



Metamagnetic transition and magnetocaloric effect in antiferromagnetic TbPdAl compound

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ABSTRACT

Magnetic properties and the magnetocaloric effect of the compound TbPdAl are investigated. The compound exhibits a weak antiferromagnetic (AFM) coupling, and undergoes two successive AFM transitions at $T_N=43$ K and $T_t=22$ K. A field-induced metamagnetic transition from AFM to ferromagnetic (FM) state is observed below T_N , and a small magnetic field can destroy the AFM structure of TbPdAl, inducing an FM-like state. The maximal value of magnetic entropy change is -11.4 J/kg K with a refrigerant capacity of 350 J/kg around T_N for a field change of 0–5 T. Good magnetocaloric properties of TbPdAl result from the high saturation magnetization caused by the field-induced AFM–FM transition.

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1. Introduction

In the recent years, magnetic refrigeration materials have been studied widely because of their potential applications in magnetic refrigeration. Room-temperature giant magnetic entropy change (ΔS_M) around the transition temperatures has been observed in many materials that experience a first-order phase transition [1–4]. Recently a number of investigations on the magnetocaloric effects (MCEs) of magnetic materials also concentrated on the rare earth (R)-based intermetallic compounds with a low-temperature phase transition, because magnetic materials exhibiting large MCEs at temperatures below 70 K are potential magnetic refrigerants for the gas liquefiers [1,2]. Some R-based compounds with ferromagnetic (FM) or antiferromagnetic (AFM) phase transitions have been found to possess not only large ΔS_M but also considerable refrigerant capacity (RC) [5–10], which are just required by magnetic refrigerant materials. Among the R-based magnetocaloric materials, the R_3TAl ($T=Ni, Cu$ and Pd) series is a subject of special attention. These compounds exhibit complex magnetic structures and possess different magnetic phase transitions, which can induce interesting magnetocaloric properties. In fact, the $RTAl$ ($T=Ni$ and Cu) compounds have been demonstrated to exhibit large MCEs [5–7]. The crystal structure, phase transition and magnetic properties of $RPdAl$ have been studied in detail by neutron diffraction and magnetic measurements [11–17]. It was found that the $RPdAl$ compounds

crystallize in two structures, i.e., the hexagonal $ZrNiAl$ -type structure (space group $P\bar{6}2m$) serving as metastable high-temperature modification and the orthorhombic $TiNiSi$ -type structure (space group $Pnma$) acting as stable low-temperature modification. The neutron diffraction investigations on TbPdAl have revealed that the compound orders antiferromagnetically below the Néel temperature $T_N=43$ K, accompanied with an additional first-order phase transition at $T_t=22$ K [12,13]. In the TbPdAl compound with a hexagonal $ZrNiAl$ -type structure the AFM nearest-neighbor exchange coupling together with a strong magnetocrystalline anisotropy gives rise to the formation of geometrically frustrated magnetic moments, which are reduced in size compared with coexisting non-frustrated moments [13,18]. To understand the effects of the complex AFM structure and the magnetic phase transition on magnetocaloric behavior, we study the magnetic property and the MCE of TbPdAl compound in the present paper. It is found that TbPdAl is a weak antiferromagnet and a field-induced metamagnetic transition from AFM to FM state below T_N leads to a high saturation magnetization, thereby inducing a large MCE.

2. Experimental

Polycrystalline TbPdAl was prepared by arc melting in a high-purity argon atmosphere. The purities of starting materials were better than 99.9% for Tb, Pd and Al. The sample was turned over and remelted several times to ensure its homogeneity. Ingots obtained by arc melting were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 1050 °C for

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10 days and then quenched to room-temperature. Room-temperature X-ray diffraction (XRD) measurements on powder samples were performed using Cu $K\alpha$ radiation to identify the crystal structure. The Rietveld refinement shows that the prepared sample is of single phase, crystallizing in a hexagonal ZrNiAl-type structure. Magnetizations were measured as functions of temperature and magnetic field using a superconducting quantum interference device (SQUID) magnetometer. The temperature dependent magnetization was measured in both zero field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic reversibility and the magnetic transition temperature. With the sample cooled down to 5 K in a zero field, the heating curve from 5 to 300 K was measured in a magnetic field of 0.05 T and the cooling curve from 300 to 5 K was also measured in the same field. In order to determine ΔS_M , the isothermal magnetization curves were measured in a temperature range of 5–89 K with a temperature step of 3 K under the magnetic fields up to 5 T. The sweep rate of the field was 0.015 T/s to ensure that the M - H curves could be recorded in an isothermal process. Using the Maxwell relation $\Delta S_M = \int_0^H (\partial M / \partial T)_H dH$, ΔS_M is calculated from the isothermal magnetization data.

