ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 343–347

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Evolution of ferromagnetism in $Y_{1-x}Pr_xInNi_4$ and its magneto caloric effect

N. Tsujii*, O. Suzuki, H. Suzuki, H. Kitazawa, G. Kido

National Institute for Material Science, Sengen 1-2-1, Tsukuba 305-0047, Japan

Available online 20 June 2005

Abstract

$PrInNi_4$ has a nonmagnetic ground state and exhibits a field-induced nonmagnetic–ferromagnetic transition by a small field of ∼0.6 T at low temperature. To clarify the origin of this novel transition, we have prepared the Y-substituted samples, $Y_{1-x}Pr_xInNi_4$ and have studied their electrical resistivity and magnetization. Resistivity suggests that the crystal-field splitting scheme is almost unchanged by dilution from that of $PrInNi_4$. Magnetic susceptibility $\chi(T)$ of the dilute sample well agrees with the calculation based on the crystal field splitting of $PrInNi_4$. It is found that $\chi(T)$ of $PrInNi_4$ is significantly enhanced at low temperatures from that of the dilute system, suggesting that intersite ferromagnetic-correlation develops at low temperatures. We also have investigated the magneto caloric effect in $PrInNi_4$. By adiabatic demagnetization from 1 T, temperature decrease from 1.4 K to 0.7 K is observed.

PACS: 75.30.Sg; 75.30.Cr; 75.30.Kz; 71.27.+a

Keywords: Intermetallics; Magnetically ordered materials; Magnetic measurements; Electronic transport

1. Introduction

Pr-based compounds are recently extensively studied due to their novel properties. For instance, $PrInAg_2$ is reported to show heavy-fermion-like behavior with a large electronic specific-heat coefficient, $\gamma = 6\,J/mol\,K^2$ [1]. $PrOs_4Sb_{12}$ exhibits superconductivity below $T_c = 1.8\,K$ [2], and this superconductivity is considered to be a non-BCS type one [3]. These phenomena cannot be explained by the conventional Kondo-lattice picture [4], because these Pr-based compounds are considered to have a nonmagnetic crystal-field ground state [1,2]. It is hence of particular importance to study new Pr-based compounds.

Recently, we have studied magnetic and electrical properties of the ternary system $PrInNi_4$ [5]. This compound has previously been reported to exist as a member of $RInNi_4$ series (*R* = Ce–Lu) with the cubic $MgSnCu_4$ structure [6]. We have found that $PrInNi_4$ has a nonmagnetic ground state due to the crystal electric field (CEF) effect, and have discovered a novel field-induced transition from nonmagnetic to ferromagnetic state by a small magnetic field of 0.6 T [5].

In this paper, we present our results on the diluted system $Y_{1-x}Pr_xInNi_4$. This diluted system is expected to shed light on the origin of the novel transition in $PrInNi_4$. In addition, we present a magneto caloric effect in $PrInNi_4$. Using the metamagnetic transition, $PrInNi_4$ can be served as a magneto cooling material that works under a small magnetic field.

In the next section, we describe the experimental procedures. In Section 3, physical properties of $PrInNi_4$ are briefly summarized. In Section 4, experimental results for $Y_{1-x}Pr_xInNi_4$ are presented. Magneto cooling effect in $PrInNi_4$ is shown in Section 5. Finally, concluding remarks are given in Section 6.

2. Experimental

Polycrystalline samples of $PrInNi_4$ and $Y_{1-x}Pr_xInNi_4$ ($x = 0, 0.1, 0.2$) have been prepared by melting pure elements

* Corresponding author.
E-mail address: tsujii.naohito@nims.go.jp (N. Tsujii).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.162

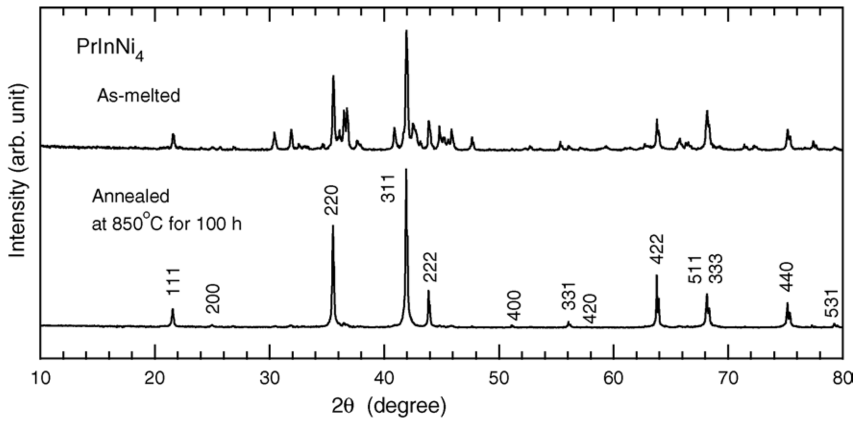

Fig. 1. Powder X-ray diffraction pattern of $PrInNi_4$. The upper and the lower patterns are those for as-melted and annealed samples, respectively.

