Specific heat of CeNi_x Pt_{1-x} pseudobinary compounds and related dilute alloys

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The low-temperature specific heat of $CEN_i Pt_{1-x}$ compounds has been investigated from $x=0$ to $x=1$. These compounds evolve from a Pauli paramagnet (CeNi) to a Kondo ferromagnet (CePt), with a crossover around $x=0.90$. The reduction of the magnetic entropy at T_c has been used to illustrate the increasing $4f$ -sd hybridization with increasing Ni content, related to a decrease of the cell volume. This effect has been confirmed by the results obtained on Y and La diluted compounds which have opposite volume effects. The relations between the jump in the specific heat at T_C , the magnetic moment, and the ratio T_K/T_c have been analyzed. The values of the electronic heat capacity γ vary as $\approx 1/T_K$ in the nonmagnetically ordered compounds in accord with the standard theory. However in the magnetically ordered compounds γ increases with T_K in accord with the resonance-level model developed by Bredl et al. [Z. Phys. B 29, 327 (1978)].

I. INTRODUCTION

The relative energy of the $4f$ levels of cerium ions with respect to the conduction band in intermetallic Ce-based alloys can give rise to a large number of observable physical phenomena, depending on the interactions in the compounds and the cerium valence state. The ion may change from a Ce^{3+} state with normal magnetic ordering to an enhanced Pauli paramagnet corresponding to an almost Ce ⁺ state. Between these extreme possibilities a wide range of so-called "anomalous phenomena" appear, among them the Kondo impurity or lattice, the heavy fermion state, and the intermediate or mixed valence state. $1-3$ The relationship between the magnetic Ruderman-Kittel-Kasuya- Yosida (RKKY), Kondo, and crystalline electric-field (CEF) interactions in these compounds plays an important role in determining their magnetic properties.

Specific-heat measurements provide a valuable method for studying the behavior of these compounds because the magnetic contribution to the heat capacity is directly related to the energy levels of the cerium ions. Furthermore, the linear electronic contribution (γ) also gives information about the conduction-band density of states at the Fermi level.^{4,5} The specific heat of nonmagnetically ordered compounds has been investigated theoretically using the Coqblin-Schrieffer model⁶ in the case of a noninteracting Fermi liquid⁷ or incorporating the effects

of the CEF on the magnetic impurity. 8 In the magnetically ordered, low-temperature regime, models have been cally ordered, low-temperature regime, models have been
developed to deal with particular cases.^{9,10} In this way a theory of Kondo systems for an $S = \frac{1}{2}$ resonant level¹¹ has been extended to Kondo lattices using a mean-field approach¹² in order to account for the specific-heat profile and the jump ΔC_{mag} at the ordering temperature. In this framework the relation between ΔC_{mag} and the ratio of the Kondo and ordering temperatures has also been analyzed.¹³ However, the combined effect of RKKY, CEF, and coherence effects has not yet been extensively stud i ed.³

Among the Ce intermetallic compounds, those with the CrB-type orthorhombic structure [such as equiatomic CeNi (Ref. 14), CePt (Ref. 15), CePd or CeRh (Ref. 16)] are particularly interesting. These compounds maintain the CrB structure both for substitutions on the d-metal site and also when Ce is replaced by nonmagnetic La or Y ions.¹⁷ The variations of cell volume give rise to changes in the properties according to a general rule: the 4f conduction-band hybridization increases with decreasing cell volume. Although this tendency is not always exhibited in other compounds [for example, $Yb(Ni_xPd_{1-x})_2Si_2$ (Ref. 18)], it has been clearly shown to apply for $CeNi_xPt_{1-x}$ (Ref. 19) and related dilute alloys.¹⁷ In this system the variation of T_K (Kondo temperature) and T_c (Curie temperature) on the increasing hybridization is in accord with the Doniach diagram and

Kondo lattice models.

