Magnetic ordering and magnetocaloric effect in PrPdIn and NdPdIn

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Abstract. Magnetic, transport, thermal and magnetocaloric properties of the hexagonal ZrNiAl-type compounds PrPdIn and NdPdIn have been studied. The results indicate that both the compounds exhibit long-range ferromagnetic ordering with the transition temperature \( T_C = 11.2 \) and \( 34.3 \) K, respectively. For NdPdIn, an additional phase transition occurs at \( T_0 = 18.3 \) K caused by the antiferromagnetic coupling. The magnetic entropy change of PrPdIn and NdPdIn, calculated from the magnetization data, shows a large peak around the temperature just above \( T_C \) suggesting the evident magnetocaloric effect. Below \( T_C \), both samples show the irreversible temperature dependence of magnetization and the long time magnetic relaxation effect, which may be the consequence of the domain-wall pinning effect and/or the intrinsic magnetic frustration due to the non-collinear ferromagnetic spin structure.

1. Introduction

Equiatomic ternary compounds \( R \)PdIn crystallize in the hexagonal ZrNiAl-type crystal structure. A great variety of interesting physical properties of them has been reported in number of works including the experimental results of fundamental properties [1-12], neutron diffraction [13-15], inelastic neutron scattering [16] and x-ray photoemission spectroscopy [17]. These results suggest that long-range ferromagnetic (FM) ordering and irreversible magnetism exist in the \( R \)PdIn compounds with the Curie temperature \( T_C \approx 26-30 \), 54, 102, 66-74, 31-38, 22-25 and 11-12.3 K for \( R = \text{Nd, Sm, Gd, Tb, Dy, Ho and Er} \) [1-7], respectively, while an additional magnetic transition is observed below \( T_C \) for the Nd, Tb, Dy and Ho compounds [2,5,14]. On the other hand, light rare earth compound CePdIn [6,8,9] and heavy rare earth compound TmPdIn [3] are found to show AFM behaviour with the lower Néel temperature \( T_N = 1.7 \) and 2.7 K, respectively. Another light rare earth compound PrPdIn [6] and heavy rare earth compound YbPdIn [12] do not show magnetic ordering down to 1.7 K. In view of the sensitivity of the magnetic properties of \( R \)PdIn to the process of sample production [2,3,5], and to get a comprehensive and complete physical information, we have preformed a systematic investigation on the well-annealed (at 600 °C for one week) polycrystalline PrPdIn and NdPdIn samples by magnetic, transport, thermal and magnetocaloric measurements. In this paper, we present the new results of our investigation including dc magnetization, ac susceptibilities, high field magnetization, magnetic relaxation, specific heat, electrical resistivity and magnetocaloric effect. The sample preparation and experimental methods employed in the present investigation are the same as that in Ref. 5.
2. Results

Figure 1 shows the temperature dependences of the dc susceptibility $\chi (= M/H)$ of PrPdIn and NdPdIn measured in $H=100$ Oe under zero field-cooled (ZFC) and field-cooled (FC) conditions. At high temperatures, the $\chi_{ZFC}(T)$ behavior can be described by the modified Curie-Weiss law for the two samples similar to that observed by Gondek et al [6,14]. At low temperatures, however, our measurements reveal clearly different behaviours comparing with the data shown in the literatures. For PrPdIn, the $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ curves show rapid increase around $T_c=11.2$ K indicating the occurrence of a magnetic phase transition. Below $T_c$, a maximum value can be observed in $\chi_{ZFC}(T)$, while the value of $\chi_{FC}(T)$ increases monotonously leading to the bifurcation between the FC and ZFC curves. This irreversible (metastable) magnetic behaviour is characteristic of the FM nature of the transition at $T_c$, and is different from the earlier observation reported for a polycrystalline PrPdIn sample (annealed in vacuum at 800 °C for one week) that remains paramagnetic behaviour down to 1.7 K [6].

