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A giant reversible magnetocaloric effect in Ho_2PdSi_3 compound

Zhao Jun Mo [a,b], Jun Shen [a,*], Li Qin Yan [c], Xin Qiang Gao [a,b], Cheng Chun Tang [b], Jian Feng Wu [a], Ji Rong Sun [c], Bao Gen Shen [c]

[a] Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
[b] School of Material Science and Engineering, Hebut University of Technology, Tianjin, China
[c] State Key Laboratory of Magnetism, Beijing National Laboratory for Condensed Matter, Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, China

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ABSTRACT

The magnetic properties and magnetocaloric effect (MCE) in Ho_2PdSi_3 compound are investigated. Ho_2PdSi_3 compound exhibits a giant reversible MCE, the value of $-\Delta S_M^{max}$ and RC are 27.5 J/kg K and 427 J/kg without thermal and field hysteresis loss, for field changes of 5 T, respectively. Especially, under field changes of 2 T, the value of $-\Delta S_M^{max}$ is 15.3 J/kg K and ΔT_{ad}^{max} is 4.2 K, respectively. The giant reversible $-\Delta S_M$, ΔT_{ad} and large RC together with the absence of thermal and field hysteresis indicate that Ho_2PdSi_3 compound could be a promising candidate for magnetic refrigeration at low temperatures.

1. Introduction

Magnetic materials with large/giant magnetocaloric effect (MCE) have been extensively studied experimentally and theoretically, not only due to its potential applications for magnetic refrigeration (higher energy-efficiency and lower environmental influence than conventional gas compression refrigeration) but also for further understanding the fundamental properties of the materials [1–11]. Usually, the magnitude of MCE can be characterized by magnetic entropy change (ΔS_M) and/or adiabatic temperature change (ΔT_{ad}) upon the variation of magnetic field. Besides, refrigerant capacity (RC) is considered as another important parameter to quantify the heat transferred between the hot and cold sinks in an ideal refrigeration cycle. However, there are some rare earth based intermetallic compounds with remarkable thermal and magnetic hysteresis, which reduce the refrigeration efficiency of the material [8]. Therefore, from the point of view of applications, it is desirable to search for materials that show giant MCE with a large RC [12,13]. In recent years, the magnetic and magnetocaloric properties in lots of rare earth based intermetallic compounds have been studied, and some of them have been found to possess not only large ΔS_M but also a small hysteresis loss [13–17].

In 1997, Pecharsky and Gschneidner reported on a giant MCE of $Gd_5Si_2Ge_2$ near room temperature ($T_C = 276$ K), which was attributed to a field induced first-order magnetic and structural transition [18]. On the other hand, the study of system with large MCE at low temperature is also important for their potential applications in special technological areas such as space science and liquefaction of hydrogen in fuel industry [4,19,20]. The series R_2PdSi_3 (R = rare earth) crystallizes in a high symmetrical AlB_2 derived hexagonal structure (space group P6/mmm). The magnetic rare earth ions occupy the Al positions of the AlB_2 structure while the non-magnetic Pd and Si atoms are assumed to be statistically distributed on the B positions [21]. Most of the R_2PdSi_3 (R = Ce, Gd, Tb, Dy, Ho, Er) compounds order antiferromagnetic (AFM) at T_N between 3 K (Ce) and 25 K (Tb) with exception of the Nd compound which orders ferromagnetic (FM) at $T_C = 17$ K [22,23]. In the present paper, we report on the magnetic properties and large reversible ΔS_M, large RC and ΔT_{ad} under a low field with no thermal and field hysteresis loss in Ho_2PdSi_3 compound.

2. Experiments

The polycrystalline sample of Ho_2PdSi_3 compound was synthesized by arc melting of stoichiometric amounts of the elements Ho (99.9%), Pd (99.9%) and Si (99.9%) under a purified argon atmosphere. In order to compensate for the loss, the content of Ho was 3% 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 1073 K for 7 days, and a subsequent quenching to room temperature was performed to obtain crystalline sample. The X-ray powder diffraction pattern confirmed the single-phase nature of the compound, and crystallizing in the hexagonal AlB_2-type structure. The lattice parameters were determined to be $a = b = 8.1072$ (4) Å and $c = 8.0214$ (2) Å with $R_{wp} = 9.6\%$ by the Rietveld technique using GSAS program, as shown in Fig. 1. Magnetizations were measured by

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[*] Corresponding author.
E-mail address: jshen@mail.ipc.ac.cn (J. Shen).

