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Antiferromagnetism and the Kondo behaviour in Ce($Pt_{1-x}Pd_x$)Ga

H.H. Cho[a], W.H. Lee[a,*], Y.Y. Chen[b]

[a]Department of Physics, National Chung Cheng University, 160 San-Hsing, Ming-Hsiung, Chia-Yi 621, Taiwan, ROC
[b]Institute of Physics, Academia Sinica, Taipei 115, Taiwan, ROC

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Abstract

We present the results of lattice parameters at room temperature, the static magnetic susceptibility and the magnetic resistivity between 1.8 and 300 K, and the low-temperature specific-heat measurements for the series Ce($Pt_{1-x}Pd_x$)Ga, ($x = 0.0$, 0.2, 0.5, 0.8 and 1.0). Two maxima in the temperature dependence of the magnetic resistive curve for each sample are observed, one above 100 K, and another at around 4 K, which due to an interplay between crystal-field effect and the Kondo effect. As determined from the peak values of the temperature dependence of the specific heat data $C(T)$, all samples exhibit antiferromagnetic ordering from 1.3 K for CePdGa to 3.4 K for CePtGa. The large reduction of entropy for each sample below T_N is associated with the Kondo effect.

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Research on the problem of the competition between the Kondo effect and exchange interactions in a Kondo-lattice model has been of interest to both theorists and experimentalists for the past 20 years [1,2]. It is well known that the anomalous physical properties of Ce-based dense Kondo systems are considered to arise from the hybridization between the localized 4f and conduction electrons, and the hybridization strength is able to be enhanced by applying either physical or chemical pressure. Recently, the equiatomic ternary compound CePtGa has been reported to be a dense Kondo system with an antiferromagnetic ordering temperature $T_N = 3.5$ K [3–8]. In this study, we explore the influence of Pd substitution for Pt in the CePtGa system, as both CePdGa and CePtGa have been known to form with the same TiNiSi-type structure. Since Pd has a smaller size than Pt, this pseudoternary system Ce($Pt_{1-x}Pd_x$)Ga provides an opportunity to investigate the effects of alloying as well as pressure on the magnetic behaviour of the compound CePtGa. In this paper, we present a detailed experimental study of the temperature dependence of the electrical resistivity for five alloys of the series Ce($Pt_{1-x}Pd_x$)Ga ($0 \leq x \leq 1$). In order to estimate the phonon contribution to the resistivities of the Ce-based samples, the temperature dependence of electrical resistivity of the La-based compounds, La($Pt_{1-x}Pd_x$)Ga, also has been measured. In addition, static magnetic susceptibility and low-temperature specific heat measurements on the compounds Ce($Pt_{1-x}Pd_x$)Ga have been made to understand magnetic ordering and Kondo interaction.

Polycrystalline samples investigated for this work were synthesized by arc melting together with stoichiometric amounts of the constituent elements in a Zr-gettered arc furnace on a water-cooled Cu hearth under purified argon of about one atmospheric pressure. Rare earth elements with a purity of 99.9%, Pd, Pt with 99.95% purity and Ga with 99.999% purity were purchased from Alfa Aesar, Gredmann and CERAC, respectively. Weight losses during several melting and turning cycles were negligible. Powder X-ray diffraction patterns with Cu K_α radiation indicated that each sample was single phase, with no additional reflections. As

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* Corresponding author. Tel.: +886-5-2720586; fax: +886-5-2720587.
E-mail address: whlee@phy.ccu.edu.tw (W.H. Lee).

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determined by the method of least squares fit of d-spacings, the lattice parameters a, b, c of the orthorhombic TiNiSi-type structure (P_{nma}) [9] and the unit-cell volume were obtained in Table 1. The crystallographic cell volume of Ce(Pt$_{1-x}$Pd$_x$)Ga are plotted in Fig. 1 as a function of the Pd content. The variation in the lattice parameters between CePtGa and CePdGa is: $\Delta a/a = -0.025\%$, Delta; $b/b = -0.107\%$ and $\Delta c/c = -0.094\%$. There is a 0.302% contraction in the unit cell volume of CePdGa compared to CePtGa. The decrease in the unit cell volume with increasing Pd concentration implies an increase in the hybridization strength between the 4f and conduction electrons.

