Magnetocaloric effect in a cluster-glass system $Ho_5Pd_{2-x}Ni_x$

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Abstract. In order to investigate the effect of chemical pressure on the large magnetocaloric effect in Ho_5Pd_2, we conducted X-ray diffraction, magnetization, and specific heat measurements on $Ho_5Pd_{2-x}Ni_x (0 \leq x \leq 1.0)$ rare-earth intermetallic compounds. The linear x dependence of the lattice constant a suggests that Ni is replaced with Pd in the case of $Ho_5Pd_{2-x}Ni_x$ $(0 \leq x \leq 0.5)$. The spin-glass transition temperature T_g and paramagnetic Curie temperature θ_p indicate a weak oscillatory x dependence. However, the magnetic entropy change $-\Delta S_m$ and the relative cooling power (RCP) are rapidly suppressed with increasing x. These large reductions in $-\Delta S_m$ and RCP cannot be explained only in terms of normal Ruderman-Kittel-Kasuya-Yoshida (RKKY)-type indirect exchange interactions.

1. Introduction

Magnetic refrigeration of magnetic materials based on the magnetocaloric effect (MCE) has attracted attention owing to its potential application in energy-efficient environment-friendly refrigeration technologies. T. Samanta *et al.* discovered that the rare-earth compound Ho_5Pd_2 exhibits a large relative cooling power (RCP) of 6.32 J/cm^3 at approximately 30 K, and suggested the possibility of antiferromagnetic ordering using magnetization data[1]. Since the temperature with the maximum RCP value is close to the boiling point of hydrogen at 20 K, it is thought that Ho_5Pd_2 is a promising material for use in hydrogen liquefaction in future societies that utilize a hydrogen energy system. Our neutron experiments confirmed that Ho_5Pd_2 belongs to a cluster-glass that is specified by short-range ordering, with an incommensurate wave vector, $\vec{q} = \{0.18, 0.18, 0.18\}$[2]. A. F. Gubkin *et al.* reported on spin-glass behaviors of Ho_5Pd_2 that were obtained using DC and AC magnetization measurements, together with the results of neutron experiments[3]. These results suggest that magnetic ordering below T_g is not antiferromagnetic and that short-range ordering with respect to the incommensurate wave vector must be caused by complex competition between ferromagnetic and antiferromagnetic interactions and partial occupancies at the Ho and Pd sites. Recently, we reported that the magnetic entropy change depends on the number of vacancies at the Ho sites in a $Ho_{5+x}Pd_2$ system $(-0.4 \leq x \leq 0.4)$[4]. Since the ionic radius of Ni is smaller than that of Pd with a similar electronic state, it is thought that the non-magnetic Ni substitution at the non-magnetic Pd sites corresponds to

a chemical pressure effect. In order to determine the way in which chemical pressure affects magnetocaloric effect, we have investigated magnetic and thermal properties using measurements of the magnetization and heat capacity of $Ho_5Pd_{2-x}Ni_x (0 \leq x \leq 1.0)$.

2. Experiment

Polycrystalline samples of $Ho_5Pd_{2-x}Ni_x$ were synthesized using an arc-melting method under a pure argon atmosphere. The mixtures of Ho (3N), Pd (3N5), and Ni (3N) with a nominal composition ($x = 0$, 0.1, 0.3, 0.5, and 1.0) were alternately melted and turned upside down five times on a water-cooled copper hearth, in order to ensure their homogenization. The as-cast samples were then annealed at 1123 K for one week in an evacuated quartz tube. The crystal structures of the annealed samples were evaluated using X-ray diffraction (XRD) with a Rigaku RINT 2100 diffractometer. The X-ray diffraction patterns were analyzed using Rietveld analysis, as implemented in the Fullprof Suite software package[5]. The magnetization measurements were conducted using a superconducting quantum interference device (SQUID) magnetometer (MPMS-5S, Quantum Design Ltd.) in the temperature range of 1.9 to 300 K, with DC magnetic field strengths ranging from 0 to 5 T. The specific heat measurements were conducted using the adiabatic heat relaxation method in the temperature range of 1.9 to 300 K, using a physical property measurement system (PPMS, Quantum Design Ltd.).