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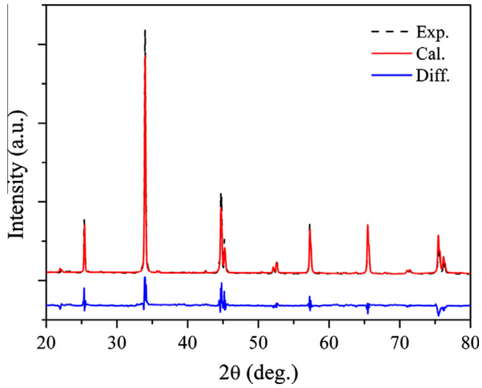

Fig. 1. Rietveld refined powder XRD patterns of Ho_2PdSi_3 compound at room temperature. The observed data are indicated by crosses, and the calculated profile is the continuous line overlying them. The lower curve shows the difference between the observed and calculated intensity.

employing a commercial superconducting quantum interference device (SQUID) magnetometer, model MPMS-7 from Quantum Design Inc. Heat capacity was measured by using a physical property measurement system (Quantum Design).

3. Results and discussions

The zero-field-cooling (ZFC) and field-cooling (FC) temperature dependence of magnetization for Ho_2PdSi_3 compound under an applied magnetic field of 0.01 T are shown in Fig. 2. It exhibits two successive magnetic transitions: the higher temperature transition is believed to be a paramagnetic (PM) to AFM transition at 8 K, and the lower temperature (<2 K) magnetic transition is possible spin reorientation effects apparently characteristic of this class of compound [24]. The ZFC and FC curves are well overlapped, indicating that there is no thermal hysteresis as usually observed in magnetic materials with a second-order magnetic transition. On the other hand, we also notice that the reciprocal magnetic susceptibility (χ_m^{-1}) of the Ho_2PdSi_3 compound follows the Curie–Weiss law ($\chi_m^{-1}) = (T - \theta_p)/C_m$ above 10 K as shown the inset of Fig. 2(a). Here θ_p is the PM Curie temperature and C_m is the Curie–Weiss constant. The effective magnetic moment $\mu_{eff} = 10.55\ \mu_B$ is obtained based on the value of C_m, which is similar to the theoretical magnetic moment value (10.60 μ_B) for the Ho^{3+} ion. This fact implies the absence of localized magnetic moment on Pd atoms in Ho_2PdSi_3, which is in agreement with the result of other R_2PdSi_3 compounds [25,26]. The PM Curie temperature is found to be $\theta_p = 7.7$ K. Fig. 2(b) shows the temperature dependences of the magnetization of Ho_2PdSi_3 in various magnetic fields. It is clearly seen that the magnetization at low temperatures increases greatly with increasing field, a field-induced metamagnetic transition is possibly the primary cause of this phenomenon.

The isothermal magnetization curves as a function of magnetic field were measured in applied fields of up to 5 T in a temperature range from 2 to 30 K, as shown in Fig. 3(a). The magnetic moment calculated for 5 T is 8.38 μ_B per Ho^{3+} atom at 2 K, which is slightly smaller than the expected value of 10.6 for Ho^{3+} ion. This discrepancy maybe attributed to the antiferromagnetism [27]. The magnetization increases rapidly at low fields for the low temperature and shows a tendency to saturate with an increase of the field. A large reversible MCE is expected around the transition temperature where the magnetization rapidly changes with varying temperature. Fig. 3(b) exhibits the field dependence of magnetization in a temperature range from 2 to 9 K with an increment of 1 K, in magnetic fields ranging from 0 to 0.5 T. It can be seen that there exist intersections among the curves. The low temperature magnetization is smaller than the high temperature value in low fields. On the contrary, this condition reverses in higher fields. This agrees with the AFM ordering of the compound below T_N [28]. Further analysis on magnetization data find that the temperature dependence of dM/dH below T_N exhibits clearly a maximum value as shown inset Fig. 3(b), also revealing the field-induced metamagnetic transition from AFM to FM states. The critical magnetic field, which is determined from the maximum of the dM/dH curve, is found to increase monotonically with the decrease of temperature and reaches a value of 0.2 T at 2 K. That is to say, the sample can change to FM phase by applying an appropriate field (about 0.2 T) in our case.