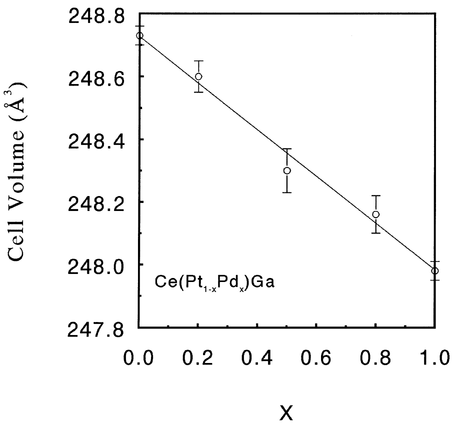

Fig. 1. Cell volume variations for Ce(Pt$_{1-x}$Pd$_x$)Ga compounds. The linear line obeys the Vegard's law.

DC electrical resistivity measurements were made between 1.8 and 300 K using a standard four-probe technique in an equipment fully automated for temperature stability and data acquisition [10]. Fine platinum wires (~2 mil diameter) were spot welded to the samples with small rectangular parallelpipeds of approximate dimensions $1 \times 1 \times 5\ \mathrm{mm}^3$, and served as the voltage and current leads. Data were taken with the current applied in both directions to eliminate possible thermal effects. All data presented are for the warming curves. Ten compositions of La(Pt$_{1-x}$Pd$_x$)-Ga and Ce(Pt$_{1-x}$Pd$_x$)Ga have been measured. Since the residual resistivity due to lattice imperfections in the series Ce(Pt$_{1-x}$Pd$_x$)Ga is very hard to determine because of the existence of Kondo scattering, we assume that the residual resistivity is approximately the same in these Ce-based and La-based compounds. The magnetic contribution to the resistivity ρ_{m} of the Ce(Pt$_{1-x}$Pd$_x$)Ga compounds was then obtained by subtracting the resistivities of the isostructural La(Pt$_{1-x}$Pd$_x$)Ga compounds. Fig. 2 displays the normalized resistivity vs. temperature for the samples Ce(Pt$_{1-x}$Pd$_x$)Ga. The most prominent feature of these resistivity curves is the presence of a narrow peak at around 4 K and a shoulder above 100 K. The data for the magnetic contribution to the resistivity ρ_{m} of Ce(Pt$_{1-x}$Pd$_x$)Ga are plotted as a function of ln(T) in Fig. 3. Two maxima in $\rho_{\mathrm{m}}(T)$ for each curve are observed, one above 100 K, and another at around 4 K, which is due to an interplay between the Kondo-effect and crystal-field. It is noted that the position of the higher-temperature peak moves toward higher temperature region, from $T = 100$ K for CePtGa to $T = 140$ K for CePdGa, which may indicate a higher energy for the first-excited state (above the ground state) due to the crystal-field effect for the Ce^{+3} ion in the compound, with the increasing Pd concentration. In fact, the inelastic neutron spectra showed the first crystal field excitation at 18.0 meV for CePtGa and 18.9 meV for CePdGa [4,6]. These curves display a logarithmic increase with decreasing temperature in the high-temperature region. Because there is no established theoretical treatment for a dense Kondo system, the $T(\rho_{\max})$ value has been assumed by some authors [11–14] to be directly related to the value of the Kondo temperature T_{K}. In this case, we obtain estimates of T_{K} for five alloys in the series Ce(Pt$_{1-x}$Pd$_x$)Ga to be nearly the same value at around 4 K. However, these values of T_{K} may be viewed with caution, as the RKKY interaction between magnetic ions may play an important or even dominant role in determining the value of $T(\rho_{\max})$ [15–19], in which case T_{K} and $T(\rho_{\max})$

Table 1
Lattice parameters, T_{N} (peak value of specific heat), effective paramagnetic moment (μ_{eff}), paramagnetic Curie temperature (Θ_{P}), coefficient of electronic specific heat (γ), Debye temperature (Θ_{D}) and the resistivity at $T = 300$ K in the series Ce(Pt$_{1-x}$Pd$_x$)Ga

	$x = 0.0$	$x = 0.2$	$x = 0.5$	$x = 0.8$	$x = 1.0$
a (nm)	0.7149(3)	0.7153(6)	0.7160(1)	0.7170(1)	0.7141(5)
b (nm)	0.4481(8)	0.4480(1)	0.4479(6)	0.4478(1)	0.4777(6)
c (nm)	0.7762(7)	0.7757(1)	0.7741(6)	0.7729(2)	0.7755(4)
v (Å^3)	248.73(1)	248.60(5)	248.30(7)	248.16(6)	247.98(3)
T_{N} (K)	3.4	2.7	1.9	1.5	1.3
μ_{eff} (μ_{B})	2.73	2.7	2.66	2.63	2.62
Θ_{P} (K)	-45	-45	-51	55	58
Θ_{D} (K)	212	200	210	203	226
γ (mJ/mol K^2)	58	40	79	119	80
ρ(300) ($\mu\Omega$ cm)	660	700	740	650	340

The number given in the parentheses is the standard deviation in the least significant digit of the reported value.