Figure 1 summarizes the characteristic behavior of the compounds we have studied, showing the evolution of the different ground states. The Ce^{3+} state of the ferromagnet CePt changes progressively through a Kondo lattice and heavy fermion state to an intermediate valence state in CeNi. The crossover from the ferromagnetic ground state to the nonmagnetic ground state occurs at $\approx 90\%$ Ni substitution. The substitution of Ce by La has the effect of a negative pressure, decreasing T_K . The variation of T_c results from the combined effects of lattice pressure and the dilution of the Ce ions. Thus although one might expect reduced hybridization to enhance T_c , the effect of dilution causes T_c to fall with increasing La concentration.²¹ Substitution of Ce by Y acts as a positiv external pressure, strongly enhancing the hybridization, and magnetic ordering disappears for compounds with Y concentrations higher than 20% .²² For the lowest Ce concentrations a tendency towards a Kondo impurity behavior is found.²³

The CePt specific-heat measurements were performed in 1981.¹⁵ Some years later a study of the lowtemperature specific heat of three $CeNi_xPt_{1-x}$ compounds $(x = 0.5, 0.8, 0.95)$ was reported.²⁴ Although the electronic and lattice specific-heat components were not separated in the latter study, the main features of the heat capacity agree with the general trends of this series, as discussed in the previous paragraph.

The aim of this paper is to present a complete study of the specific heat of the CeNi_xPt_{1-x} system, including the

FIG. 1. Schematic evolution of the magnetic behavior of $CeNi_xPt_{1-x}$ and related Y- and La-diluted alloys. Full circles represent the compounds studied by other techniques (Refs. 17, 19, and ²¹—23). Open circles denote the compounds studied by specific-heat measurements.

La- and Y-diluted alloys. This has allowed us to investigate the interplay of the interactions across the diagram on Fig. 1. We have paid particular attention to the changing behavior of the specific heat in the ferromagnetic phase as the relative importance of RKKY and Kondo interactions varies.

II. EXPERIMENTAL

Polycrystalline ingots were prepared by direct melting of stoichiometric amounts of the constituents in a cold crucible induction furnace under an argon atmosphere and were annealed for two days at 700'C. The samples prepared were CePt, $CeNi_{0.7}Pt_{0.3}$, $CeNi_{0.8}Pt_{0.2}$, $\text{CeNi}_{0.85}\text{Pt}_{0.15}$, $\text{CeNi}_{0.9}\text{Pt}_{0.1}$, $\text{Ce}_{0.7}\text{La}_{0.3}\text{Ni}_{0.8}\text{Pt}_{0.2}$, $Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$, and $LaNi_{0.8}Pt_{0.2}$. The composition were checked by x-ray microanalysis electron microscopy, and the crystal structure was confirmed by x-ray diffraction to be the orthorhombic CrB-type (C_{mem} space group) (Ref. 25} for all the compounds. Those with $x \ge 0.80$ showed a broadening of the diffraction peaks, probably due to inhomogeneities in the samples or structural disorder at either Ni/Pt or Ce/La/Y sites. Samples were cut by spark erosion or diamond saw from the annealed polycrystalline ingots, and then polished to reduce the thickness. Typical sample masses were \sim 7 mg.

The specific heat at constant pressure was measured using the microcalorimeter at Birkbeck College. The heater and thermometers are made from a $0.45-\mu m$ layer of Si(P}, grown epitaxially on a sapphire substrate which serves as the sample holder. Samples are attached to the calorimeter with Wakefield Thermal Compound and the calorimeter is suspended in vacuum by its four electrical connections. The leads, which are made from $20-\mu m$ diam gold-plated tungsten wire, are spot-welded onto aluminum contact pads. The leads form a thermal link to a temperature-stabilized copper enclosure with a thermal resistance of typically 10^6 K W⁻¹. This assembly is then screwed onto the bottom of a 3 He cryostat and measurements made by one of the many variants of the relaxation technique.

