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From Ferromagnetic to Non-Magnetic Singlet Ground State in $CePd_{1-x}Ni_x$*

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Magnetic, resistivity and specific heat measurements were performed on the $CePd_{1-x}Ni_x$ system, which ranges between a ferromagnetic (CePd) and non-magnetic (CeNi) singlet ground state. The Curie temperature (T_c) grows with Ni concentration, reaching a maximum value of $T_c = (10.5 \pm 0.1)$ K for $0.5 \leqslant x \leqslant 0.8$. Both, the concentration dependence of T_c and the Curie-Weiss temperature (θ_P) follow the predicted competition between the magnetic exchange interactions and the Kondo effect. In the crossover region ($x \cong 0.9$) the entropy gain shows that only the doublet crystal field ground state is involved in the singlet ground state formation.

Introduction

From its reduced volume with respect to the RE-Ni series, CeNi was early recognized as belonging to the Instable Valence compounds [1]. Such a feature was later confirmed by magnetic [2], thermal and transport properties [3, 4]. On the other hand CePd, which also shows the orthorhombic CrB crystalline structure, orders ferromagnetically at $T = 6.6$ K and does not show any volume anomaly with respect to the RE-Pd series [5]. Moreover, the valence of Ce studied through L_{III} X-ray spectroscopy in the Ce-Pd system shows that the CePd compound is one of the best examples of the coexistence of a non-integral valence ($V = 3.10$) and a low temperature magnetic ordering [6].

The possibility of a continuous alloying among both systems, together with a strong change in the molar volume, gives the chance for studying the competition between the magnetic exchange interaction and the Kondo effect. Similar studies were recently performed in Ce systems such as $CePt_{1-x}Ni_x$ [7], $CeSi_{2-x}Ge_x$ [8], $CeInAg_{2-x}Cu_x$ [9] and $CeCu_{2-x}Ni_xSi_2$ [10].

In this paper we present magnetic and resistivity measurements, performed on polycrystalline samples in the whole concentration range, together with some reference $LaPd_{1-x}Ni_x$ alloys. In order to gain further insight into the regime crossover region, specific heat measurements were carried out for the $x = 0.5$, 0.9 and 0.92 concentrations.

Experimental Details

The samples were prepared by melting together the proper amount of components in an arc furnace under argon atmosphere. The weight loss in this procedure was negligible. The starting elements were 99.99% pure Ce, Pd and Ni. The X-ray patterns performed on both $CePd_{1-x}Ni_x$ and $LaPd_{1-x}Ni_x$ compounds are characteristic of the CrB structure. The magnetization measurements were performed in a vibrating sample magnetometer, operating in magnetic fields up to 2 Tesla and between 1.5 and 300 K, and by an induction method at 4.2 K in fields up to 15 T (Service

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National des Champs Intenses, Grenoble). A conventional four-probe a.c. technique, with a lock-in detection was used for resistivity measurements. Specific heat measurements were performed in a semi adiabatic He^3 calorimeter, using the standard heat pulse method, within a range of 0.4 to 60 K.

Experimental Results

a) Volume Contraction

The cell volume of the $CePd_{1-x}Ni_x$ system is reduced from 189.4 Å^3 at $x=0$, to 172.5 Å^3 at $x=1$. Its concentration dependence shows a regular variation as function of the Ni content in the range of $0 \leqslant x \leqslant 0.8$, as displayed in Fig. 1. For $x > 0.8$ the volume decreases faster, as a signal of a further Ce volume contraction. Such deviation from the Vegard's law was already found in other Ce compounds [7, 10].

b) Magnetic Measurements

The field dependence of the magnetization, measured at 4.2 K up to 15 T is shown in Fig. 1. The saturation magnetization M_s, extracted following the usual approaching law $M(H) = Ms(1 - A/H) - (C/H^2)\ldots) + \chi_{vv}H$, where χ_{vv} is the Van Vleck contribution, is given in Fig. 2 and in Table 1 as a function of the Ni concentration.

The thermal variation of the low field magnetization ($H < 0.02$ T) shows the characteristics of a ferromagnetic transition for $x \leqslant 0.92$. In all cases the ordering temperature T_c is defined as the extrapolated $M(T)_{M \to 0}$ value. These Curie temperature T_c (see Table 1 and Fig. 3) increases in the concentration range $0 < x < 0.5$, reaching a plateau at $T_c \cong 10.5$ K for $0.5 \leqslant x \leqslant 0.8$ and then steeply drops, becoming zero for an extrapolated Ni concentration of $x \cong 0.95$. Note that the same concentration dependence characterises the $CePt_{1-x}Ni_x$ system with a plateau at $T_c \cong 8.5$ K [7].

