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Evolution from Kondo ferromagnet to intermediate valence in the $\text{Ce}_x\text{Y}_{1-x}\text{Ni}_{0.8}\text{Pt}_{0.2}$ system

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Abstract. The effect of substitution of cerium by yttrium on the $\text{CeNi}_{0.8}\text{Pt}_{0.2}$ dense Kondo ferromagnet has been studied by means of magnetic and electrical resistivity measurements. The evolution from Kondo ferromagnetic behaviour to a non-magnetic ground-state regime is interpreted according to the theoretical Kondo lattice model.

Anomalies in the temperature dependence of the electrical resistivity such as those observed in $\text{CeSi}_{1.85}$ are also found in this system.

1. Introduction

The $\text{CeNi}_y\text{Pt}_{1-y}$ compounds are an interesting system in which a continuous evolution from a Ce^{3+} magnetic state, in CePt , to an intermediate-valence state, in CeNi , was observed, passing through a ferromagnetic Kondo regime [1]. This behaviour is in agreement with the theoretical Kondo lattice model [2–4], confirming the predicted variations in T_C (Curie temperature) and T_K (Kondo temperature) with $|\Gamma N(E_F)|$, this product increasing with increasing Ni content. Γ is the negative coupling constant between the 4f shell and the conduction band and $N(E_F)$ is the density of the states at the Fermi level.

Among the compounds of this series, two are especially exciting, namely CeNi and $\text{CeNi}_{0.8}\text{Pt}_{0.2}$. CeNi [5] exhibits, under a small applied pressure ($P_c \approx 2$ kbar), a first-order transition between a high and low magnetic state of the 4f electrons analogous to the γ -to- α transition in Ce metal. The chemical substitution of Ce by Y in CeNi [6] by decreasing the lattice parameters has the same effects on the magnetic properties as does a weak applied pressure: a decrease in the susceptibility maximum χ_{\max} and an increase in the temperature T_{\max} of this susceptibility maximum. This substitution leads to an enhancement of the intermediate-valence character. However, in a $\text{Ce}_{0.9}\text{Y}_{0.1}\text{Ni}$ single crystal the γ -to- α transition evidenced in CeNi is no longer observed even under a pressure of 5 kbar.

$\text{CeNi}_{0.8}\text{Pt}_{0.2}$ is a dense Kondo ferromagnet [7], with a large Curie temperature ($T_C = 8.6$ K) and a huge reduction in the Ce magnetic moment ($0.54\mu_B$) mainly due to a large Kondo effect. In this compound, $|\Gamma N(E_F)|$ is close to the critical value which subdivides

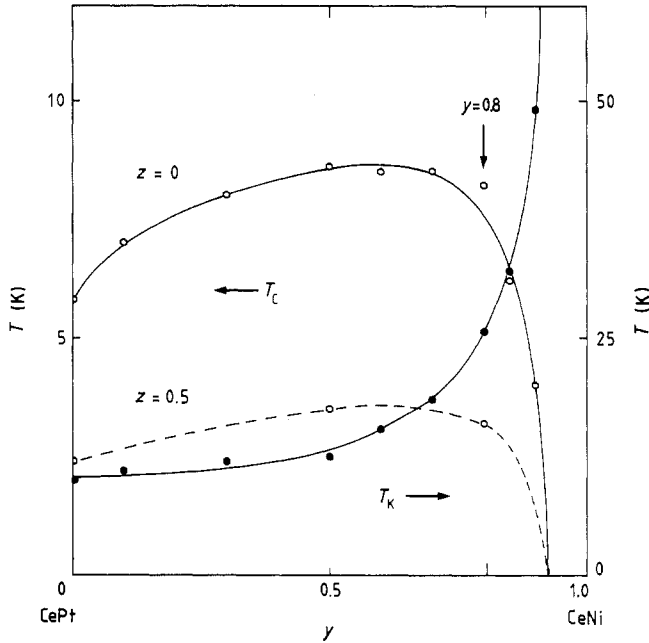


Figure 1. Curie temperature T_C and Kondo temperatures T_K of $Ce_{1-z}La_2Ni_yPt_{1-y}$ compounds. (Taken from [5].)

the $CeNi_yPt_{1-y}$ phase diagram into magnetically ordered Kondo compounds and those with mainly a Fermi liquid behaviour.