3. Results and Discussion

Figure 1 shows the XRD patterns of $Ho_5Pd_{2-x}Ni_x (0 \leq x \leq 1.0)$ at room temperature. The Rietveld analysis was performed assuming that a normal composition of Ni was substituted for the Pd. This analysis revealed that the main phase of all the samples ($0 \leq x \leq 1.0$) exhibited a cubic Dy_5Pd_2-type structure (space group: $Fd3m$)[6]. In the cases of $x = 0.5$ and 1.0, a small amount of unknown phases (denoted by •) were also clearly detected. The lattice constant a as a function of x is shown in Fig.2 and tabulated in Table 1. The amplitude of a linearly decreased with the replacement of Pd sites with Ni, up to a value of $x = 0.5$, as shown in Fig.2. However, it is of note that the amplitude of a above $x = 0.5$ began to deviate from the linear curve. This implies that the lattice constant a in $Ho_5Pd_{2-x}Ni_x (0 \leq x \leq 0.5)$ follows the well-known Vegard's law and that the majority of the Ni replaced Pd.

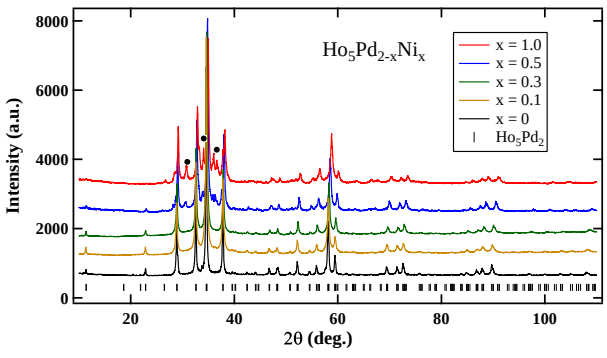

Figure 1. X-ray diffraction patterns of $Ho_5Pd_{2-x}Ni_x$ at the room temperature. The XRD pattern is shifted along the y-axis direction.

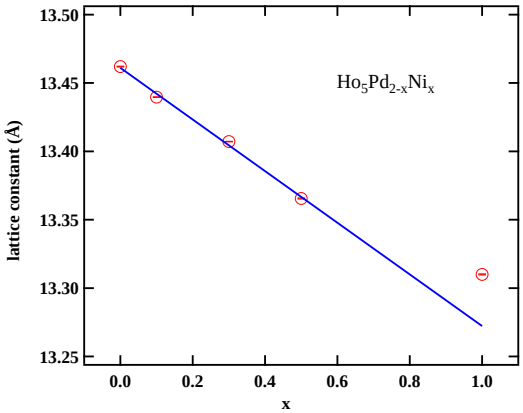

Figure 2. Lattice constant a as a function of x in $Ho_5Pd_{2-x}Ni_x$.The line indicates the least-squares fitting line for $0 \leq x \leq 0.5$.

Table 1. The lattice constant a, the spin-glass transition temperature T_g, the maximum values of the magnetocaloric parameters ($-\Delta S_m^{max}$ and RCP) under 5 T, the effective magnetic moment μ_{eff}, and the paramagnetic Curie temperature θ_p for $Ho_5Pd_{2-x}Ni_x$.

x	lattice constant a (Å)	T_g (K) (from C_p)	$-\Delta S_m^{max}$ (J/kg K)	RCP (J/kg)	μ_{eff} (μ_B/Ho)	θ_p (K)
0.0	13.4620	25.5	15.4	678	11.07	29.7
0.1	13.4397	24.9	12.0	492	10.65	29.2
0.3	13.4071	22.9	11.0	462	10.76	27.5
0.5	13.3655	23.4	9.4	389	10.72	30.9
1.0	13.3099	24.8	8.5	332	10.59	33.8

