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Magnetic, magnetocaloric and magnetoresistance properties of Nd_7Pd_3

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Abstract
Magnetic, magnetocaloric and magnetoresistance properties of the intermetallic compound Nd_7Pd_3 have been investigated. It exhibits a first-order magnetic phase transition at its ferromagnetic ordering temperature ($T_C = 34$ K). Just above the T_C, the magnetization isotherms exhibit a metamagnetic transition from the paramagnetic to a ferromagnetic state. In the immediate vicinity of T_C, a field change of only 10 kOe leads to the giant magnetocaloric effect of 13 J mol^{-1} K^{-1}. For a field change of 50 kOe a large magnetoresistance of $\sim$21% is observed near T_C. First-principles electronic structure calculations indicate that the first-order phase transition in Nd_7Pd_3 may originate from the peculiar nature of the density of states near the Fermi level.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The rich variety of magnetic phenomena exhibited by rare-earth-(R) based intermetallics makes them a unique play-ground for both fundamental studies and for applications based on the magnetostriction, magnetoresistance and magnetocaloric effect (MCE) [1–4]. Among various applications, the one based on the MCE is still in its infancy. MCE is an intrinsic property of magnetic materials and it can be measured in terms of the isothermal magnetic entropy change (ΔS_M) and/or the adiabatic temperature change (ΔT_{ad}) [4]. MCE is the underlying physical property for an energy-efficient and environmentally friendly technology, namely magnetic refrigeration, and, therefore, the materials exhibiting a large MCE are of great importance.

Although the phenomenon of the MCE has been known for over 100 years, the research in the field received impetus only after the discovery of the giant magnetocaloric effect (GMCE) in $Gd_5Si_2Ge_2$ [5]. Further investigations showed that the GMCE is not a peculiar property of $Gd_5Si_2Ge_2$ but is also exhibited by several other members of the $R_5(Si, Ge)_4$ series of compounds [6, 7]. The continued effort in the field has revealed that the GMCE occurs in other families of compounds such as $La(FeSi)_{13}$ [8], MnAs [9], FePMnAs [10], RCo_2 [11, 12], Heusler alloys [13], manganites [14] and a few others as well. In all these materials, the GMCE arises due to the occurrence of first-order magnetic phase transitions. It has been shown that, owing to a large contribution from the structural entropy, the low field MCE of materials exhibiting a first-order transition (FOT) may be enhanced drastically [15]. Furthermore, owing to the structural transformation, the compounds having FOT show a dramatic change in the density of states near the Fermi level and thereby exhibit large magnetoresistance (MR) [16, 17]. Therefore, materials exhibiting FOT are promising for both fundamental studies and applications based on MCE and MR.

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In this paper we report on the magnetic, magnetocaloric and magnetoresistance properties of the intermetallic compound Nd_7Pd_3. The compound exhibits an FOT at its ferromagnetic ordering temperature (T_C) of 34 K. At temperatures close to T_C in the paramagnetic state, the magnetization isotherms of Nd_7Pd_3 show a metamagnetic transition leading to the field-induced formation of the ferromagnetic phase. As a consequence of FOT, Nd_7Pd_3 shows a GMCE of 13 J mol^{-1} K^{-1} for a field change of only 10 kOe, which is about twice as large as that of $ErCo_2$ [12]. Furthermore, for a field change of 50 kOe the Nd_7Pd_3 exhibits a magnetoresistance of about 21% at 36 K. First-principles calculations indicate that the presence of a pronounced peak in the density of states just below the Fermi level is likely to be the reason for the metamagnetism of Nd_7Pd_3.

2. Experimental details

The Nd_7Pd_3 alloy was prepared by arc melting of the stoichiometric mixture of the constituent elements under an argon atmosphere. The Nd and Pd used for the synthesis were 99.9 wt% and 99.99 wt% pure, respectively. To ensure homogeneity the ingot was re-melted five times with the button flipped after every melting, and then annealed at 873 K for a week. The Rietveld refinement of the room temperature x-ray diffraction pattern collected using Cu Kα radiation revealed that Nd_7Pd_3 crystallizes in the hexagonal Th_7Fe_3-type structure (space group $P6_3mc$) with lattice parameters $a = b = 10.1369(8)$ Å and $c = 6.383\,54(6)$ Å. The lattice parameters obtained from refinement compare well with the previously reported values [18]. The sample contained a trace (<5%) of an impurity phase—Nd_3Pd_2. The magnetization (M) measurements under zero-field-cooled (ZFC), field-cooled–cooling (FCC) and field-cooled–heating (FCH) modes were performed using a SQUID magnetometer and a vibrating sample magnetometer. The magnetization isotherms were collected after reaching the target temperature in the ZFC mode from temperatures well above the ordering temperature. The electrical resistivity was measured using a physical property measurement system (PPMS) by employing a four-probe technique.