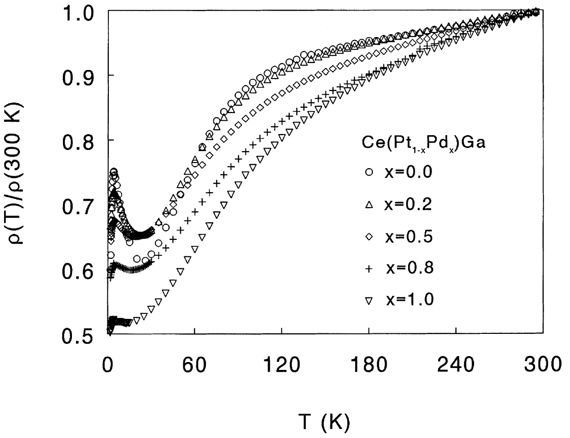

Fig. 2. Electrical resistivity normalized to the value at room temperature as a function of temperature for five alloys in the system Ce($Pt_{1-x}Pd_x$)Ga.

would not be proportional. According to the theory of Cornut and Coqblin [20], the ratio of the high- and low-temperature logarithmic slopes is

$$[(2J+1)^2-1]/(\lambda_0^2-1),$$

where $J = 5/2$ and λ_0 is the degeneracy of the ground state. From the data in Fig. 3, we calculate the ratio of the five logarithmic slopes to be 2.0, 3.52, 4.35, 3.2 and 11.5 for the samples with $x = 0.0$, 0.2, 0.5, 0.8 and 1.0. The ratio value of 11.5 corresponds to $\lambda_0 = 2$. This indicates that the decrease of ρ_m just above 4 K for CePdGa may originate from the Kondo effect on a ground-state doublet, whereas the decrease at high temperature is due to the Kondo effect on the entire multiplet. Similar results also have been observed in the nonmagnetic Kondo lattice $CePtSi_2$ [21] and antiferromagnetic Kondo lattice $CePdSi_2$ [22,23]. While the agreement is not as convincing as the fit to the magnetic resistivity for the rest four samples, it shows that either the theory of Cornut and Coqblin may be not valid for some magnetically ordering Kondo lattices or the subtraction procedure to obtain magnetic contribution to resistivity is not free from ambiguities. In fact, the magnetic resistivity of CePtGa has been previously well described on the basis of Fischer's theory [6,24].

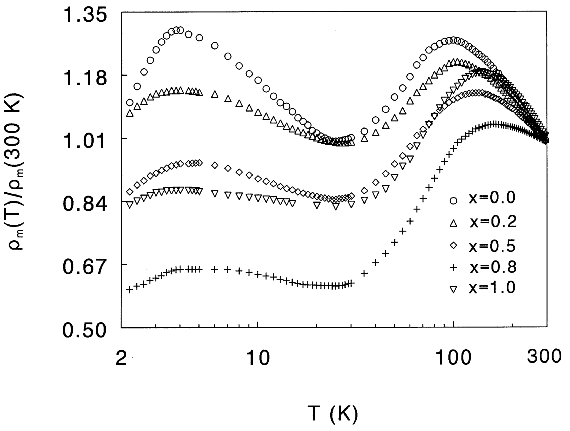

Fig. 3. Magnetic resistivity normalized at 300 K vs. ln(T) for the five alloys in the series Ce($Pt_{1-x}Pd_x$)Ga.