3. Results and discussion

Fig. 1(a) shows the temperature dependences of ZFC and FC magnetizations for TbPdAl in a magnetic field of 0.05 T. The results in Fig. 1(a) show that TbPdAl undergoes a second-order AFM-paramagnetic (PM) transition as temperature increases and

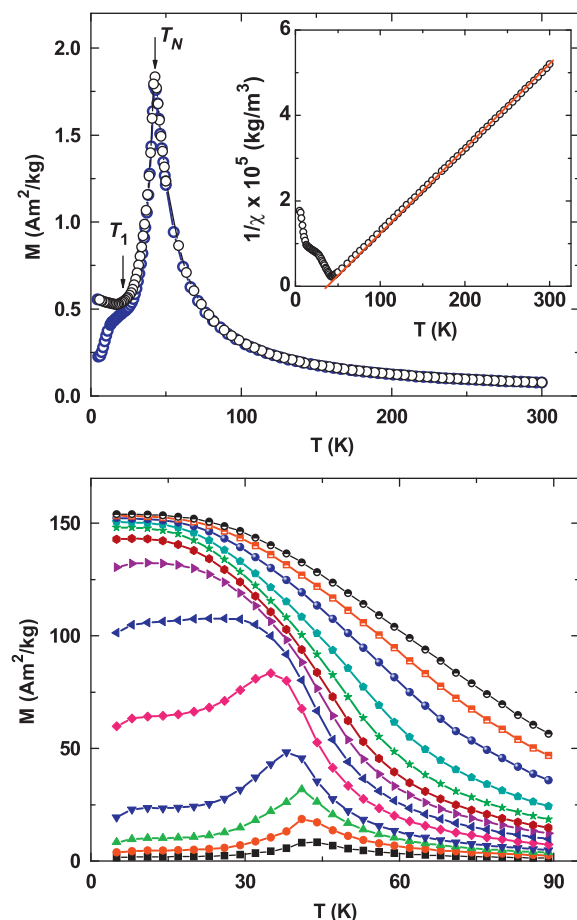


Fig. 1. Temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetizations for TbPdAl in a magnetic field of 0.05 T. The inset shows the reciprocal magnetic susceptibility χ^{-1} versus temperature in a field of 0.05 T.

its Néel temperature T_N is determined to be 43 K, which is in good agreement with the previous results [12,13]. The neutron diffraction investigations reveal that the TbPdAl compound has two successive magnetic phase transitions at $T_N=43$ K and $T_t=22$ K. The phase transition at T_t , for which no clear peak is observed in the M - T curves as reported in Refs. [12,13], is associated with the AFM structure transition. In hexagonal TbPdAl, one-third of the Tb moments (at Tb2) are highly frustrated between T_N and T_t . The geometrically frustrated Tb2 spins in TbPdAl lead to the change from a purely commensurate AFM structure at higher temperature to a purely incommensurate magnetic structure at a lower temperature of T_t . Two-third of the non-frustrated Tb moments (at Tb1 and Tb3) show commensurate AFM ordering below T_N [15,16]. In addition it can be found from Fig. 1(a) that considerable differences between the ZFC and the FC M - T curves at temperatures lower than about 30 K are observed and gradually increase with the decrease in temperature, which is related to the frustration effects of the magnetic structures [12,15,16]. The temperature dependences of the magnetization at different magnetic fields are shown in Fig. 1(b). A field-induced metamagnetic transition from AFM to FM state is clearly observed below T_N . When the applied magnetic field is higher than about 0.6 T the magnetization as a function of temperature for TbPdAl exhibits stepwise behavior above T_N , which corresponds to the FM-PM transition. A similar result is observed usually in AFM materials with a low critical field (B_C) required for metamagnetism [9,19]. The reciprocal magnetic susceptibility χ^{-1} versus temperature for TbPdAl in a field of 0.05 T is shown in the inset of Fig. 1(a). It can be seen from the inset that the magnetic susceptibilities of TbPdAl compound at temperatures above ~ 150 K perfectly follow the Curie-Weiss law $\chi^{-1}=(T-\theta_p)/C$, where θ_p is the PM Curie temperature and C is the Curie-Weiss constant. The value of θ_p is estimated to be about 38 K. The positive value of θ_p implies the presence of FM interactions above T_N in TbPdAl compound because θ_p reflects the collective exchange interactions in the compound. From the value of C the effective magnetic moment μ_{eff} per Tb ion for TbPdAl, obtained from the linear temperature dependence of χ^{-1} at 150–300 K, is $9.66 \mu_B$, which is close to the value expected for a free Tb^{3+} ion ($\mu_{eff}=9.72 \mu_B$).