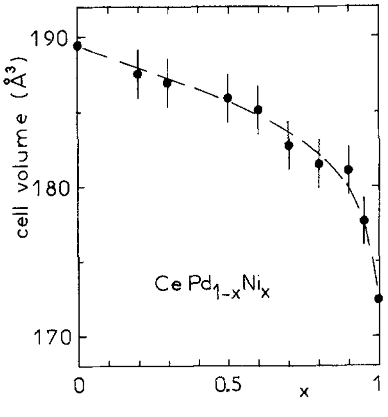

Fig. 1. Cell volume dependence with concentration

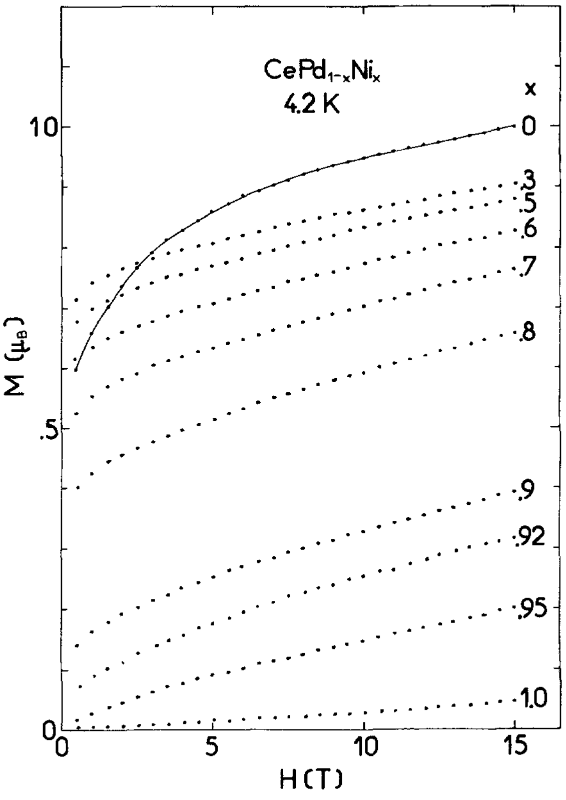

Fig. 2. Magnetization as function of the magnetic field up to 15 T. For $x=0$, $\chi = 1.8 \cdot 10^{-3}$ emu/mole is independent of magnetic field up to 18 T

Table 1. Curie temperature T_c, saturation magnetization M_s, Curie-Weiss temperature θ_P, maximum of the resistivity $\Delta\rho_{max}$ at the temperature T_{max} as a function of x in the $CePd_{1-x}Ni_x$ system. (*) is the value at 300 K

x	T_c (K)	M_s (μ_s)	θ_P (K)	T_{MAX} (K)	$\Delta\rho_{MAX}$ ($\mu\Omega$cm)
0.	6.6	0.84	22	—	14*
0.30	9.5	0.77			
0.50	10.3	0.74	28	145	22
0.60	10.6	0.67			
0.70	10.3	0.57			
0.80	10.2	0.46	42	85	45
0.90	8.4	0.20	78	80	65
0.92	6.3	0.14	77	90	57
0.95	2<	0.04	128		
1.	—	0	198		

The susceptibility study shows that, in the $0 \leqslant x \leqslant 0.8$ region, the Curie constant extracted at $T > 100$ K is close to the Ce^{3+} value. In addition the change of the slope of χ^{-1} vs T at low temperature, together with the $M_s(x)$ decrease, suggests the weakening of the Ce magnetic moment for $x>0.9$. The paramagnetic Curie-Weiss temperature (θ_P), displayed in Table 1, also defines two different regions in its concentration dependence, being nearly constant for $x \leqslant 0.5$, and rapidly increasing for $x \geqslant 0.8$.

