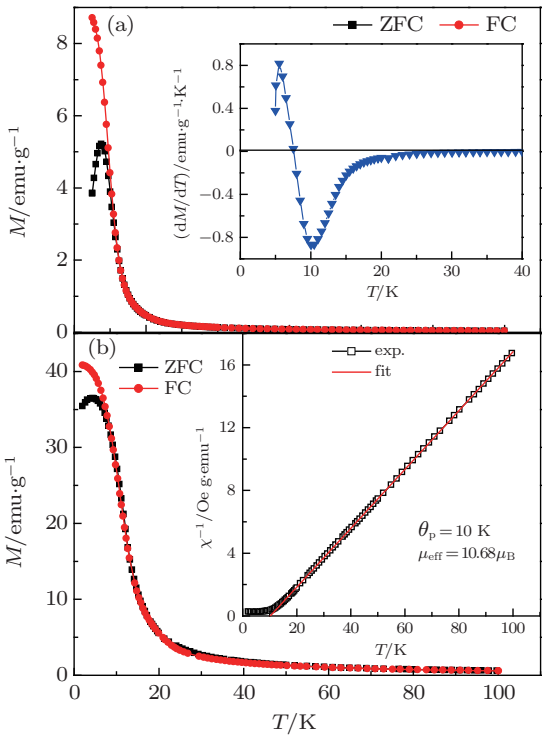


Fig. 1. (color online) Temperature dependences of ZFC and FC magnetizations under the magnetic fields of (a) 0.01 T and (b) 0.1 T. The inset in panel (a) is dM/dT–T curve; that in panel (b) is reciprocal magnetic susceptibility χ_m^{-1} versus temperature.

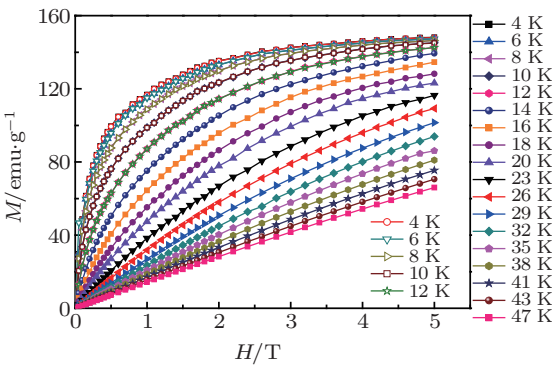


Fig. 2. (color online) Magnetization isotherms of HoPd collected in the temperature range of 4–47 K; the M–H curves in decreasing field mode around T_C (open symbols) are also shown.

Figure 3 shows the Arrott plots of the HoPd compound in the temperature range of 4–20 K. According to the Banwejee criterion,[27] a magnetic transition is expected to be of

the first order when the slope of M^2 versus H/M is negative, whereas it is of the second order when the slope is positive. Neither negative slope nor inflection point is observed in the Arrott plots of the HoPd compound, indicating a second-order FM–PM magnetic transition.

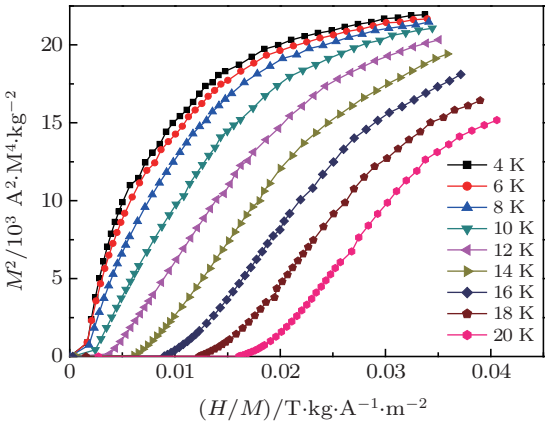


Fig. 3. (color online) Arrott plots of HoPd in the temperature range of 4–20 K.