Fig. 2(a) shows the isothermal magnetization as a function of magnetic field for TbPdAl around T_N . The magnetization of TbPdAl below T_N is found to increase slowly with the increase of magnetic field in a very low field range due to the existence of AFM ground state. However a field-induced metamagnetic transition from AFM to FM state occurs below T_N , which leads to a sharp increase of magnetization when the applied field exceeds a certain value. The critical field (B_C) required for metamagnetism for TbPdAl is determined from the maximum of dM/dH - H curve, as shown in Fig. 2(b). The value of B_C is found to decrease first slowly below T_t and then rapidly between T_t and T_N with the increase of temperature (see the inset of Fig. 2(b)). A similar result has been reported previously [13]. The B_C value at 9 K is 0.55 T, which is in good agreement with the value reported by Kitazawa et al. [14]. The low B_C indicates that the TbPdAl compound is a weak antiferromagnet, and a small magnetic field can destroy the AFM structure of TbPdAl, inducing an FM-like state. Therefore, the magnetization of TbPdAl is easily saturated below T_N and above the critical field due to the field-induced FM state; thus a high saturation magnetization is observed. The saturation moment at 5 K and in a magnetic field of 5 T is found to be $8.1 \mu_B$. Therefore, this is expected to be capable of achieving a large ΔS_M for TbPdAl.

Fig. 3 shows the Arrott plots of TbPdAl compound at different temperatures and its inset indicates the magnified Arrott plots in a temperature range of 9–39 K. According to the Banerjee criterion [20] a magnetic transition is expected to be of the

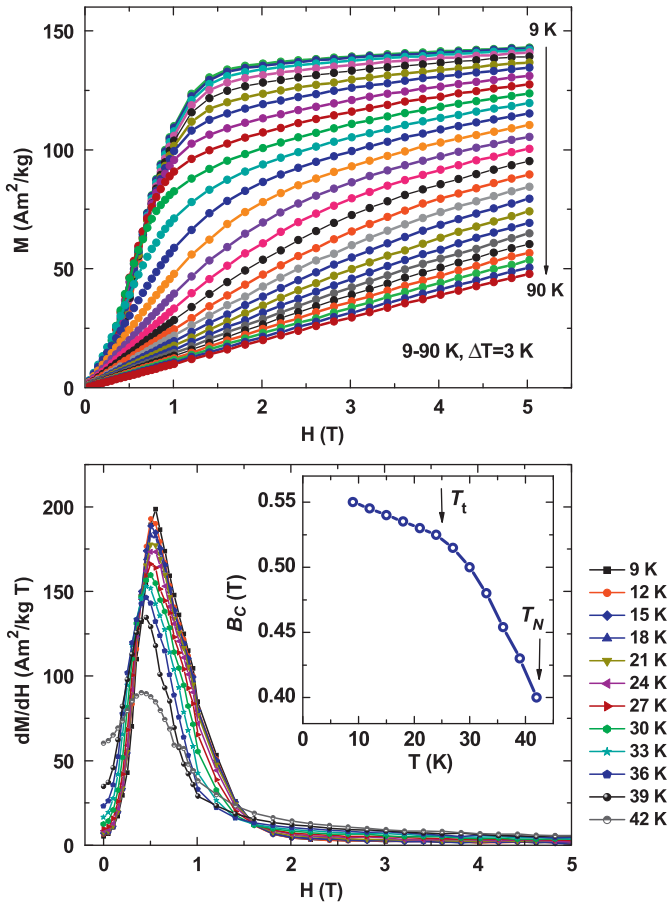


Fig. 2. Isothermal magnetization (M) and dM/dH as functions of magnetic field for TbPdAl around T_N . The inset shows the temperature dependence of the critical field (B_c) required for metamagnetic transition.

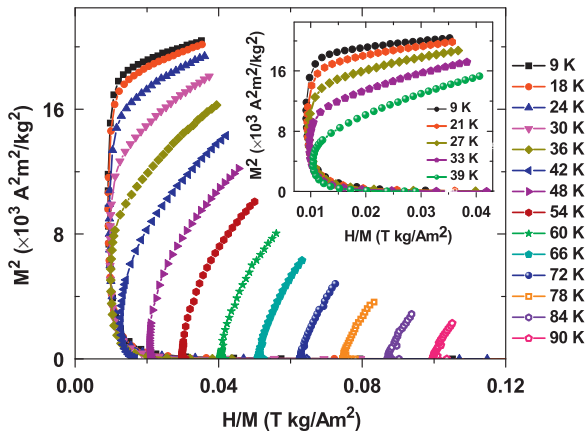


Fig. 3. Arrott plots of TbPdAl at different temperatures. The inset displays magnified Arrott plots in a temperature range of 9–39 K.

first-order when the slope of Arrott plot is negative, whereas it will be of the second-order when the slope is positive. It can be clearly seen from the inset of Fig. 3 that the Arrott plot of TbPdAl exhibits obviously a negative slope below T_N , confirming the existence of the field-induced first-order AFM–FM transition. However, the positive slope above T_N indicates a characteristic of field-induced second-order FM–PM transition.