c) Resistivity Measurements

The thermal variation of the magnetic contribution to the resistivity $\Delta\rho(T)$ is obtained by subtracting the respective $LaPd_{1-x}Ni_x$ resistivity, which accounts for the phonon and alloying contribution. The Fig. 4 shows the $\Delta\rho(T)$ variation for some typical Ni concentration in a $\ln T$ representation up to 300 K. The $\rho(T_c)$ related to the magnetic transition is well-defined in the $x \leqslant 0.8$ range but for higher Ni concentration only a shoulder is observed at $T=T_c$. This feature suggests that the magnetic phase is not the dominant one in this concentration range, therefore the conduction electron scattering mechanism is governed by other kind of processes. At high temperature the $x \geqslant 0.5$ samples show the characteristic $\Delta\rho(T)$ maximum due to the crystal field and Kondo effect competition. For the CePd compound no maximum appears up to 300 K, within the uncertainties of the absolute magnetic resistivity determination. This $\Delta\rho(T)$ variation is typical of the spin disorder resistivity (ρ_{sd}) originated in the crystal field levels (CF) only; the thermal variation of ρ_{sd} is defined by

$$\rho_{sd}(T) = A \sum_{ij} B_{ij} p_i f_{ij}, \quad (1)$$

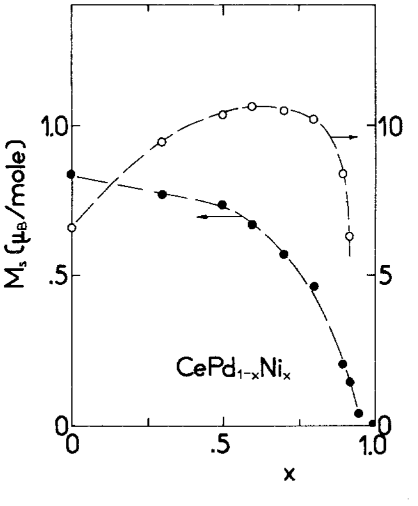

Fig. 3. Concentration dependence of: the saturation magnetization (M_s) and the Curie temperature (T_c). The dashed lines are guides to the eye

with $A=(3\pi Nm^*/h e^2 \varepsilon_F) J^2 (g-1)^2$, $B_{ii}=\langle m_s j J_z m_s i\rangle^2$, the matrix element concerning the initial and final states, p_i the Boltzman factor and f_{ij} the Fermi function [11]. For the system under study, where the ground and first excited state CF levels are equally degenerated, the spin disorder resistivity can be written as:

$$\rho_{sd}(T) \alpha A \operatorname{sech}^2(y), \quad (2)$$

where $y=\delta/2T$, with $T<\delta$, and δ is the CF splitting. The inflexion point of $\rho_{sd}(T)$, i.e. $\delta^2\rho_{sd}(T)/\delta T^2=0$, gives $y=0.13$ which leads to the relation $T=0.385\delta$. From the experimental $\Delta\rho(T)$ results we obtain a value of $\delta \cong 200$ K. Any other contribution or vicinity of the second excited doublet would imply a larger δ value.

d) Specific Heat Measurements

The phonon and conduction electron contributions to the specific heat (C_p) of the $x=0.90$ and 0.92 $CePd_{1-x}Ni_x$ samples are evaluated from the reference $LaPd_{0.1}Ni_{0.9}$ compound. For this compound the classical $C_p=\gamma T+\beta T^3$ behaviour is found at the low temperature limit ($T<\theta_D/20$ K, θ_D=Debye temperature) with $\gamma=5.8$ mJ/mole K^2 and $\beta=0.615$ mJ/mole K^4, i.e. $\theta_D=185$ K. These values are close to the LaNi ones: $\gamma=5$ mJ/mole K^2 and $\theta_D=190$ K [3]. The Fig. 5 displays the Ce contribution, i.e. $\Delta C(T)=C_{meas}(T)-C_p(T)$. A well-defined second order transition is found for $x=0.5$ with a jump of $\delta C(T_c) \cong 12$ J/mole K at $T=10.3$ K. In the $x \leqslant 0.5$ range, the magnetic transition leads to the theoretical value of $\delta C(T_c)=3R/2$ and to a good agreement between the ordering temperature obtained by both magnetic and specific heat measurements [5]. For $x=0.5$ the total entropy of the magnetic phase is $\Delta S \cong 0.9 R \ln 2$. At low temperature ($T \ll T_c$) two distinct magnetic regions are observed, namely *i*) up to $T \cong 1.4$ K, the classical ferromagnetic Bloch behaviour ($\Delta C=AT^{3/2}$), *ii*) at $T>4$ K the characteristic one for an anisotropic ferromagnet with a gap in the magnon spectrum ($\Delta C=BT^{3/2}\exp(-D/T)$) with $D=9.6$ K.