The MCE in terms of isothermal magnetic entropy change has been determined by utilizing Maxwell's relationship $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$, where T is the absolute temperature and H is the applied field. The values of $-\Delta S_\mathrm{M}$ for different magnetic field changes as a function of temperature are shown in Fig. 4. The $-\Delta S_\mathrm{M}^\mathrm{max}$ is found to increase monotonically with the increase of the applied magnetic field. Under the magnetic field change of 5 T, $-\Delta S_\mathrm{M}^\mathrm{max}$ is 20 J/(kg·K) for the HoPd compound around T_C, which is near the boiling point of hydrogen (20.4 K). The $-\Delta S_\mathrm{M}^\mathrm{max}$ is found to be 11.3 J/(kg·K) for HoPd under a low magnetic change of 2 T. Meanwhile, the HoPd compound has confirmed a characteristic of second-order FM–PM magnetic transition, no thermal hysteresis, and zero field hysteresis. The permanent magnets in the present market can only provide a maximum field of ∼ 2 T; this indicates that a large MCE under a low magnetic field change is desirable for the fulfillment of a magnetic refrigerator simply using permanent magnets. The low field MCE parameters of HoPd are comparable to or larger than those of most potential magnetic refrigerant materials with a similar magnetic transition temperature, as listed in Table 1.

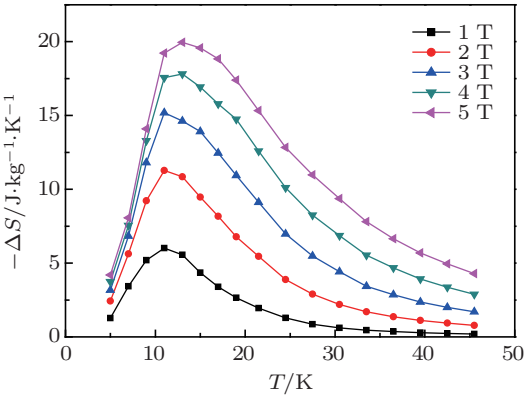


Fig. 4. (color online) Temperature dependences of magnetic entropy change in HoPd for different magnetic field changes.

Table 1. Magnetic ordertransition temperature T, $-\Delta S_\mathrm{M}^\mathrm{max}$ and RC with the field change of 2 T for HoPd and other MCE materials around 10 K.

Compound	T/K	Order of transition	$-\Delta S_\mathrm{M}$/J·/kg^{-1}·K^{-1}	RC/J·kg^{-1}	Ref.
$ErRu_2Si_2$	5.5	first	11	55	[28]
$HoNi_2B_2C$	6.5	first	5.7	62	[29]
$DyCo_2B_2$	10	second	4.5	0.9 J/cm^3	[30]
DyCuSi	10	first	∼ 10.5	∼ 160	[31]
$Eu_8Ga_{16}Ge_{30}$	10	second	8.0	80	[32]
Er_3Co	13	second	12	163	[33]
$Dy_{0.9}Tm_{0.1}Ni_2B_2C$	9.2	first	4.05	52	[34]
HoPd	10	second	11.3	142	present

A high RC is another important requirement of a potential magnetic refrigerant, which is a measure of how much heat can be transferred between the cold and hot sinks in one ideal refrigerant cycle.[35] It is defined as $RC = \int_{T_1}^{T_2} |\Delta S_\mathrm{M}| \mathrm{d}T$, where T_1 and T_2 are the temperatures corresponding to the half-maximum values at the two sides of the $-\Delta S_\mathrm{M}$ peak, respectively. One can find that the RC of the HoPd compound increases with increasing field change and reaches to 142 J/kg and 342 J/kg for the field changes of 0–2 T and 0–5 T, respectively. This RC value is comparable to or larger than that of many magnetic refrigerant materials with a similar magnetic transition temperature. Our results suggest that the HoPd compound could be a very attractive candidate material for the magnetic refrigerator working at low temperature.

4. Conclusion

The polycrystalline HoPd compound with a single phase has been synthesized. A reversible MCE without thermal and magnetic hysteresis loss has been observed in the compound, which originates from the second order magnetic phase transition from PM to FM. With the magnetic field change of 0–5 T, $-\Delta S_\mathrm{M}^\mathrm{max}$ is evaluated to be 20 J/(kg·K) and RC is 342 J/kg. In particular, for the HoPd compound, $-\Delta S_\mathrm{M}^\mathrm{max}$ and RC are 11.3 J/(kg·K) and 142 J/kg under a magnetic field change of 0–

2 T at low temperature. The present results indicate that HoPd is one of the promising candidates for magnetic refrigeration at low temperature, particularly for helium liquefaction.

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