The ΔS_M of TbPdAl is calculated based on the isothermal magnetization data. Fig. 4 shows $-\Delta S_M$ as a function of temperature for different magnetic field changes up to $H=5$ T. It is found that the

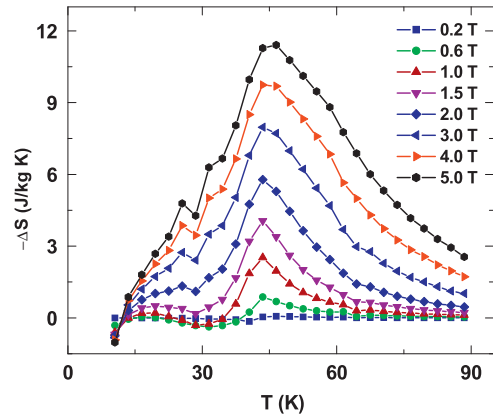


Fig. 4. Magnetic entropy change $-\Delta S_M$ as a function of temperature for TbPdAl for different magnetic field changes up to $H=5$ T.

values of ΔS_M of TbPdAl are positive at temperatures below T_N and under lower magnetic fields, but they change to negative values with temperature and applied field increasing due to the field-induced AFM–FM transition. The negative values of ΔS_M in the FM and the PM states result from magnetically more ordered configuration, with an external magnetic field applied [21]. However, the positive value of ΔS_M in the AFM ordering is due to disordered magnetic sublattices antiparallel to the applied magnetic field [22]. A small positive value of ΔS_M for TbPdAl indicates a weak dominance of AFM ordering at low temperatures. It can also be seen from Fig. 4 that the ΔS_M – T curve exhibits a small peak around T_t , which is associated with the frustrated AFM structure [15,16]. When the temperature is increased to T_N , the field-induced AFM–FM transition leads to a large negative ΔS_M . The maximum value of $-\Delta S_M$ is found to increase monotonically with applied magnetic field increasing and reaches a value of 11.4 J/kg K around T_N for a magnetic field change from 0 to 5 T, which is comparable to those of TbNiAl compound [5] and amorphous GdNiAl alloy [23], but it is much larger than those of RAI_2 ($R=Nd$ and Gd) compounds [24]. The RC value of TbPdAl compound has also been calculated using the approach suggested by Gschneidner et al. [25]. The RC is defined as $RC = \int_{T_1}^{T_2} |\Delta S_M| dT$, where T_1 and T_2 are the temperatures corresponding to both sides of the half-maximum value of ΔS_M peak. The estimated RC value for TbPdAl is 350 J/kg with $T_1=30.6$ K (temperature of the cold reservoir) and $T_2=69$ K (temperature of the hot reservoir) for a field changing from 0 to 5 T. It is interesting to note that although some compounds with a first-order phase transition exhibit large ΔS_M around their phase transition temperatures, their RC values are much smaller than that of TbPdAl due to the fact that the ΔS_M peaks of the first-order phase transition materials are relatively high and narrow; for instance $ErCo_2$ exhibits a ΔS_M value of 33 J/kg K, but an RC value of only 270 J/kg around its Curie temperature $T_c=35$ K for a field change of 0–5 T (the RC value is estimated from the temperature dependence of ΔS_M in the literature) [26]. The relatively large ΔS_M value and the considerable RC value around T_N for TbPdAl are due to the high saturation magnetization caused by the field-induced metamagnetic transition.

4. Conclusions

The TbPdAl compound orders antiferromagnetically below the Néel temperature $T_N=43$ K, accompanied with an additional first-order phase transition at $T_t=22$ K. The compound is a weak antiferromagnet and undergoes a field-induced metamagnetic transition from AFM to FM state below T_N , which gives rise to a large MCE. Sign change of MCE from negative to positive with

magnetic field and temperature increase is observed below T_N near the critical field at which the metamagnetic transition occurs. The maximal values of ΔS_M and RC are determined to be -11.4 J/kg K and 350 J/kg around T_N for a field change of $0-5$ T, respectively. The good magnetocaloric properties suggest that TbPdAl may be an appropriate candidate for magnetic refrigerant in low-temperature ranges.

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