Moreover, for $0.4 \leqslant T \leqslant 1.4$ K, a linear contribution of $\Delta C/T=21$ mJ/mole K^2 is extracted. Its origin is uncertain accounting the overlap of magnon and electron spectra in this range of temperature. At high temperature ($T \geqslant 40$ K) an enhancement of ΔC is observed in this compound. Within the experimental dispersion, we can evaluate such a contribution as a Schottky anomaly due to the thermal population of the first excited level, with a splitting larger than $\delta \cong 200$ K, in agreeemnt with the resistivity analysis of the CePd compound.

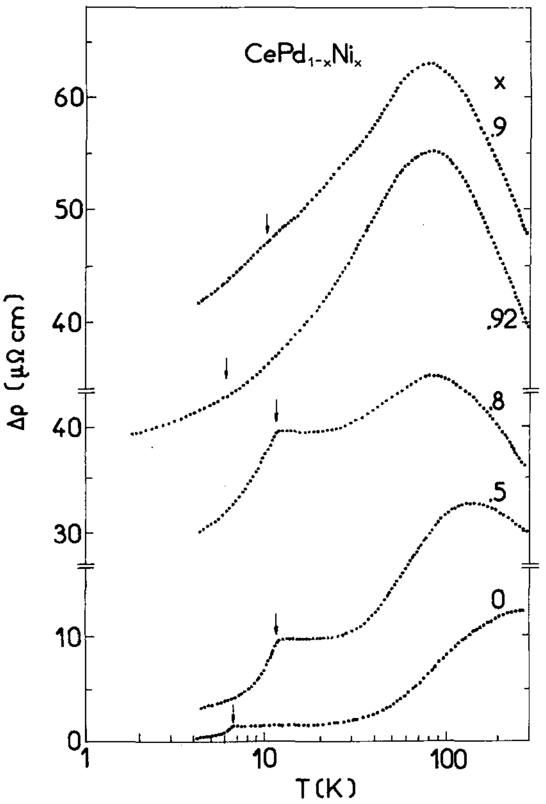

Fig. 4. Magnetic contribution to the resistivity as a function of lnT. The arrows indicate the T_c temperature from Table 1

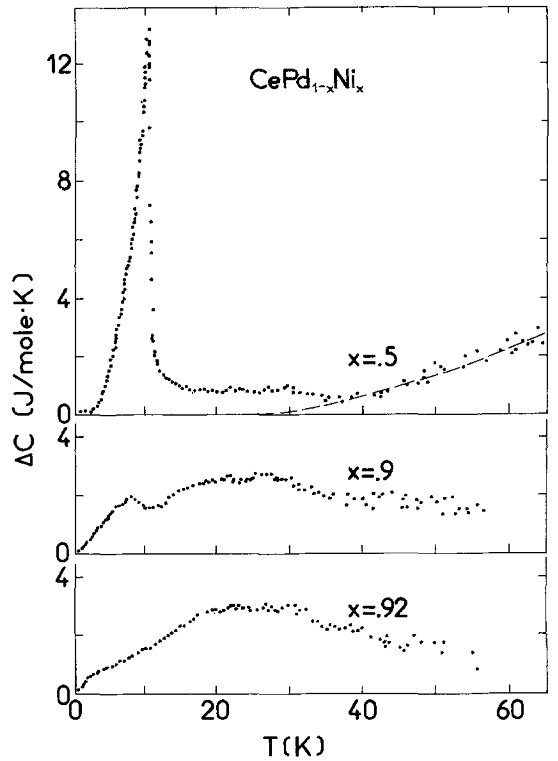

Fig. 5. Cerium contribution to the specific heat ΔC as a function of T. The dashed line correspond to a Schottky contribution with $\delta = 200$ K

Also in Fig. 5, the thermal specific heat variation of $x = 0.90$ and 0.92 shows a broad maximum at $T = (23 \pm 2)$ K. This anomaly will be discussed later within the framework of the Kondo ground state. Another maximum, in the specific heat, is observed at $T \cong 8$ K for $x = 0.90$, meanwhile only a shoulder appears around $T \cong 3$ K for $x = 0.92$. These two anomalies should be related to the onset of magnetic order observed in the magnetic measurements. The entropy gain as a function of T is shown in Fig. 6. The $\Delta S = R \ln 2$ value is reached at $T \cong 40$ K for $x = 0.50$ and at $T \cong 50$ K for $x = 0.90$ and 0.92. By comparison, we show also in Fig. 5 the entropy gain of CeNi and LaNi evaluated from the Ref. [3].