in Ar arc-furnace and subsequent annealing in evacuated silica tubes at 850°C for several days. Samples were analyzed by using X-ray diffraction (XRD) and an energy dispersive X-ray spectrometer (EDS) equipped in a scanning electron microscope (SEM). The as-melted sample of $PrInNi_4$ was found to consist of several phases. After the annealing procedure, single phased $PrInNi_4$ with the cubic $MgSnCu_4$ structure is formed. In Fig. 1, powder XRD patterns of as-melted and annealed $PrInNi_4$ samples are shown. The XRD pattern of the annealed sample is consistent with that of the cubic $MgSnCu_4$ structure, whereas that of the as-melted one is of multi-phases. Then, annealed samples were used for all the physical property measurements.

Magnetic susceptibility and magnetization measurements were performed using a superconducting quantum interference device magnetometer. Electrical resistivity was measured by a four-probe method. Magneto caloric effect was evaluated by measuring the temperature of the sample by a Cernox resistance thermometer attached on the sample.

3. Field-induced ferromagnetic transition in $PrInNi_4$

In Fig. 2, temperature dependence of the magnetization divided by field, M/H, of $PrInNi_4$ is shown. For $H = 0.1\,T$, M/H shows no evidence of magnetic transition, consistent with the nonmagnetic crystal-electric-field (CEF) level. On the other hand, M/H above $H = 0.5\,T$ shows a jump at low temperatures. For $H = 0.5\,T$, this jump is seen at $T_c = 1.8\,K$, and shifts to higher temperatures with the increase of applied field. Below T_c, it is found that the magnetization reaches to $\sim 1.5\mu_B$. These results indicate that ferromagnetic transition is induced by fields above 0.5 T.

In the inset of Fig. 2, the value of T_c is plotted against the applied field. It is found that T_c linearly decreases with the decrease of applied fields, and the extrapolation predicts that the ferromagnetic transition occurs even for $H = 0\,T$ at $T = 0.7\,K$. This has been actually demonstrated by recent magnetization measurements [7]. Interestingly, the transition has been found to be first-order.

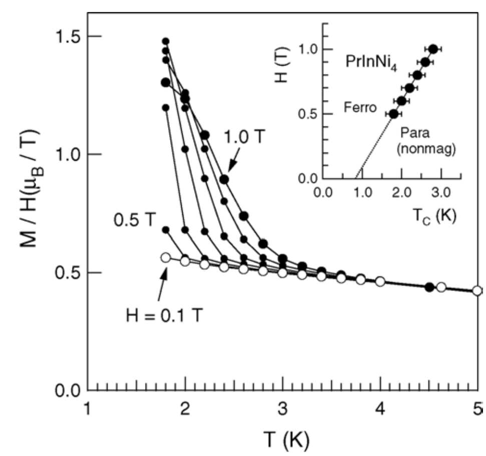

Fig. 2. Temperature dependence of the magnetization divided by field of $PrInNi_4$. Data measured at $H = 0.1$, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 T are shown. Inset shows the field variation of the transition temperature T_c.

These ferromagnetic transition may be compared with that of so-called ‘induced-ferromagnets’, which have a nonmagnetic ground state but have ferromagnetic transition due to a mixing with magnetic excited-states. Such examples are Pr_3Tl [8], PrPtAl [9], Pr_3Se_4 [10], etc. and their ferromagnetic moments are less than $1\mu_B$. On the other hand, $PrInNi_4$ has a large moment of $\sim 2\mu_B$ [5], almost the saturation value of the first excited level [7]. We, therefore, conclude that the crystal field scheme drastically changes at this transition.

4. Properties of $Y_{1-x}Pr_xInNi_4$

In order to study the mechanism of the novel transition in $PrInNi_4$, dilute system $Y_{1-x}Pr_xInNi_4$ has been investigated. Dilution with $LaInNi_4$ would be ideal if available. However, preparation of $LaInNi_4$ was found to be unsuccessful.