III. RESULTS AND ANALYSIS

A. General trends

Figure 2 shows the specific heat versus temperature for all the compounds studied. For $x = 0.5$ and $x = 0.95$ the data are taken from Ref. 24. The CePt and $CeNi_{0.8}Pt_{0.2}$ results of this paper are in good agreement with those reported earlier.^{15,24}

CePt $(x=0)$ shows a clear λ -type anomaly characterized by a Curie temperature of $T_c=6.2$ K, defined as the inflexion point above the maximum of the $C(T)$ curve. For the other compounds the anomaly broadens and its maximum value decreases with increasing Ni content. The Curie temperatures (reported in Table I) rise up to 8.8 K for $x = 0.8$, and then decrease rapidly for $x \ge 0.9$. $CeNi_{0.95}Pt_{0.05}$ does not show any magnetic order.

Figure 2(b) illustrates the effect of dilution on the Ce site in $CeNi_{0.8}Pt_{0.2}$. We note that whereas the compound

with 30% La dilution shows a clear anomaly around T_c =5.1 K, the anomaly is strongly reduced for the 10% Y compound. The broadening of the peaks might be related to the inhomogeneity effects caused by substitutions as was suggested by x-ray analysis.

The nonmagnetic compounds LaPt (data from Ref. 15) and $\text{LaNi}_{0.8}\text{Pt}_{0.2}$ follow a well-defined Debye behavior in the temperature range studied. The LaPt specific heat has been taken as the phonon contribution C_{ph} for CePt whilst after taking into account the mass corrections,²⁶ the specific heat of $\text{LaNi}_{0.8}\text{Pt}_{0.2}$ has been used as C_{ph} for the remaining compounds.

FIG. 2. Specific heat versus temperature of (a) the CeNi_xPt_{1-x} series and (b) CeNi_{0.8}Pt_{0.2} and diluted La and Y compounds.

B. C_{mag} above T_C

Figure 3 displays the magnetic contribution to the specific heat, $C_{\text{mag}} = C - C_{\text{ph}}$, as a function of the reduced temperature T/\tilde{T}_C . It can be seen that C_{mag} remain finite above the magnetic transition. Apart from shortrange-order correlations that might be present above T_c , contributions to C_{mag} may arise from both Kondo resonance¹² and crystal-field effects.²⁷ In these low-symmet systems the $J = \frac{5}{2}$ multiplet splits into three doublets with the excited states separated from the ground state by energy gaps Δ_1 and Δ_2 . A Schottky-type anomaly is expected at temperatures above T_c . The behavior of C_{mag} above T_c is almost the same for all the compounds.

The effect of dilution on the specific heat, noted in Sec. III A, is shown again in Fig. 3(b). When the phonon contribution has been subtracted, and the data are plotted on the normalized scale, the specific-heat jump $\Delta \dot{C}_{\text{mag}}$ at T_C for $Ce_{0.7}La_{0.3}In_{0.8}Pt_{0.2}$ is almost the same as that of the nondiluted CeNi_{0.8}Pt_{0.2}, while for Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2} it is drastically reduced. The values of ΔC_{mag} obtained in this way are given in Table I. They are all lower than 12.48 $J K^{-1}$ mol⁻¹, the value for a purely magnetic two-level system in a conventional mean-field calculation. The magnetic entropies have been calculated from $\Delta S_{\text{mag}} = \int_0^T (C_{\text{mag}}/T) dT$, and are shown in Fig. 4. In all the compounds the magnetic entropy at T_c is lower than R ln2=5.76 JK⁻¹ mol⁻¹ corresponding to the double

FIG. 3. C_{mag} versus reduced temperature (T/T_C) of (a) the $CeNi_xPt_{1-x}$ series and (b) $CeNi_{0.8}Pt_{0.2}$ and diluted La and Y compounds.

TABLE I. Magnetic characteristics of the compounds studied: Curie temperature (T_C) ; jump of the specific heat at $T_C \, (\Delta C_{mag})$; reduced magnetic entropy at T_c [S_{mag} (T_c) /R ln2]; Kondo temperature (T_K) estimated from (i) the magnetic entropy (S_{mag}), (ii) the reduced magnetic entropy at T_c [S_{mag} (T_c) /R ln2]; Kondo temperature (T_K) e magnetic susceptibility ($|\theta_P|/2$), and (iii) quasielastic neutron scattering (QENS); linear electronic specific-heat coefficient (γ), without CEF corrections and with CEF corrections ($\Delta_1 = 100$ K); magnetic moment per Ce ion (M_0) obtained from magnetization (Refs. 19, 21, and 22).