Discussion

As the relative Pd-Ni concentration is changed the strong dependence of M_s (Fig. 3) evidences that the system $CePd_{1-x}Ni_x$ undergoes a continuous transition from a magnetic dominant ground state ($0 \leqslant x \leqslant 0.5$) to a nonmagnetic ground state ($x = 1$). The question arises here whether the magnetization is homogeneous or not when both magnetic and non-magnetic ground state compete. For such a purpose we tentatively apply the Wohlfarth criterium for the region close to the critical concentration [12]. From the Landau theory of a second order transition the magnetization can be written as:

$$M(O, T, x) = (a(T)/b(T))^{1/2}(x - x_0(T))^B, \qquad (3)$$

where x_0 is the critical concentration for the onset of ferromagnetism, and a and b the Landau parameters. In the mean field approximation β equals 1/2 only in the homogeneous case. In the system under study the saturation magnetization follows the $M_s^2 = A(x - x_0)$ law within the $0.5 \leqslant x \leqslant x_0 = 0.95$ range of concentration, which evidences the homogeneous character of the magnetic transition.

In order to discuss the non-magnetic ground state contribution, the characteristic Kondo temperature can be extracted by using the Krishna-Murthy relationship, $T_K = \theta_P/2$, for the local moment regime ($T_K < T < 20\, T_K$) [13]. Because the molecular field in a ferromagnet is originated in a $J_{ex} > 0$ exchange interaction and the Kondo effect in a $J_{ex} < 0$, the measured θ_P depends on the difference of both contributions. Therefore the ferromagnetic Curie-Weiss temperature has to be added to the measured θ_P, i.e.

$2T_K = T_c + \theta_{P(\mathrm{meas})}$, this implies that the Curie-Weiss temperature of the ferromagnet equals T_c. With this procedure we obtain $T_K = 43$ K and 41 K for $x = 0.9$ and 0.92 respectively.

The magnetic contribution to the electrical resistivity $\Delta\rho$, also reflects a regime change by developing a maximum ($\Delta\rho_{\mathrm{MAX}}$ at T_{MAX}) which grows as T_{MAX} is reduced by concentration variation. Its maximum value (and minimum T_{MAX}) is observed for the x value where $T_c(x)$ drops down. Such a $\Delta\rho_{\mathrm{MAX}} \propto T_{\mathrm{MAX}}^{-1}$ relationship is characteristic of systems which undergo these changes of regime (or valence variation) [14]. The system at hand reaches $\Delta\rho_{\mathrm{MAX}} = 65\,\mu\Omega$cm at $T_{\mathrm{MAX}} = 80$ K as extreme values for $x = 0.90$.

The increase of θ_P and the large $\Delta\rho_{\mathrm{MAX}}$ values appear in the concentration range where the magnetic order is still observed, which implies that both contributions are simultaneously present. This is confirmed by the specific heat results that allow to evaluate their relative contribution, via the entropy gain of the electron involved in each one. As it can be seen in Fig. 7 the samples with $x = 0.90$ and 0.92 show the typical $\Delta C(T)/T =$ Const. behaviour for a Fermi Liquid system for $10 < T < 15$ K, i.e. $T_c < T < T_K$, and for $T < 10$ K the onset of the magnetic order is superimposed. The fraction of magnetic entropy ΔS is found to be 19% and 11% of the total $R \ln 2$ entropy for $x = 0.90$ and 0.92 and the $\Delta C/T$ of the Kondo contribution are 0.145 and 0.156 J/mole K^2 respectively. Because these $\Delta C/T$ measured values correspond to a fraction of electrons, they have to be normalized to the total expected entropy of $R \ln 2$. In this way the $\Delta C/T \cong 0.17$ J/mole K^2 value is obtained for the $x = 0.90$ and 0.92 concentration.