In Fig. 3, electrical resistivity $\rho(T)$ of $Y_{1-x}Pr_xInNi_4$ is shown. $\rho(T)$ of $PrInNi_4$ shows a downturn below 20 K. The downturn is explained as due to the decrease of magnetic scattering since the lowest CEF level is nonmagnetic. This is

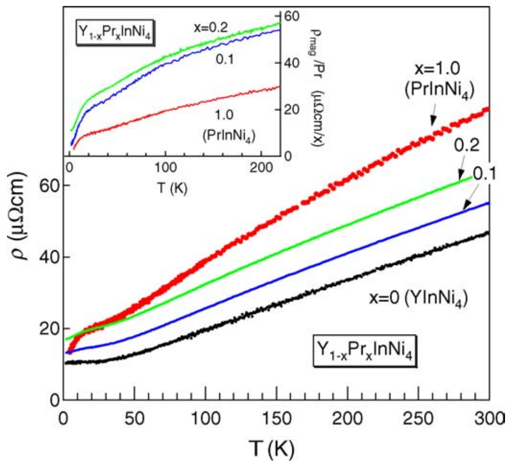

Fig. 3. Temperature dependence of the electrical resistivity $\rho(T)$ of $Y_{1-x}Pr_xInNi_4$. Inset shows magnetic contribution of resistivity $\rho_{mag}(T)$ normalized by the Pr-concentration x.

consistent with the CEF splitting of about 20 K observed by specific heat and neutron scattering [7]. Notably, similar behavior is seen for the dilute systems, $x = 0.1$ and 0.2, though the extent of downturn is not so pronounced. This feature is more clearly seen in the inset of Fig. 3, where the magnetic contribution of resistivity, ρ_{mag} is plotted. Here, ρ_{mag} is derived from $(\rho_{observed} - \rho_{YInNi_4})/x$. The similarity of ρ_{mag} demonstrates that the CEF level schemes of the dilute systems are almost the same as that of $PrInNi_4$. The absolute value of ρ_{mag} of $PrInNi_4$ is smaller than those of $x = 0.1$ and 0.2. This would be due to the difference in the phonon contribution between $YInNi_4$ and $PrInNi_4$.

In Fig. 4, magnetic susceptibility $\chi(T)$ of $Y_{1-x}Pr_xInNi_4$ is shown. $\chi(T)$ of $PrInNi_4$ shows a saturation behavior at low temperatures due to the nonmagnetic CEF level. This saturation is also seen in $\chi(T)$ of $x = 0.1$ and 0.2. This is consistent with the conclusion mentioned above; i.e., the same crystal field scheme as that of $PrInNi_4$. The solid line is a calculation using the CEF scheme of $PrInNi_4$ obtained from the specific heat and neutron scattering experiments [7]. At high temperatures (>100 K), all the $\chi(T)$ curves ($x = 1.0$, 0.2, and 0.1) agree well with the CEF calculation. Here, note that the $\chi(T)$ are normalized by the Pr-concentration x. The coincidence of $\chi(T)$ curves at $T > 100$ K indicates that the magnetic moments of Pr ions are dominated by the single-site CEF effect, and the intersite correlations are not so important above 100 K.

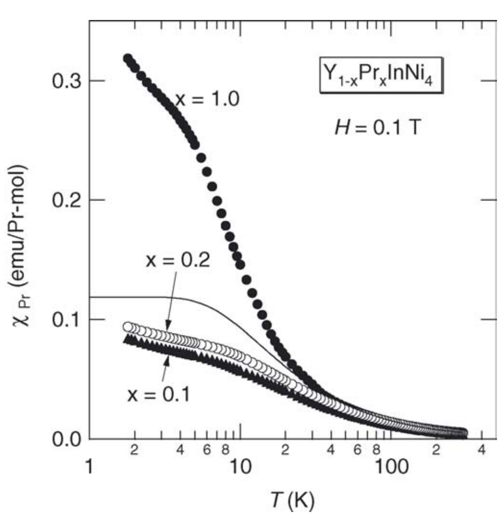

Fig. 4. Temperature dependence of the magnetic susceptibility $\chi(T)$ of $Y_{1-x}Pr_xInNi_4$ measured at $H = 0.1$ T. Solid line is a calculation. See text for details.