At low temperatures, $\chi_{ZFC}(T)$ curve of NdPdIn shows “two-peak structure” suggesting two magnetic transitions near the peak temperatures. Note that similar two-peak structure in $\chi_{ZFC}(T)$ was early reported for NdPdIn [14], and the first anomaly was connected with FM ordering, whereas the second one was considered to originate from the reorientation of the easy axis. Here, we would like to emphasize that our NdPdIn sample shows the FM transition at $T_c=34.3$ K, in addition, the nature of the transition seen at low temperature ($T_0=18.3$ K) is AFM like. As a typical character of the AFM transition at $T_0$, $\chi_{ZFC}(T)$ shows a peak near $T_0$ followed by continuous decrease down to the lowest temperature measured. On the other hand, the irreversible magnetic behaviour below $T_c$, i.e. bifurcation between the FC and ZFC curves, can be observed also in this system.

The insets of Fig. 1 show the high-field isothermal magnetization, $M(H)$, of PrPdIn and NdPdIn measured at 4.2 K. At low fields, $M(H)$ shows a fast increase, a behavior typical for ferromagnets. With a further increase of the field, $M(H)$ passes through a bend at about 2.5 kOe for NdPdIn and at 3 kOe for PrPdIn and than increases slowly. At $H=230$ kOe, $M(H)$ achieves a value of 2.01 $\mu_B$/Pr for PrPdIn and 2.38 $\mu_B$/Nd for NdPdIn, much smaller than 3.20 $\mu_B$/Pr and 3.27 $\mu_B$/Nd, the expected saturation values for PrPdIn and NdPdIn, respectively. This may arise due to the canted structure of the Pr/Nd magnetic moments as well as the presence of magnetocrystalline anisotropy.

Figure 2 shows the time ($t$) dependence of remanent magnetization $M$ of PrPdIn and NdPdIn. The samples were first ZFC from 150 K to the desired temperatures, then, a field of 0.5 kOe (for PrPdIn) and 1 kOe (for NdPdIn) was applied for 5 min and switched off at $t=0$. Clearly, for both the samples, the decay of $M(t)$ is remarkably slow, nonzero remanence could be detected after 3 h. Using a logarithmic function, $M(T, t)=M_0(T, 0)−S(T)\ln(t+t_0)$, the $M(t)$ behaviour of both compounds can be fitted very well with three $T$-dependent fitting parameters: initial zero-field magnetization $M_0(T)$, magnetic viscosity $S(T)$ and characteristic time $t_0$. The best fitting results are shown by the solid lines in Fig. 2 with positive $S$ values, which decrease with increasing $T$ for both compounds.

![Figure 1. Temperature dependences of the dc susceptibility of PrPdIn (a) and NdPdIn (b) in $H=100$ Oe. The insets show the high field magnetizations.](image)

![Figure 2. Time dependences of the isothermal remanent magnetization normalized to the value at $t=0$ for PrPdIn (a) and NdPdIn (b).](image)

![Figure 3. Temperature dependences of the real component of the ac susceptibility of PrPdIn (a) and NdPdIn (b) measured at various frequencies.](image)
Magnetic measurements on our polycrystalline PrPdIn sample (annealed at 600 °C) revealed a peak near 70 kOe at the temperatures around $T_C$. The evident peak observed in $\Delta S_m$ entropy change of PrPdIn was found down to 1.7 K [6]. This, to the best of our knowledge, is the solitary literature reported on PrPdIn. For NdPdIn, no anomaly can be detected in $\Delta S_m$ at $T_0$ (not shown here). These properties are also characteristic of the AFM nature of the low temperature transition.

The temperature dependence of electrical resistivity $\rho(T)$ and specific heat $C(T)$ of PrPdIn and NdPdIn are illustrated in Fig. 4. For both the samples, $\rho(T)$ shows a rapid decrease at $T_C$, while $C(T)$ exhibits an evident peak near $T_C$. On the other hand, for NdPdIn no anomaly can be detected in $\rho(T)$ and $C(T)$ curves near $T_0$=18.3 K. These results provide new evidence for the existence of FM order at $T_C$ in PrPdIn and NdPdIn, and the short range AFM correlations below $T_0$ in NdPdIn.