The magnetic hysteresis loop at 2 K indicates no hysteresis effect in Ho_2PdSi_3 compound as shown in Fig. 4, which is very favorable for the actual application of magnetic refrigerant. The inset of Fig. 4 shows the magnified hysteresis loop at 2 K, in magnetic field up to 0.25 T. We can find that there exists an obvious change in the slope of the curve in a field of 0.2 T, which also confirms a phase transition under this magnetic field.

Fig. 5 displays the heat capacity (C_P) curves for Ho_2PdSi_3 under the fields of 0 and 2 T, respectively. The obvious λ-shape peak around 8 K in zero field $C_p(T)$ is believed to be due to the magnetic ordering transition which was consistent with those deduced from the magnetization measurement. With the increase of magnetic field, the peak turns a broader and shifts toward higher temperature. It is known that the heat capacity peak is caused by the absorption of heat which is utilized in randomization of magnetic moments around transition temperature. With the application of field, the randomization of moments would spread out over a wide temperature region, and the maximum peak moves towards higher temperature [18,29].

The ΔS_M value of Ho_2PdSi_3 compound calculated from the magnetization isotherms by using an integral version of Maxwell's thermodynamic relation $\Delta S(T,H) = \int_0^H (\partial M/\partial T)_H dH$ and from the heat capacity C_p (T, H) data using the equation $\Delta S_M(T)_{\Delta H} = \Delta S_M(2.5K)_{\Delta H} + \int_{2.5\ K}^{T} \frac{\Delta C_H}{T} dT$ [30]. When we use the equation

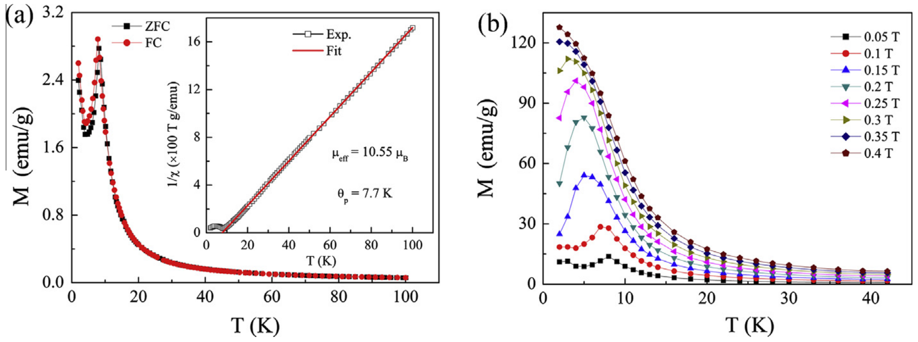

Fig. 2. (a) Temperature dependences of ZFC and FC magnetizations under the magnetic fields of 0.01 T; inset: the temperature variation of the ZFC inverse susceptibility fitted to the Curie–Weiss law and (b) temperature dependences of ZFC and FC magnetizations under different magnetic field.

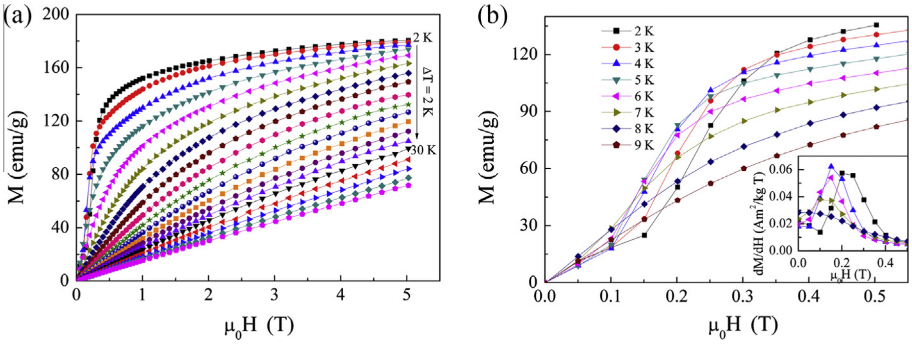

Fig. 3. (a) Magnetization isotherms of Ho_2PdSi_3 collected in the temperature range of 2–30 K and (b) the low field magnetization isotherms for Ho_2PdSi_3 at 2–9 K; inset: magnetic field derivatives of magnetization data (dM/dH) as a function of the magnetic field at different constant temperatures.