3. Results and discussion

The temperature (T) dependence of magnetization (M) data of Nd_7Pd_3 has been collected in various applied fields (H) under ZFC, FCC and FCH conditions. Figure 1(a) shows ZFC, FCC and FCH $M(T)$ of Nd_7Pd_3 collected in $H = 1$ and 10 kOe whereas figure 1(b) shows the temperature dependence of the FCH inverse magnetic susceptibility and the Curie–Weiss ($M/H = C/(T - \theta_P)$) fit to it. We note that the compound exhibits only a ferromagnetic (FM) transition at the ordering temperature (T_C) of 34 K. This is in contrast to observations of Kadomatsu *et al* [18] where the Nd_7Pd_3 was reported to order antiferromagnetically at 38 K and then ferromagnetically below 33 K. It may be seen from figure 1(a) that, at T_C, the $M(T)$ shows a sharp change and the $M(T)$ data obtained in FCC and FCH conditions show large thermal hysteresis. It

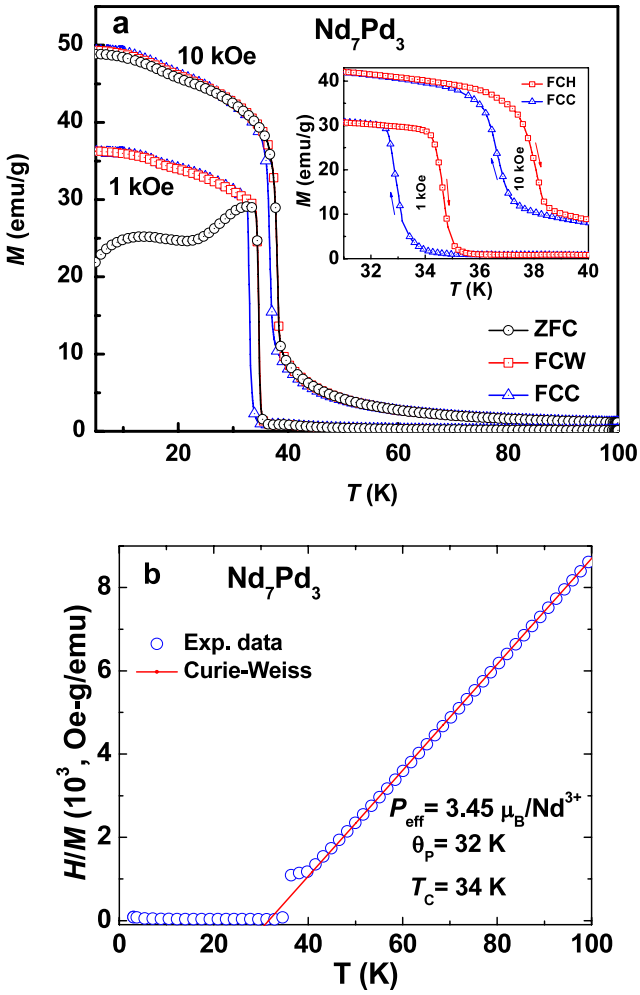

Figure 1. (a) Temperature (T) dependences of the magnetization (M) of Nd_7Pd_3 collected under zero-field-cooled (ZFC), field-cooled–cooling (FCC) and field-cooled–heating (FCH) modes in applied magnetic fields (H) of 1 and 10 kOe. (b) Temperature variation of the inverse magnetic susceptibility (H/M) obtained in $H = 500$ Oe along with the Curie–Weiss fit. The inset in (a) shows the $M(T)$ data under FCC and FCH modes expanded near the magnetic ordering temperature.

is well known that the thermal hysteresis is a characteristic feature associated with FOT [19]. Therefore, the observation of a sharp transition at T_C and the thermal hysteresis is attributed to the first-order transition at T_C. This is in accord with a large discontinuity in the temperature dependence of linear thermal expansion at the FM ordering in Nd_7Pd_3 [18].