The temperature dependencies of the heat capacity $C(T)$ and $C(T)/T$ of $Ho_5Pd_{2-x}Ni_x$ under a magnetic field of $B = 0$ are shown in Fig.3 and Fig.4, respectively. The $C(T)$ of Lu_5Pd_2 is also plotted as a reference substance for the lattice part of the specific heat provided in Fig.3. The spin-glass transition temperature T_g is defined as the temperature at the maximum value of $C(T)/T$. A λ-shaped anomaly for $x \geq 0.5$ appears at 45 K, which originated from the phase transitions of unknown phases. When x was changed from 0 to 1.0, the amplitude of T_g initially decreased, with a minimum at $x = 0.3$, and then began to increase again. The increase of $C(T)$ and $C(T)/T$ below 3.5 K suggests either the occurrence of other phase transitions or the nuclear contribution of Ho at lower temperatures[7]. We will confirm this using heat capacity experiments at lower temperatures. Note that the large magnetic contribution of the specific heat remains above T_g.

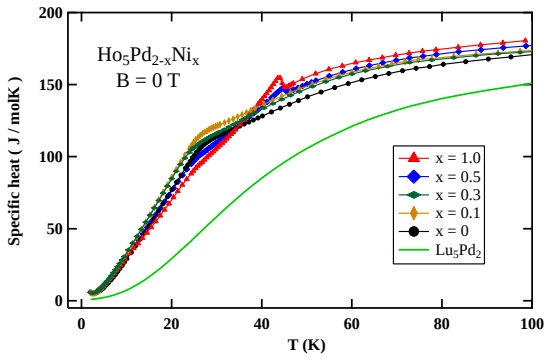

Figure 3. Temperature dependences of the heat capacity $C(T)$ in $Ho_5Pd_{2-x}Ni_x$.

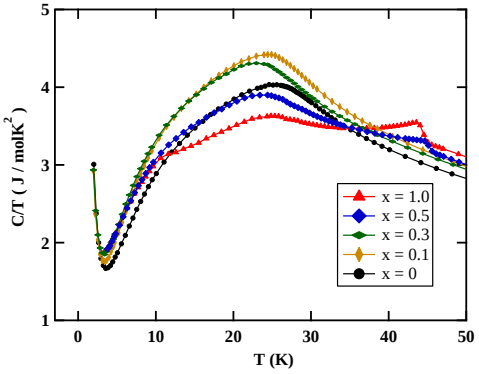

Figure 4. $C(T)/T$ as a function of temperature T in $Ho_5Pd_{2-x}Ni_x$.

The temperature dependence of the magnetic susceptibility $\chi(T)$ of $Ho_5Pd_{2-x}Ni_x$ under a magnetic field of $B = 0.1$ T is shown in Fig.5. The spin-glass transition temperature T_g obtained from the $\chi(T)$ data should be located at approximately the shoulder of the $\chi(T)$ curve. The $\chi(T)$ values obtained in the zero-field cooled (ZFC) and field cooled (FC) processes began to differ below T_g. However, A. F. Gubkin *et al.* reported that the amplitude of T_g is affected by the magnetic field [3]. Therefore we will adopt the T_g as defined using the $C(T)$ data under zero magnetic field as the spin-glass transition temperature of $Ho_5Pd_{2-x}Ni_x$ in this study. A small hump in the data at 45 K can be seen in the cases of $x = 0.5$ and 1.0. Judging from the

anomalies related to $C(T)$ and $\chi(T)$ at 45 K and the existence of unknown phases in the XRD patterns, the unknown phases in $x = 0.5$ and 1.0 undergo an amount of magnetic ordering below 45 K. The amplitude of $\chi(T)$ follows the Curie-Weiss law in the temperature range of 60 K to 300 K (not shown in Figure). The Curie-Weiss law is expressed as