Below about 30 K, it is clearly seen that $\chi(T)$ of $x = 1.0$ enhances remarkably compared to those of $x = 0.1$ and 0.2. This deviation indicates that ferromagnetic interaction starts to develop between the Pr ions for $x = 1.0$ below about 30 K. It should be noted that the magnetic interaction is considered to be antiferromagnetic at high temperatures ($T > 100$ K), as was suggested by the negative Curie–Weiss temperature $\theta = -11.4$ K [5]. Although this contradiction seems to be difficult to explain, it may be useful to point that the enhancement of $\chi(T)$ of $PrInNi_4$ is most prominent below 30 K, which is the same order of the CEF splitting between the lowest and the first excited levels. Furthermore, the neutron scattering experiments have revealed that the lowest CEF level is Γ_3, which is nonmagnetic but has a quadrupolar moment. It is, therefore, suggested that intersite quadrupolar correlation can be responsible for the evolution of ferromagnetic interactions.

In contrast to the data of $x = 1.0$, such ferromagnetic enhancement is not observed in the $\chi(T)$ curves of $x = 0.1$ and 0.2, which appear to be rather consistent with the CEF calculation. Although the observed $\chi(T)$ is smaller than the CEF calculation especially below 30 K, this deviation can be attributed to the quantitative difference in the CEF parameter: CEF splitting in $x = 0.1$ and 0.2 would be somewhat larger than that in $PrInNi_4$ due to the smaller lattice parameters in the former than the latter. This causes the decrease in the Van–Vleck contribution to $\chi(T)$, which decreases with the increase of the splitting energy between the CEF levels.

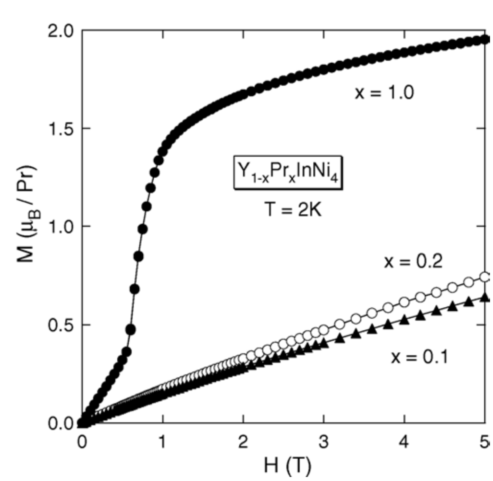

Fig. 5. Field dependence of the magnetization of $Y_{1-x}Pr_xInNi_4$ measured at $T = 2$ K.

In Fig. 5, field dependence of the magnetization $M(H)$ of $Y_{1-x}Pr_xInNi_4$ is shown. $M(H)$ for $x = 0.1$ and 0.2 does not show a metamagnetic transition up to 5 T. Previous CEF calculation has predicted an S-shaped $M(H)$ curve for fields applied parallel to the (1 0 0) axis [11]. The predicted S-shaped $M(H)$ is due to the CEF level crossing. As the consequence of a cooperative effect of the S-shaped $M(H)$ and the intersite ferromagnetic interaction, the field-induced ferromagnetic transition of $PrInNi_4$ was explained phenomenologically [11]. Such S-shaped $M(H)$ curve should also be observed for the dilute systems, since the level crossing is intrinsically a single-site phenomenon. However, this has not been observed in the present study. This may be due to the powder averaged data, because such behavior is predicted only for the (1 0 0) direction. To observe such field dependence of M, single crystalline $Y_{1-x}Pr_xInNi_4$ samples should be needed.

In addition, it would be also interesting to measure the physical properties of $Y_{1-x}Pr_xInNi_4$ down to much lower temperatures. Since the systems of dilute limit ($x \sim 0$) would not exhibit any magnetic or quadrupolar ordering, the quadrupolar degree of freedom of the Γ_3 ground state persists to the lowest temperatures. In such cases, the quadrupolar–Kondo effect can be observed, that has been proposed for the anomalous properties of U-based compounds [12], but has not been experimentally established. For Pr-based systems, the dilute system (Pr,La)Pb_3 has been studied as a candidate for the quadrupolar–Kondo system [13]. However, other examples are not yet provided, since Pr-based compounds with the Γ_3 ground state are quite rare. It is, therefore, meaningful to perform precise experiments on the $Y_{1-x}Pr_xInNi_4$ system as well.

5. Magneto cooling effect in $PrInNi_4$

As is mentioned before, the field-induced transition of $PrInNi_4$ is considered to accompany a drastic change of the CEF scheme. Below H_c, the ground state is a nonmagnetic doublet, whereas above H_c the lowest level would be a magnetically-polarized singlet. This transition therefore causes a large change of magnetic entropies. Furthermore, the transition occurs very steeply at a relatively small external field. This feature would be useful for a magnetocaloric application with this compound. We, thus, have measured the magnetocaloric effect in $PrInNi_4$ at low temperature.