Besides the thermal hysteresis between the FCH and FCC, the $M(T)$ data collected between ZFC and FCH/FCC modes also show considerable difference. This thermomagnetic irreversibility decreases with increasing applied field and disappears completely for $H = 5$ kOe. It is well known that the magnetic materials with large magnetocrystalline anisotropy and low T_C possess narrow domain walls and, owing to the domain wall pinning effect, such systems show thermomagnetic irreversibility [20]. The low T_C and large magnetocrystalline anisotropy associated with an Nd sublattice may be responsible for the large thermomagnetic irreversibility in Nd_7Pd_3 [20].

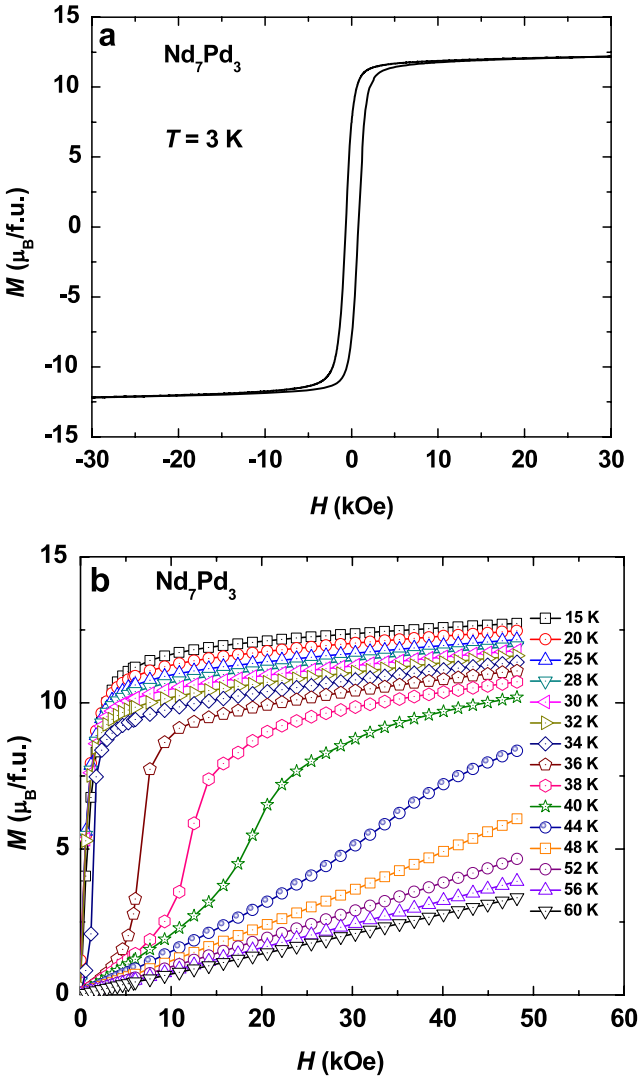

Figure 2. (a) Field (H) dependence of magnetization (M) isotherm of Nd_7Pd_3 at $T = 3$ K. (b) $M(H)$ isotherms collected at various temperatures near the magnetic ordering temperature ($T_C = 34$ K).

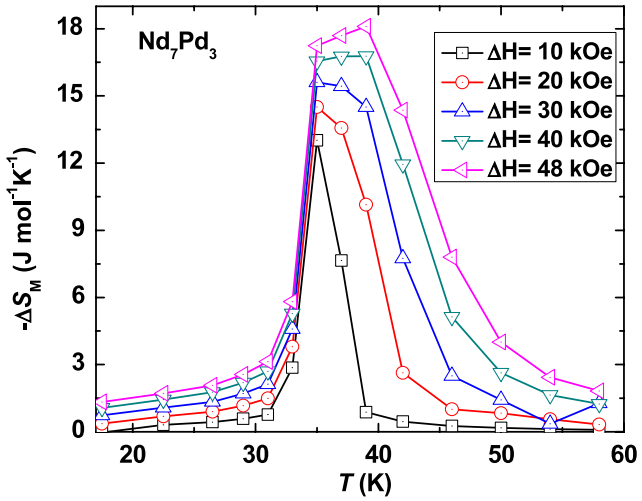

Figure 3. Temperature dependences of the isothermal magnetic entropy change (ΔS_M) of Nd_7Pd_3 for various field changes.