							$(mJ K^{-2} mol^{-1})$		M_{0}
	T_c	$\Delta C_{\rm mag}(T_C)$	$S_{\text{mag}}(T_C)$				Not CEF	CEF	(μ_B)
Compound	(K)	$(J K^{-1} Ce mol^{-1})$	$\lceil R \ln(2) \rceil$	S_{mag}	$\frac{T_K({\bf K})}{\left \theta_P\right }$	OENS	corrected	corrected	per Ce ion
CePt	6.2 ± 0.1	10.6 ± 0.1	0.77	7.6	10	2.3	71 ± 10	105 ± 10	1.43
CeNi _{0.5} Pt _{0.5}	8.6 ± 0.1	5.3 ± 0.1	0.71	12.3	12.5	3.8	$135 + 7$	$160 + 7$	1.09
CeNi _{0.7} Pt _{0.3}	8.7 ± 0.1	4.2 ± 0.1	0.62	14.7	15		$167 + 17$	$180 + 17$	0.78
$CeNi_{0.8}Pt_{0.2}$	8.8 ± 0.1	2.4 ± 0.1	0.57	16.3	24.5	4.5	200 ± 10	223 ± 10	0.55
CeNi _{0.85} Pt _{0.15}	8.3 ± 0.2	1.1 ± 0.2	0.40	20.4	32		193 ± 15	$217 + 15$	0.29
CeNi _{0.9} Pt _{0.1}	7.8 ± 0.2	0.3 ± 0.2	0.23	42.5	49		$180 + 11$	205 ± 11	0.09
$CeNi_{0.95}Pt_{0.05}$					61		$120 + 7$	$120 + 7$	
$Ce_{0.7}La_{0.3}Ni_{0.8}Pt_{0.2}$	5.1 ± 0.2	2.2 ± 0.2	0.57	9.5	12		110 ± 13	$137 + 13$	
$Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$	4.5 ± 0.2	0.2 ± 0.2	0.26	15.4	40.5		$168 + 7$	$188 + 7$	

ground state. The magnitude of the reduction increases with Ni content $[Fig. 4(a)]$ or with Y dilution $[Fig. 4(b)],$ and may be interpreted as a consequence of the increasing importance of the Kondo interaction.

C. Estimating T_K and T_C

We have estimated T_K by several methods (see Table I). Firstly, we consider the reduction of the magnetic en-

FIG. 4. Magnetic entropy S_{mag} versus reduced temperature (T/T_C) of (a) the CeNi_xPt_{1-x} series and (b) CeNi_{0.8}Pt_{0.2} and diluted-La and Y compounds.

tropy at T_c from the value of R ln2. Using a simple two-level model with an energy splitting of $k_B T_K$,²⁸ we can deduce the reduced entropy at T_c as²⁹:

$$
\frac{\Delta S}{R} = \ln \left[1 + \exp\left(\frac{-T_K}{T_C} \right) \right]
$$

$$
+ \frac{T_K}{T_C} \left[\frac{\exp(-T_K/T_C)}{1 + \exp(-T_K/T_C)} \right]
$$

The entropy per Ce mol of the La-diluted compound at T_C remains the same as the undiluted $CeNi_{0.8}Pt_{0.2}$ [see Fig. 4(b)], indicating a similar ratio of T_K/T_c in both materials. However, dilution with Y decreases the entropy per Ce mol at T_c to about half that of CeNi_{0.8}Pt_{0.2}, and T_K is significantly larger than for the La-diluted compound. These results and the ΔC_{mag} values are a clear confirmation of the validity of the Doniach diagram when the hybridization is related to the cell volume as occurs in our system.