$$\chi = \frac{N\mu_{\rm eff}^2}{3k_{\rm B}\,(T-\theta_{\rm p})}, \tag{1}$$

where N, $\mu_{\rm eff}$, $k_{\rm B}$, and $\theta_{\rm p}$ are the number of magnetic atoms per mole, the effective magnetic moment, the Boltzmann constant, and the paramagnetic Curie temperature, respectively. The obtained values of $\mu_{\rm eff}$ and $\theta_{\rm p}$ are listed in Table 1. The positive $\theta_{\rm p}$ of the $Ho_5Pd_{2-x}Ni_x$ indicates that the ferromagnetic interaction dominates.

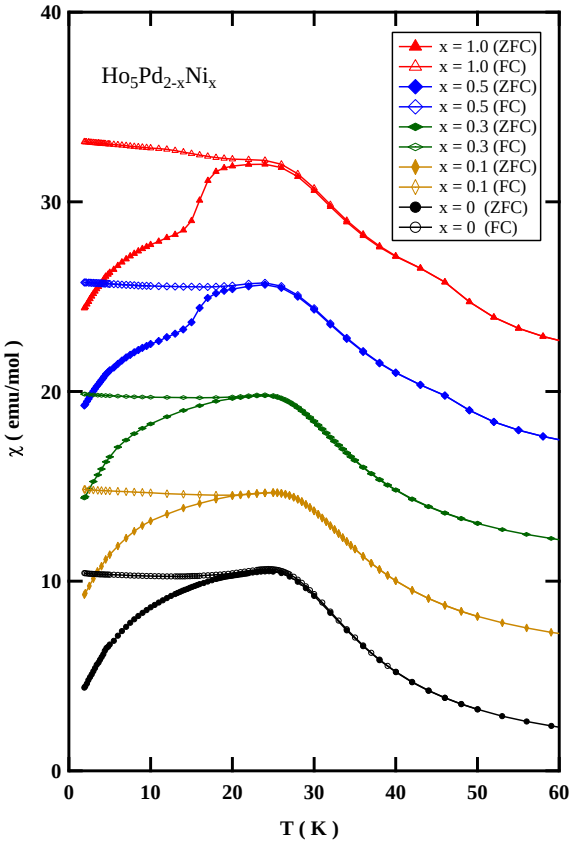

Figure 5. Temperature dependence of the magnetic susceptibility $\chi(T)$ in $Ho_5Pd_{2-x}Ni_x$. Each $\chi(T)$ curve is shifted by +5 emu/mol along the y-axis direction.

In order to clarify the effect of chemical pressure on the MCE, we evaluate two crucial quantities related to MCE. The first crucial quantity is the magnetic entropy change $-\Delta S_{\rm m}$ defined by

$$\Delta S_{\rm m} = \int_0^B \left(\frac{dM}{dT}\right)_B dB, \tag{2}$$

which is calculated using the temperature T and magnetic field B dependence of the magnetization M, according to the Maxwell relation. The second crucial quantity is the RCP[8]. The RCP is an important quality factor for magnetic refrigeration materials, which is related to the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle.

The value of RCP is evaluated using the product of the maximum value $-\Delta S_{\rm m}^{\rm max}$ and the full width at half maximum $\delta T_{\rm FWHM}$ of the magnetic entropy change :

$$\mathrm{RCP} = \Delta S_{\rm m}^{\rm max} \times \delta T_{\rm FWHM}. \tag{3}$$

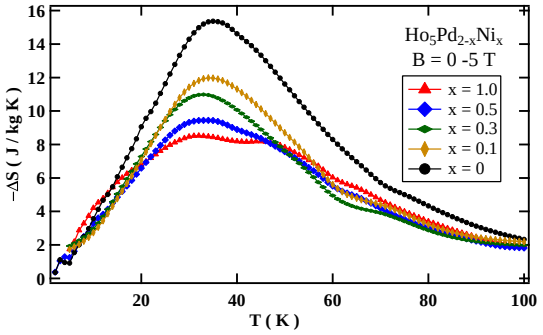

Figure 6. Magnetic entropy changes $-\Delta S_{\rm m}$ as a function of T in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ ($B = 0-5$ T).