Figure 1(b) shows that above 45 K the magnetic susceptibility obeys the Curie–Weiss law with the paramagnetic Curie temperature (θ_P) and effective magnetic moment (P_{eff}) of 32 K and 3.45 μ_B/Nd^{3+}, respectively. The positive value of θ_P indicates that the ground state of Nd_7Pd_3 is ferromagnetic. We note that the experimentally determined P_{eff} is close to the theoretical value $[g\{J(J+1)\}^{1/2}]$ of 3.62 μ_B expected for non-interacting Nd^{3+} ions. Therefore, this observation indicates that the Pd sublattice of the title compound is nonmagnetic.

Figure 2 shows the magnetization isotherms of Nd_7Pd_3 at various temperatures. $M(H)$ isotherms below T_C show hysteresis consistent with the FM nature of the ground state of Nd_7Pd_3. The isotherm at $T = 3$ K (figure 2(a)) yields a saturation moment of 1.8 μ_B/Nd^{3+}, which compares well with the previous report [18]. The lower value of the saturation moment as compared to that of the expected moment $[gJ = 3.3\ \mu_B/Nd^{3+}]$ can be attributed to the crystalline electric field effect.

We note that for low magnetic fields (<4 kOe) the $M(H)$ isotherms of Nd_7Pd_3 above 34 K show nearly linear dependence on H (figure 2(b)). However, above a certain critical field (H_C), these isotherms exhibit a metamagnetic transition with hysteresis (not shown) between the field increasing and decreasing branches. The hysteresis associated with metamagnetic transition is consistent with the first-order character of the metamagnetic process. The magnetization above H_C shows a tendency towards saturation, which indicates that the field-induced state is FM. This behavior is consistent with the metamagnetic transition reported by Kadomatsu *et al* [18]. Based on the 16 kOe magnetization data, the authors of [18] argued that the FM state of Nd_7Pd_3 exists below 33 K and that the compound is antiferromagnetic (AFM) between 33 and 38 K. They have suggested that the paramagnetic (PM) state exists only above 38 K and that above T_C the metamagnetic transition arises from a field-driven conversion of the AFM to FM state [18]. Our $M(T)$ data indicate that Nd_7Pd_3 exhibits only the FM–PM transition at 34 K and that the metamagnetic feature in the $M(H)$ data has been observed up to $T = 44$ K, which is higher than the AFM ordering temperature determined by Kadomatsu *et al* [18]. Hence this proves that the metamagnetic transition in the Nd_7Pd_3 originates from a field-induced PM–FM transition and not from an AFM–FM transition. A similar field-driven PM–FM transition has been reported in several other intermetallic compounds [8, 12, 21].

Using the $M(H)$ data collected at various temperatures the magnetocaloric behavior of Nd_7Pd_3 has been determined in terms of the isothermal magnetic entropy change (ΔS_M) and shown in figure 3. We note that Nd_7Pd_3 exhibits reversible MCE and for field changes (ΔH) of only 10 kOe, the maximum value of $\Delta S_M(\Delta S_M^{max})$ is 13 J mol^{-1} K^{-1}. For $\Delta H = 20$ and 48 kOe, the ΔS_M^{max} values are 14.5 and 18 J mol^{-1} K^{-1}, respectively. In $ErCo_2$, which is a noted potential magnetic refrigerant material around 35 K, $\Delta H = 10$ kOe gives rise to ΔS_M^{max} of ~4.8 J mol^{-1} K^{-1} [22]. For $\Delta H = 50$ kOe, the ΔS_M^{max} values of $ErCo_2$, $(Dy_{0.7}Er_{0.3})Al_2$,

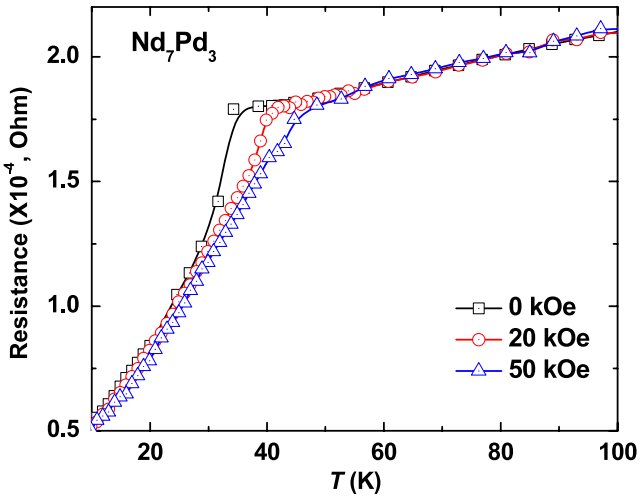

Figure 4. Temperature (T) dependences of the electrical resistance (R) of Nd_7Pd_3 measured in various applied magnetic fields.