In Table I, the values of T_K obtained by other methods are also presented. From the paramagnetic Curie temperatures, which are negative for all the compounds, the T_K values are estimated as $|\theta_n|/n$. The values presented in Table I are taken from Ref. 19 with $n = 2$. However, other authors have proposed values of *n* from $n = 4$ (Ref. 31) to $n = 1$ (Ref. 32). From quasielastic neutron experiments³³ the deduced T_K values are much smaller. The most interesting feature in all these estimates of T_K is that the relative values and the general trend are always the same across the series in spite of being determined by different experimental methods. Such a difference between the values of T_K found from neutron and bulk property experiments has been observed in other Ce systems^{34,35} and may reflect the differing time scales of the experimental techniques.

As discussed in the Introduction, some theories have attempted to account for the reduction of ΔC_{mag} in terms of the relative importance of the Kondo and magnetic in-

FIG. 5. ΔC_{mag} versus T_K/T_C . The solid line represents the analytical variation of ΔC_{mag} (see text).

teractions. In particular, the $S = \frac{1}{2}$ resonant level mod el^{12} has provided a good description of $C_{mag}(T)$. Using Eqs. (12), (13), and (15) of Ref. 12, we have calculated explicitly the jump ΔC_{mag} at T_C , which is given by

$$
\Delta C_{\text{mag}} = \frac{6k_B}{\psi''(\frac{1}{2} + \zeta)} [\psi'(\frac{1}{2} + \zeta) + \zeta \psi''(\frac{1}{2} + \zeta)]^2
$$

where $\xi = (T_K/T_C)/2\pi$ and ψ' , ψ'' , and ψ''' are the first three derivatives of the digamma function. In Fig. 5 we compare the dependence of ΔC_{mag} vs T_K/T_C given by the above expression with the values obtained for our compounds, using T_K deduced from S_{mag} as in Table I. The agreement is quite good, especially considering the uncertainties in T_K , except for CePt, where the magnetic interactions are more important $(T_C \geq T_K)$. In this case, the above expression starts to break down due to the ferromagnetic order and strong CEF effects.

D. Estimating Δ_1 and γ

Estimates of the electronic coefficient of the specific heat γ depend strongly on assumptions made about the importance of CEF effects, and the contribution of the related Schottky anomaly.²⁷ Several attempts have been made to determine the correct CEF level scheme in CePt compounds, most of which lead to a total splitting of at least 200 K. Thermal-expansion measurements³⁶ and specific-heat measurements in $Ce_x La_{1-x} Ni$, ³⁷ have indicated the existence of a first excited doublet at around 65 K. Inelastic neutron scattering³³ provides evidence for a broad contribution centered around 160 K which decreases with Q, roughly as the magnetic form factor, and broadens out with increasing temperature. However it is not possible to say if this contribution accounts only for the first transition, or for the total CEF effects. In Fig. 6 we show the Schottky contributions for $\Delta_1=65$ K and Δ_1 =100 K together with the C_{mag} for one of the compounds (i.e., CeNi_{0.8}Pt_{0.2}). It is clear that the $\Delta_1 = 65$ K Schottky anomaly is too large, and the first excited doublet should be at a higher temperature. $\Delta_1=100$ K provides a more plausible estimate for the CEF contribution.

We now consider the effect of the CEF contribution on

FIG. 6. C_{mag} for $\text{CeNi}_{0.8}\text{Pt}_{0.2}$, compared to the CEF Schottk contributions for $\Delta_1 = 65$ K and $\Delta_1 = 100$ K.

the estimate of γ . In Fig. 7 the C/T versus T^2 curve for $CeNi_{0.8}Pt_{0.2}$ is compared with that obtained by subtract ing a Schottky contribution for $\Delta_1=100$ K. As can be seen, the γ value is about 10% larger than that obtained without the CEF correction. Table I lists the values of γ deduced with and without assuming a CEF contribution.

In Fig. 8 we plot the corrected values for γ as a function of Ni content (x) . The coefficient is enhanced for compounds with increasing hybridization, reaching values of more than 200 mJ K^{-2} mol⁻¹ around the crossover point $x \approx 0.9$. The maximum in this region corresponds to the strongest hybridization of 4f and sd states. For compounds with higher Ni concentration, delocalized Pauli paramagnetism is predominant.