The static magnetic susceptibility of the sample was measured in a field of 1.0 kOe between 1.80 and 300 K with a commercial SQUID magnetometer [10]. Fig. 4(a) depicts the molar magnetic susceptibility χ_m vs. temperature T for the Ce($Pt_{1-x}Pd_x$)Ga alloys with $x = 0$, 0.2, 0.5, 0.8, and 1.0 between 1.8 and 20 K. It is seen that a transition from nonmagnetic to magnetic ordering is seen below 3.6, 3.0 and 2.0 K (peak values) for the samples with $x = 0$, 0.2 and 0.5, respectively. As shown in Fig. 4(b), the high-temperature (>70 K) susceptibility data of all the samples can be fitted very well with the Curie–Weiss law $\chi_m = C/(T+\Theta)$, where C is the Curie constant and Θ may be considered as a temperature characteristic of the s–f mixing interaction. Below about 10 K, all samples show a rather sharp increase in the magnetic susceptibility (see Fig. 4(a)). We attribute these deviations from the high temperature Curie–Weiss law to the combined results of the crystal-field splitting of

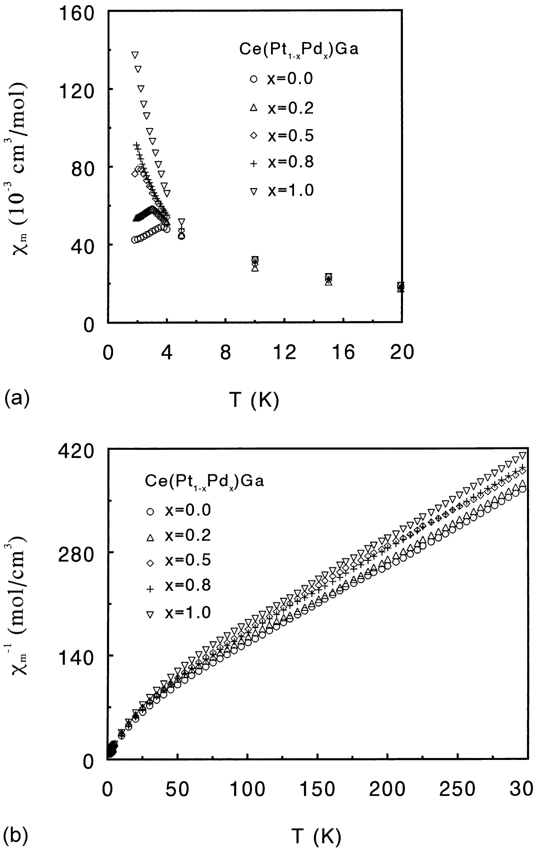

Fig. 4. (a) Molar magnetic susceptibility χ_m vs. temperature T for five alloys in the series Ce($Pt_{1-x}Pd_x$)Ga between 1.8 and 20 K. (b) Inverse molar magnetic susceptibility χ_m^{-1} vs. temperature of the series Ce($Pt_{1-x}Pd_x$)Ga between 1.8 and 300 K.

the $J = 5/2$ multiplet level of Ce and the spin fluctuation (Kondo state) of the Ce 4f level. The fitted effective moment per Ce atom and paramagnetic Curie temperature for the five alloys are listed in Table 1. From Table 1, it is seen that all the samples are characterized by an effective moment per Ce atom close to the theoretical free Ce^{+3} ion value (2.54 μ_B) and a large Θ_P. These large Θ_P are consistent with the presence of the Kondo effect.

The low-temperature specific-heat measurements were made using a thermal-relaxation microcalorimeter. Detailed measurement procedures can be found in [25]. The sample, which has two flat sides after polishing, was wiped with ~50 μg N grease for good thermal contact and was attached to a sapphire holder on an over-all precision and accuracy is reproducible within ~3%. As indicated in Fig. 5, the specific heat vs. T data curve for each sample in the series $Ce(Pt_{1-x}Pd_x)Ga$ shows a Landa-type of antiferromagnetic ordering peak centering at 3.4, 2.7, 1.9, 1.5 and 1.3 K for the sample with $x = 0$, 0.2, 0.5, 0.8 and 1.0, respectively, in agreement with the inference from the dc susceptibility data. To determine the electronic and lattice specific-heat contributions, the specific heat data in the paramagnetic state at temperatures above 8 K were fitted to the expression $C_n = \gamma T + \beta T^3$ for each sample in the series $Ce(Pt_{1-x}Pd_x)Ga$. Thus, the obtained coefficients of electronic specific heat γ and β, which determines the Debye temperature of the compound, are listed in Table 1. Valuable information can be obtained from the entropy associated with the magnetic ordering. Fig. 6 shows the temperature dependence of the ratio of specific heat to temperature, C/T, for five alloys in the series $Ce(Pt_{1-x}Pd_x)Ga$. Each data curve in Fig. 5 has a minimum around 7 K and a λ-type anomaly peak which corresponds to antiferromagnetic ordering. From the data of Fig. 6, the entropy estimated by integrating the temperature dependence C/T curve for each sample is displayed in Fig. 6. It is seen that the entropy value for each sample reaches to $R \ln 2$ around 10 K, implying that Ce^{+3} ion in these compounds $Ce(Pt_{1-x}Pd_x)Ga$ is in a doublet ground state. If we neglect the phonon contribution, the estimated magnetic entropy $S_m(T_N)$ as shown in Fig. 7 is about 69, 57, 45, 41 and 38% of Rln(2), corresponding to a reduction of ~31, 43, 55, 59 and 62% of the cerium moment for the samples with $x = 0$, 0.2, 0.5, 0.8 and 1.0, respectively. The large magnetic reduction may be able to be attributed to Kondo effect.