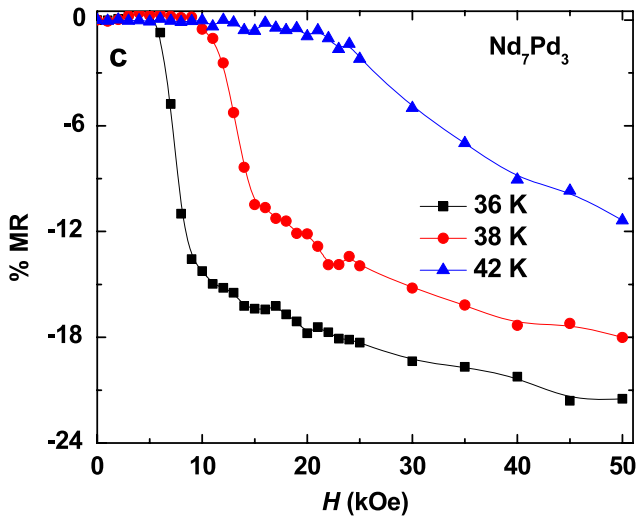

Figure 5. Field dependence of the magnetoresistance (MR) at temperatures close to the magnetic ordering temperature ($T_C = 34$ K).

$TbNi_2$, DyCoAl, $TbCoC_2$, DySb and Gd_2PdSi_3, which have magnetic ordering temperatures comparable to that of Nd_7Pd_3, are 9.2, 4, 4.1, 3.6, 4.6 and 6 J mol^{-1} K^{-1} [4, 22–26]. These values are significantly smaller than that of Nd_7Pd_3. However, the ΔS_M^{max} value of Nd_7Pd_3 is about half of that of the giant magnetocaloric $R_5(Si_{1-x}Ge_x)_4$ series. For example, the ΔS_M^{max} values of Dy_5Si_3Ge and $Gd_5Si_{0.33}Ge_{3.67}$ are 34 and 37 J mol^{-1} K^{-1}, respectively, for $\Delta H = 50$ kOe [4]. Thus, the ΔS_M^{max} of Nd_7Pd_3 lies between that of materials which exhibit the usual MCE and GMCE.

It is well known that a change in the magnetic state is also reflected in electrical resistivity behavior. Thus, to further understand the magnetic properties of Nd_7Pd_3 we have measured the temperature dependence of electrical resistance under various applied fields and the results are shown in figure 4. We note that the compound exhibits metallic character over the entire temperature range and, owing to the loss of spin disorder scattering brought about by the spontaneous magnetic ordering, the electrical resistivity shows a faster drop at $T_C = 34$ K. Furthermore, except for the anomaly at T_C, no additional anomalies in the resistivity data are seen. This indicates that the Nd_7Pd_3 possesses only one magnetic transition, which is in accord with the magnetization measurements. With the increase in the field strength, the suppression of the spin disorder scattering occurs at temperatures above T_C as well.

Figure 5 shows the field dependence of magnetoresistance (MR), defined as $[\{R(T, H) - R(T, 0)\}/R(T, 0)]$, of Nd_7Pd_3 at various temperatures just above T_C. At 36 K, for low fields ($H < 5$ kOe) the MR is negligible; however, it shows a sudden increase in the absolute value at $H = 6$ kOe and for $H = 50$ kOe it attains a negative value of ∼21%. A similar behavior is seen at 38 and 42 K also. However, at these latter two temperatures, the field at which the MR shows discontinuity increases to 11 and 25 kOe, respectively. For $H = 50$ kOe the MR attains a negative value of 18% and 11.5% at 38 K and 42 K, respectively. It is well known that, because of the Lorentz force term, in a metallic system the application of magnetic field gives rise to a positive contribution to MR [17, 27] and, therefore, the existence of large negative MR at temperatures above T_C indicates that there is considerable spin scattering involved in the electronic transport process, which is suppressed by the field. Furthermore, we note that the fields associated with the discontinuity in MR match well with the critical fields for PM–FM transition determined from magnetization data (see figure 2(b)). Thus, these results further support that in Nd_7Pd_3 the large negative MR above T_C arises from a suppression of spin disorder scattering contribution to the electrical resistivity brought about by the field-induced PM–FM transition. Here, we would like to emphasize that the MR data clearly shows that the metamagnetic transition occurs at 42 K, which is higher than the AFM ordering temperature reported by Kadomatsu *et al* [18]. Therefore, the MR data also indicates that the metamagnetic transition in Nd_7Pd_3 originates from a field-induced PM–FM transition and not from an AFM–FM transition.