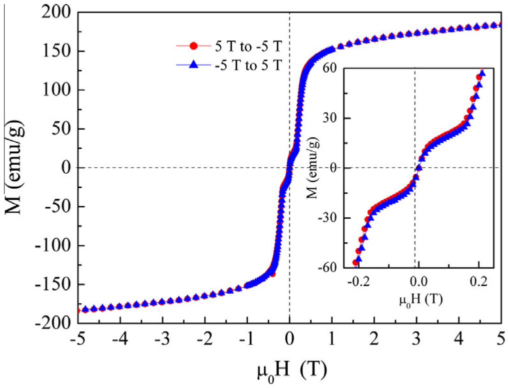

Fig. 4. Magnetic hysteresis loop at 2 K up to 5 T, with the inset showing the enlarged part of magnetic hysteresis loop.

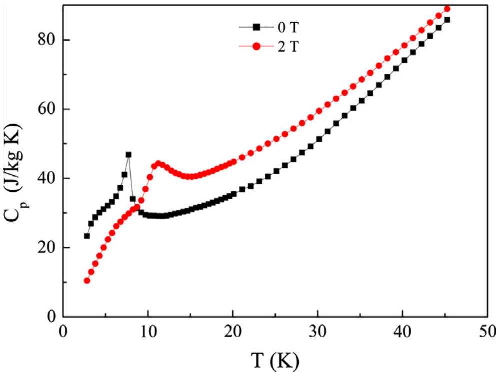

Fig. 5. Temperature dependence of heat capacity (C_P) for Ho_2PdSi_3 measured in the fields of 0 and 2 T.

$\Delta S(T)=\int_0^T \frac{\Delta C_H}{T}dT$ from the heat capacity C_p (T, H) data, heat capacity needs to be measured at extremely low temperature ($C_H(T)=C_0(T)$), so now the question is whether we may use the above standard method. Considering the fact that the starting temperature of heat capacity measurement for Ho_2PdSi_3 compound is 2.5 K, the standard method of calculating ΔS_M from C_H data will not hold true in this case anymore. In fact, the problem can be solved as long as we make some modifications to this method. The key point of modification is to replace the original point, such as the $S_M(2.5\ K)+S_M(2.5–40\ K)$ reference $S_M(0–40\ K)$. We suppose that the $\Delta S_M(2.5\ K)$ calculated from the magnetization isotherms and from C_H data are equal. The new steps are as follows:

$$S_M(T)_0 = S_M(2.5\ \mathrm{K})_0 + \int_{2.5\ \mathrm{K}}^{T} \frac{C_0}{T}dT \tag{1}$$

$$S_M(T)_H = S_M(2.5\ \mathrm{K})_H + \int_{2.5\ \mathrm{K}}^{T} \frac{C_H}{T}dT \tag{2}$$

So we can get the $\Delta S_M(T)_{\Delta H}$ from Eqs. (1) and (2)

$$\Delta S_M(T)_{\Delta H} = \Delta S_M(2.5\ \mathrm{K})_{\Delta H} + \int_{2.5\ \mathrm{K}}^{T} \frac{\Delta C_H}{T}dT \tag{3}$$

Fig. 6(a) shows the values of $-\Delta S_M$ for different magnetic field changes as a function of temperature. The maximum value of $-\Delta S_M$ ($-\Delta S_M^{\max}$) is found to increase monotonically with applied magnetic field increasing and reaches a value of 27.5 J/kg K for a magnetic field change from 0 to 5 T at 9.5 K. Particularly, under the magnetic field changes of 2 T, which can be realized by permanent magnet and advantageous to applications, a large value of $-\Delta S_M^{\max}$ is evaluated to be 15.3 J/kg K. It is much larger than those of most potential magnetic refrigerant materials in a similar magnetic transition temperature under the same field change, such as ErFeSi (14.2 J/kg K) [31], $ErRu_2Si_2$ (11 J/kg K) [15] and DyCuSi