To conclude, the decrease in the unit cell volume with increasing Pd concentration increases the hybridization of the 4f and conduction electrons monotonically, which results in the decrease of T_N from 3.4 K for CePtGa to 1.3 K for CePdGa. The variation of the product $|\Gamma N(E_F)|$, where Γ is the coupling constant between the 4f and conduction electrons and $N(E_F)$ is the density of the electronic states at the Fermi level as a function of the Pd content, is probably not large enough and no pure Kondo state has been observed in the Kondo lattice $Ce(Pt_{1-x}Pd_x)$-Ga. However, the substitution of Pd in the CePtGa indeed not only broadens the energy levels between the doublet ground state and the first excited state as revealed in the

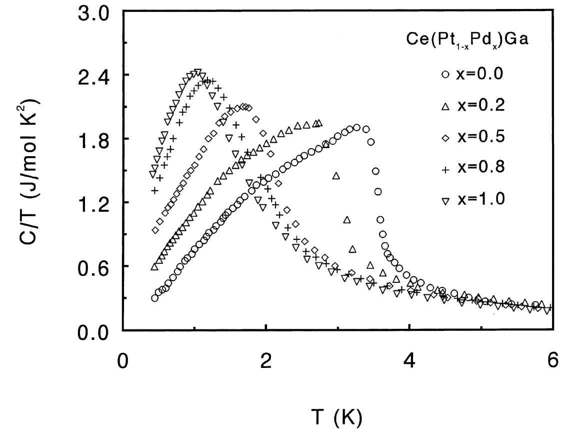

Fig. 6. Specific heat divided by temperature C/T vs. T for five alloys in the series $Ce(Pt_{1-x}Pd_x)Ga$.

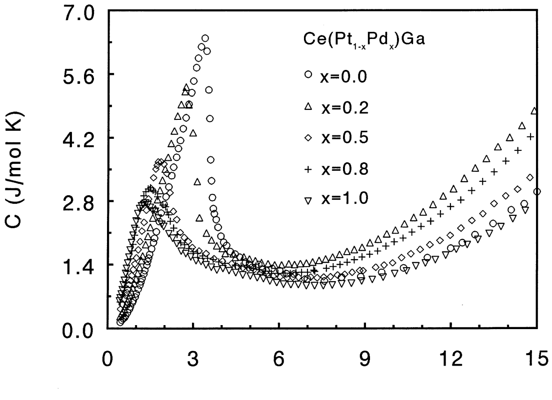

Fig. 5. Heat capacity vs. T for five alloys in the series $Ce(Pt_{1-x}Pd_x)Ga$.

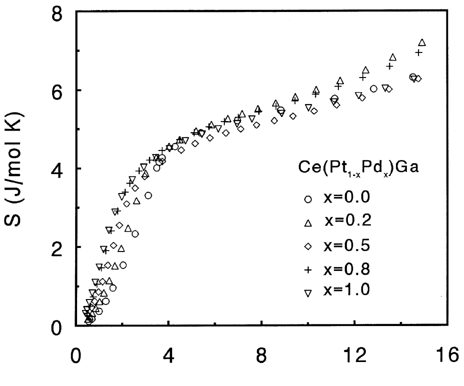

Fig. 7. The temperature dependence of entropy S for five alloys in the series $Ce(Pt_{1-x}Pd_x)Ga$.

magnetic resistivity data but also reduces magnetic entropy, which is associated with the enhanced hybridization strength between the localized 4f and conduction electrons.

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