In order to determine the possible origin of the first-order transition at the magnetic ordering temperature and, therefore, the GMCE and large MR in Nd_7Pd_3, the paramagnetic and ferromagnetic self-consistent total energy and density of states (DOS) calculations have been performed by employing the tight binding linear muffin tin orbital method within the local spin density approximation by treating 4f electrons as core electrons [28]. The results are shown in figure 6. The FM total energy calculated by assigning 3 μ_B 4f spin moments in each Nd atom is lower than the PM total energy calculated by assigning equal spin-up and spin-down 4f moments in each Nd atom. This confirms the FM state as the ground state for Nd_7Pd_3.

We note that in Nd_7Pd_3 the Fermi energy (E_F) lies on the rapidly decaying slope of a pronounced peak. According to Rhodes and Wohlfarth [29], such a feature in DOS is necessary for the occurrence of a metamagnetic phase transition and has been observed in other metamagnetic compounds such as $ErCo_2$ [30]. As follows from figure 6, most of the 4d electrons of the Pd atom are localized at −4 eV. The paramagnetic

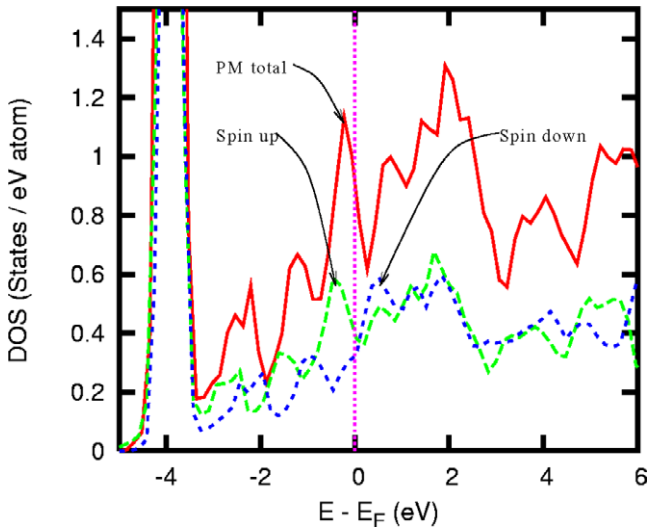

Figure 6. Paramagnetic (solid line) and spin polarized (dashed lines) total density of states (DOS) of Nd_7Pd_3. The Fermi level has been shifted to zero of the energy scale.

DOS at the Fermi level, which has a 75% contribution from Nd and a 25% contribution from Pd, is 0.9 states/eV atom. The spin polarized calculation indicates that, because of the indirect 4f–4f exchange interactions between Nd atoms, the peak of the paramagnetic DOS just below the Fermi level splits into spin-up (at −0.4 eV) and spin-down (at 0.57 eV) bands. Interestingly, the product of the paramagnetic spd DOS at the Fermi level and the exchange splitting of Nd 5d is 0.87, indicating that the Stoner criterion of ferromagnetism is nearly satisfied in Nd_7Pd_3. Therefore, the presence of the pronounced peak in the paramagnetic DOS just below the Fermi level and the splitting of the conduction bands when 4f moment order may be the origin of the metamagnetic transition in Nd_7Pd_3.

4. Conclusions

To summarize, the Nd_7Pd_3 possesses a first-order transition at its ferromagnetic ordering temperature of 34 K and, above T_C, it exhibits a field-driven reconstruction of ferromagnetic phase. For a field change of only 10 kOe, it exhibits a giant magnetocaloric effect of 13 J mol^{-1} K^{-1}. Associated with the suppression of the spin disorder scattering that arises from field-induced PM–FM transition, a large negative magnetoresistance is observed near T_C. First-principles calculations show that the presence of a pronounced peak in DOS just below the Fermi level may account for the origin of the metamagnetism.

Acknowledgments

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