From the specific heat, given by Desgranges-Schotte in the $S = 1/2$ Kondo model [15], the T_K temperature can be evaluated using the following independent relationships, *i*) for the low temperature limit ($T \ll T_K$), $T_K = \pi R T / 3\Delta C$ and *ii*) for the high temperature region ($T \cong T_K$), $0.45\,T_K = T(\Delta C_{\mathrm{MAX}})$. For both limits a value of $T_K = 50$ and 52 K are respectively obtained, in good agreement with those extracted from the magnetic properties. We should note that there is no major T_K change between these two different concentrations because the Kondo ground state is the dominant one and the relative enrichment of this component from $x = 0.90$ and 0.92 is not significative, whereas the magnetic component suffers a strong relative reduction (from 19% to 11%) which is clearly reflected in the T_c and M_s drop in this concentration range.

A theoretical approach on the study of this change of regime is based on the fact that the binding energy of both, the Kondo singlet and the magnetic state, depends on the strength of the 4*f*-conduction electron exchange constant (J) [16, 17]. The binding energy of the magnetic state, $T_{\mathrm{RKKY}} \sim n_f J^2$, has to be compared with that of the Kondo singlet, $T_K \sim \exp(-1/n_f J)$, where n_f is the density of the conduction states. For small $n_f J$ values of RKKY state dominates, while above a critical value the non magnetic Kondo singlet is expected as the ground state. Both limits were already well documented for Ce compounds [18]. In the system at hand the critical value for $n_f J$ is found on the rich Ni side (i.e. $0.85 < x < 0.95$).

In conclusion, we have shown that the CePd$_{1-x}$Ni$_x$ system moves from a magnetic to a Kondo-like regime as the chemical potential (or Fermi Energy) is changed by alloying. This behaviour is reflected in the four independent physical properties: volume, magnetization, resistivity and specific heat.

The first crystal field excited state lies at about

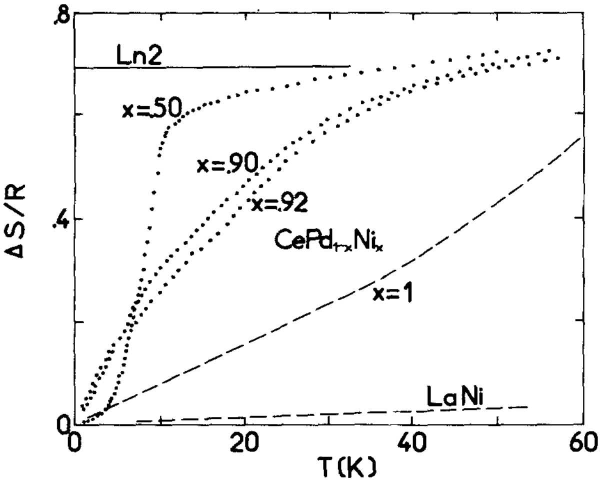

Fig. 6. Thermal variation of the entropy $\Delta S/R$. The CeNi and LaNi values (dashed lines) are extracted from [3]

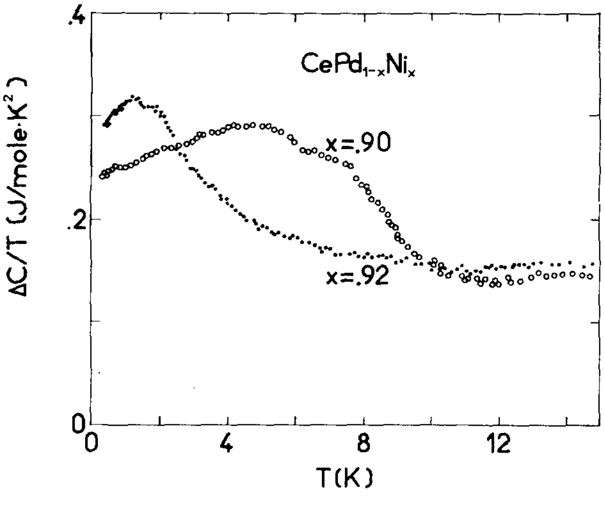

Fig. 7. Thermal variation of the $\Delta C/T$ ratio

$\delta \cong 200$ K, at least from low x values, in agreement with the entropy gain ($R \ln 2$) at $\cong 50$ K. This is a clear indication that only the doublet ground state is involved in the magnetic or Kondo like ground state formation. The magnetic contribution arises from an homogeneous magnetization of the system. Finally, the two contributions coexist in the sense that, if their respective entropies are taken as additive, the T_K temperature extracted from specific heat and magnetic measurements are in good agreement.

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