Indications of a similar behavior of γ have been found for other series going from a localized to a delocalize state, e.g., in $CeSi_x$, $3\bar{8}-40$ a ferromagnetic Kondo lattice system, and in Ce($\overline{R}h_{1-x}Ru_{x})_{2}Si_{2}$,⁴¹ an antiferromagne cally ordered system which presents a similar γ variation
with increasing Ru concentration. However the with increasing Ru concentration. CeNi_xPt_{1-x} shows the variation of γ more clearly than any other system of which we are aware.

A $\gamma \propto 1/T_K$ dependence is commonly assumed (see, for example, Yoshimori⁴² or Rajan⁷), but this is found for Kondo impurity and heavy fermion systems in which no magnetic order occurs. In Kondo lattice systems, in the

FIG. 7. C/T versus T^2 plot for $CeNi_{0.8}Pt_{0.2}$ showing the different estimates of the electronic specific-heat coefficient (γ) depending on the CEF corrections.

FIG. 8. Electronic specific-heat coefficient (γ) as a function of composition. The solid line is drawn as a guide only. The x values of the points for the two dilutions (\Box and Δ) have been adjusted to make them lie near the line. The difference between the adjusted x values and the actual value ($x = 0.8$) reflects the sensitivity of γ to cell volume changes due to Y and La dilution.

presence of RKKY-induced magnetic order, it is possible for T_k and γ to increase at the same time. From a theoretical point of view, this effect can be understood on the basis of the resonance model as modified by Bredl, Steglich, and Schotte.¹² Within this framework, the electronic specific-heat coefficient becomes according to Eq. (10) of Ref. 12

$$
\gamma \sim \frac{T_K}{T_K^2 + H^2}
$$

where H is the Zeeman energy of the magnetic moment associated with a Ce^{3+} ion within the molecular field created by the other ions. By taking the variation of T_K with Ni concentration from Table I, and assuming a decrease of H with increasing Ni content, we are able to account qualitatively for the experimental variation of γ .

IV. CONCLUDING DISCUSSION

The general analysis developed above, looking at the evolution of γ and the magnetic entropy, confirms the close correlation between the increasing hybridization and the decrease of the cell volume. This makes the Doniach diagram valuable in understanding the "anomalous" behavior of this series of compounds in the framework of an available model. The diluted compounds with La and Y are significant examples of the validity of such an analysis. The agreement of the ΔC_{mag} values with the analytical expression for ΔC_{mag} vs T_K/T_C indicates that the $S = \frac{1}{2}$ resonant-level model is appropriate when the Kondo interactions become more important than the

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FIG. 9. ΔC_{mag} versus magnetic moment M_0 , taken from Refs. 21 and 22. The solid line joins the origin with the Ce^{3+} free ion values $(M_0=2.14\mu_B/\text{atom},$ $\Delta C_{\text{mag}} = 12.48$ $J K^{-1}$ mol⁻¹).

RKKY coupling. We have noted the need to take into account the Schottky contributions from both Kondo and CEF effects in order to estimate correctly the γ values.

An extension of the single-ion impurity resonant-level model considering strong magnetic interactions and CEF effects would be needed to account for our experimental results. In Fig. 9, we present the relationship between ΔC_{mag} at the transition temperature and the magnetic moment M_0 . The results are in accord with a simple linear dependence from the origin to the $Ce³⁺$ free ion state with $M_0 = 2.14 \mu_B$ and $\Delta C_{\text{mag}} = 12.48 \text{ J K}^{-1} \text{ mo}$ indicating that ΔC_{mag} and M_0 depend in the same way on the hybridization. Once again, we see that the dilution with Y has more important consequences than dilution with La.

In conclusion the CeNi_xPt_{1-x} system and in particular $CeNi_{0.8}Pt_{0.2}$ and the related diluted alloys provide an excellent example of increasing hybridization in a Kondo lattice with strong anisotropy. The competition between RKKY and Kondo interactions leads to a γ variation with a maximum at the crossover from nonmagnetic to the magnetically ordered regimes, which can be understood in terms of the resonance-level model as developed by Bredl, Steglich, and Schotte.¹²

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