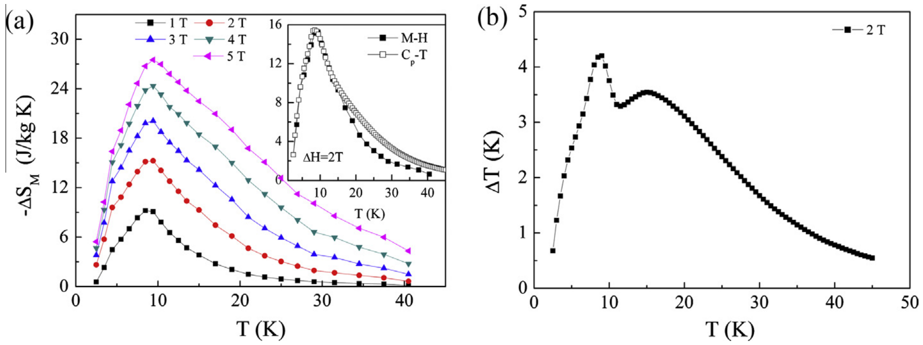

Fig. 6. (a) Temperature dependences of magnetic entropy change in Ho_2PdSi_3 for different magnetic field changes; inset: magnetic entropy changes calculated from magnetizations (full symbols) and heat capacity measurements (open symbols) as a function of temperature under field change 2 T and (b) temperature dependence of adiabatic temperature change under field change 2 T.

(10.5 J/kg K) [32]. The ΔS_M values were determined from both methods under magnetic field change 2 T as shown inset of Fig. 6(a), and it is clearly seen that the ΔS_M curves obtained from two methods match well with each other. As another important parameter to evaluate the MCE of magnetocaloric materials, the adiabatic temperature change ΔT_{ad} was calculated from the C_p (T, H) data by using the equation $\Delta T_{ad} = -\frac{T}{C_H}\Delta S_H$. Fig. 6(b) shows the maximum value of ΔT_{ad} is 4.2 K for the field change of 2 T. The RC is an important quality factor of the refrigerant materials, which defined as a cooling capacity of $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, is calculated by numerically integrating the area under the $-\Delta S_M{-}T$ curve, where T_1 and T_2 are the temperatures at half maximum of the peak [33]. The values of RC are evaluated to be 150 and 427 J/kg for the magnetic field changes of 2 and 5 T, respectively. These values are comparable or larger than those of recently reported potential magnetic refrigerant materials in a similar magnetic transition temperature under the same field change, such as TmCuAl (372 J/kg at 4 K) [34], $ErMn_2Si_2$ (365 J/kg at 4.5 K) [14], ErRuSi (416 J/kg at 9 K) [35], $DyNi_2B_2C$ (290 J/kg at 12 K) [36], TmGa (364 J/kg at 16 K) [7], for a field change of 0–5 T. The large $-\Delta S_M^{max}$ and RC indicate that the Ho_2PdSi_3 compound appears to be a very attractive candidate material for use in a magnetic refrigerator working in low temperature.

4. Conclusion

In summary, a giant reversible MCE and large RC in Ho_2PdSi_3 compound were observed by magnetization and heat capacity measurements. It possesses an AFM–PM transition and undergoes spin-glass behavior above temperature. Ho_2PdSi_3 compound exhibits large MCE around Neel temperature, the value of $-\Delta S_M^{max}$ (27.5 J/kg K) and RC (427 J/kg) are obtained without thermal and field hysteresis loss for field changes of 5 T, respectively. A field-induced metamagnetic transition from AFM to FM states is observed in these compounds and the large reversible MCE is attributed to AFM–PM and FM–PM the transitions. Especially, for the magnetic field changes of 2 T, the value of $-\Delta S_M^{max}$ is 15.3 J/kg K and RC is 150 J/kg, respectively. The low magnetic field can be realized by permanent magnet. Additionally, the maximum values of ΔT_{ad} reach 4.2 K for the field change of 2 T. Therefore, the giant reversible MCE, large RC and ΔT_{ad} make the Ho_2PdSi_3 a promising candidate for magnetic refrigeration.

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