First, $PrInNi_4$ was cooled down to about 1.4 K under the field of 1 T. At this stage, the system is in the ferromagnetic state with magnetically polarized singlet. Next, the external field was switched off adiabatically, and the change of the temperature was measured. Details will be published elsewhere [14]. The result is shown in Fig. 6. It is clearly seen that the temperature rapidly decrease down to 0.7 K. If the adiabatic condition is improved, it is expected that the temperature can be decreased to much lower values. We stress that this effect is observed with external field as small as

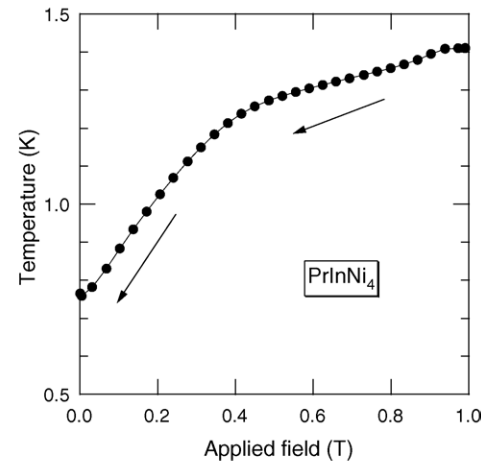

Fig. 6. Magneto cooling effect in $PrInNi_4$.

~0.6 T, which is easily obtained by a conventional permanent magnet or a resistive electromagnet. Hence, $PrInNi_4$ is promising as a magneto cooling material that can generate low temperatures below 1 K without superconducting magnets nor ^{3}He-refrigerators.

It is also notable that the entropy of Γ_3 state $R \ln 2$ (R is the gas constant) is responsible for this magneto cooling effect. This may be the first example in which the quadrupolar degree of freedom is used for application.

6. Conclusion

The magnetic susceptibility and magnetization of $Y_{1-x}Pr_xInNi_4$ have revealed that these properties are enhanced for peculiarly $x = 1.0$ at low temperatures. This enhancement should be responsible for causing the field-induced ferromagnetism. At high temperatures, interestingly, magnetic interaction between Pr ions is antiferromagnetic, but below 30 K such ferromagnetic interaction seems to be dominant and susceptibility starts to be enhanced. These results imply that the quadrupolar interaction of the lowest Γ_3 state plays an important role for the evolution of ferromagnetic enhancement in $PrInNi_4$.

Magneto cooling effect is also observed in $PrInNi_4$. This effect occurs with relatively small fields (~0.6 T) and at liquid ^{4}He temperature range ($\gtrsim$1.4 K). $PrInNi_4$ can be useful to generate low temperatures below 1 K without superconducting magnets or ^{3}He.

References

[1] A. Yatskar, W.P. Beyermann, R. Movshovich, P.C. Canfield, Phys. Rev. Lett. 77 (1996) 3637.
[2] E.D. Bauer, N.A. Frederick, P.C. Ho, V.S. Zapf, M.B. Maple, Phys. Rev. B 65 (2002) 100506R.

[3] Y. Aoki, A. Tsuchiya, T. Kanayama, S.R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, R. Kadono, Phys. Rev. Lett. 91 (2003) 067003.
[4] N.B. Brandt, V.V. Moshchalkov, Adv. Phys. 33 (1984) 373.
[5] N. Tsujii, H. Kitazawa, H. Suzuki, M. Imai, G. Kido, J. Phys. Soc. Jpn. 71 (2002) 1852.
[6] Ya.M. Kalychak, J. Alloys Compd. 262–263 (1997) 341.
[7] H. Suzuki et al., in preparation.
[8] K. Andres, E. Bucher, S. Darack, J.P. Maita, Phys. Rev. B 6 (1972) 2716.
[9] H. Kitazawa, A. Dönni, L. Keller, J. Tang, F. Fauth, G. Kido, J. Solid State Chem. 140 (1998) 233.
[10] E. Bucher, K. Andres, F.J. di Salvo, J.P. Maita, A.C. Gossard, A.S. Cooper, G.W. Hull Jr., Phys. Rev. B 11 (1975) 500.
[11] H. Suzuki, N. Tsujii, O. Suzuki, H. Kitazawa, H. Abe, M. Imai, G. Kido, Acta Phys. Pol. B 34 (2003) 1055.
[12] D.L. Cox, Phys. Rev. Lett. 59 (1987) 1240.
[13] T. Kawae, T. Yamamoto, K. Yurue, N. Tateiwa, K. Takeda, T. Kitai, J. Phys. Soc. Jpn. 72 (2003) 2141.
[14] O. Suzuki et al., in preparation.