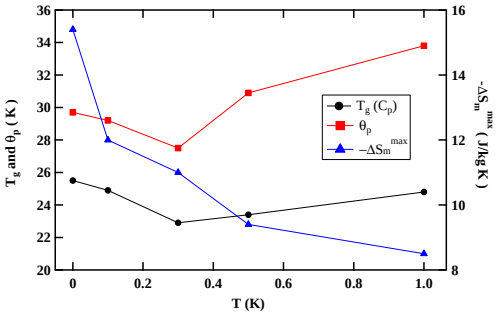

Figure 7. x dependencies of the spin-glass transition temperature $T_{\rm g}$, the paramagnetic Curie temperature $\theta_{\rm p}$, and the maximum magnetic entropy change $-\Delta S_{\rm m}^{\rm max}$ ($B = 0-5$ T).

The magnetic entropy changes $-\Delta S_{\rm m}$ as a function of temperature in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ are shown in Fig.6. The maximum magnetic entropy change $-\Delta S_{\rm m}^{\rm max}$ is located at approximately 35 K, which is above $T_{\rm g}$. The maximum magnetic entropy change $-\Delta S_{\rm m}^{\rm max}$ and the RCP values are listed in Table 1. The magnetic parameters $T_{\rm g}$, $\theta_{\rm p}$, and $-\Delta S_{\rm m}^{\rm max}$ are plotted as a function of x in Fig.7. The maximum $-\Delta S_{\rm m}^{\rm max}$ value of 15.4 J/kgK was obtained for $\mathrm{Ho_5Pd_2}(x = 0)$. The amplitudes of $-\Delta S_{\rm m}^{\rm max}$ and RCP rapidly decreased with increasing x. However, $T_{\rm g}$ and $\theta_{\rm p}$ exhibited different x dependencies. When x increased from 0 to 1.0, both values decreased, with a minimum at approximately $x = 0.3$, before beginning to increase again. The spin-glass behavior represented by $T_{\rm g}$ is well correlated with the strength of magnetic interactions which is characterized by $\theta_{\rm p}$. However, the chemical pressure effect in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ does not monotonically tune the amplitude of the magnetic interactions. Since the magnetic properties in rare-earth intermetallic compounds are mainly governed by Ruderman-Kittel-Kasuya-Yoshida (RKKY)-type indirect exchange interactions, which exhibit an oscillatory dependence on the distance between magnetic ions, the obtained chemical pressure effect on $T_{\rm g}$ and $\theta_{\rm p}$ in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ may be explained using a model based on complex RKKY interactions. However, the large reduction in $-\Delta S_{\rm m}$ in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ cannot be explained using this method. It is necessary to perform neutron scattering experiments on $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ in order to collect further microscopic information and elucidate the chemical pressure effect.

4. Conclusion

Since the lattice constant follows Vegard's law in $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x (0 \le x \le 0.5)$, a portion of the Pd sites of $\mathrm{Ho_5Pd_2}$ must have been replaced with Ni. The magnetic entropy change and RCP of $\mathrm{Ho_5Pd_{2-}}_x\mathrm{Ni}_x$ were greatest at $x = 0$, under a magnetic field change of 5 T. The Ni substitution in $\mathrm{Ho_5Pd_2}$ rapidly reduced the amplitudes of the magnetic entropy change and RCP. Since the amplitudes of $T_{\rm g}$ and $\theta_{\rm p}$ exhibited weak oscillatory behavior, the large reduction of magnetic entropy change and RCP cannot be explained by referring only to RKKY interactions.

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