Magnetocaloric effect of the title compounds was also studied by measured $M(H)$ isotherms up to 70 kOe at the temperatures around $T_C$. Usually, magnetocaloric effect is characterized by magnetic entropy change $\Delta S_m$ caused by a field change. Using the Maxwell relation, $\Delta S_m(H) = \int [\partial (\rho M^2 / \partial T)]_H dH$, $\Delta S_m$ can be calculated from the $M(H)$ data. The measurements of $M(H)$ and the calculated results of $\Delta S_m$ are shown in Figs. 5 and 6, respectively. The $\Delta S_m$ vs $T$ plot for PrPdIn shows a large and broad peak near $T_C$ with the value of $\Delta S_m$=-6.35 J kg$^{-1}$ K$^{-1}$ for $\Delta H$=70 kOe. This is a further evidence for the FM transition occurring in PrPdIn. For NdPdIn, evident peak is also clear in $\Delta S_m(T)$ near $T_C$ followed by broad bending around $T_0$. This observation indicates that the system from the short range AFM correlation state could also lead to evident magnetic entropy change. Both the compounds show positive MCE (negative $\Delta S_m$) as usually observed in conventional FM materials.

3. Discussion and conclusions

The temperature dependences of specific heat and dc magnetization (in $H$=1 kOe) were early reported for the polycrystalline PrPdIn (annealed at 800 °C for one week), and no sign of magnetic ordering was found down to 1.7 K [6]. This, to the best of our knowledge, is the solitary literature reported on PrPdIn with respect to its magnetic properties up to date. Magnetic measurements on our polycrystalline PrPdIn sample (annealed at 600 °C for one week), however, show different magnetic behavior. The evident peaks observed in $M(T)$, $\chi''(T)$, $C(T)$ and $\Delta S_m(T)$ curves as well as the rapid decrease in $\rho(T)$ curve near $T_C$=11.2 K strongly suggest that the PrPdIn sample undergoes a FM phase transition. To further confirm this conclusion neutron diffraction study is necessary. For NdPdIn, the existence of FM transition near ~30 K has been confirmed by neutron diffraction measurements [14].
Moreover, we observed the clear anomalies in $M(T)$, $\chi''(T)$ and $\Delta S_m(T)$ curves near $T_c (=18.3$ K), which may be originate from the short range AFM ordering due to a change in the direction of the Nd magnetic moments. Note that the neutron diffraction patterns collected at 15 K reveal that the Nd magnetic moments in NdPdIn are tuned out from the basal plan for an angle of about 50° [14].

A finding of emphasis here is that both PrPdIn and NdPdIn show the metastable magnetism manifesting as the difference between FC and ZFC magnetizations and long time magnetic relaxation effect below $T_C$. Such a metastable magnetic behavior has been reported in some other intermetallic compounds with long range magnetic order [18]. We believe that both the domain-wall pinning effect and the intrinsic magnetic frustration may be responsible for this behavior. The frustrated magnetic moments in PrPdIn and NdPdIn could be induced by the topology and the partially AF coupling between nearest neighbours of Pr/Nd moments similar to that confirmed in the isostructural compound DyPdIn [13].

In conclusion, magnetic, transport, thermal and magnetocaloric properties are measured on PrPdIn and NdPdIn. In particular, the ac susceptibility, high field magnetization, magnetic relaxation and electrical resistivity measurements are first reported in this work. Our PrPdIn sample was found to be FM system with Curie temperature $T_C=11.2$ K unlike the results reported early. This suggests that magnetic behavior of PrPdIn is sensitive to the heat treatment conditions. The $M(T)$, $\chi''(T)$, $\rho(T)$, $C(T)$ and $\Delta S_m(T)$ measurements of NdPdIn indicate the presence of complex magnetic state with long range FM ordering below $T_C (~34.3$ K) as well as short range AFM correlations below $T_N (~18.3$ K). For both PrPdIn and NdPdIn, irreversible temperature dependence of magnetization and the long time magnetic relaxation are observed below $T_C$. Taking into account the neutron diffraction results of NdPdIn and some other RPdIn systems, we believe that the ground state of either PrPdIn or NdPdIn is not collinear ferromagnet, but some canted one with AFM spin component.

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