The substitution of Ce by La in $CeNi_{0.8}Pt_{0.2}$ [8] which increases the cell volume, gives rise to a decrease in $|\Gamma N(E_F)|$, having an effect opposite to the effect of the applied pressure. The importance of the Kondo effect decreases when the La content increases, whereas the T_C -values are mainly related to dilution effects. These results, as well as those previously reported for $Ce_xLa_{1-x}Pt$ and $Ce_xLa_{1-x}Ni_{0.5}Pt_{0.5}$ [9], can be interpreted in the framework of the theory of competition between the Kondo effect and exchange interactions (figure 1).

In order to complete this study, it seems interesting to substitute Y for Ce in $CeNi_{0.8}Pt_{0.2}$. This substitution should allow us to investigate the evolution from a Kondo ferromagnetic behaviour to a non-magnetic ground-state regime, increasing the $|\Gamma N(E_F)|$ -value as is expected owing to the decrease in the cell volume with increasing Y content.

In this paper we report and discuss the crystallographic, magnetisation and resistivity measurements performed on polycrystalline samples of $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ for $x = 1, 0.9, 0.8, 0.7$ and 0.5 . These results together with the previous results give us a deeper understanding of the dilution and pressure effects on the $CeNi_xPt_{1-x}$ system.

2. Experimental details

The polycrystalline samples were prepared in a cold-crucible induction furnace, under an argon atmosphere. The phase purity was checked using the Debye-Scherrer method

Table 1. Lattice parameters and unit-cell volume of the $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ alloys. The V -value of 183.1 \AA^3 from [1] was obtained by the Debye–Scherrer method.

Ce concentration x	a (\AA)	b (\AA)	c (\AA)	V (\AA^3)
0.5	3.783	10.434	4.343	171.4
0.7	3.796	10.488	4.374	174.2
0.8	3.817	10.551	4.380	176.4
0.9	3.852	10.589	4.403	179.6
1.0	3.868	10.688	4.443	183.5
1.0	3.830	10.790	4.430	183.1 [1]

(Cr $K\alpha$ radiation) as well as high-resolution powder diffractometry (Cu $K\alpha$ radiation). No extra phases were observed. The lattice parameters were determined from the powder diffractograms by a least-squares method using 10 reflections. The resistivities were measured by an alternating-current four-probe method between 1.5 and 300 K at the Laboratoire Louis Néel of Grenoble and at the Laboratorio de Física del Estado Sólido of the Universidad de Cantabria. The samples were reduced by spark cutting in a parallelepiped shape having a typical dimension of $5 \text{ mm} \times 2 \text{ mm} \times 2 \text{ mm}$. Magnetic measurements were performed between 1.5 and 300 K at the Laboratoire Louis Néel.

3. Crystallographic analysis

All the studied samples crystallise in the CrB-type orthorhombic structure (space group, Cmc m).

The lattice parameters and the cell volume are reported in table 1. In figure 2, we compare the cell volume variation of $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ with those previously obtained for the $Ce_xLa_{1-x}Ni_{0.8}Pt_{0.2}$ and $Ce_xY_{1-x}Ni$ series.

As expected, the introduction of Y has an effect opposite to that of La dilution, and the relative volume variation $[V(x = 1) - V(x = 0.6)]/V(x = 1) = \Delta V/V$ is more drastic in the Y case. Within the experimental accuracy, the interesting fact is the different behaviours of the Ce_xY_{1-x} and the $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ series. In the first case, the variation is almost linear with an initial variation $\Delta V/V$ of 1.0% between $x = 1$ and $x = 0.9$. For the second case a positive curvature is observed and the initial decrease is larger ($\Delta V/V = 2.1\%$ between $x = 1$ and $x = 0.9$).

4. Resistivity measurements

Resistivity measurements were performed for compounds with $x = 0.9, 0.8, 0.7$ and 0.5 . For each compound, the measurements were repeated on at least two different pieces, in order to minimise metallurgical problems in the samples. In fact the brittleness and the existence of possible cracks in the samples lead to some dispersion in the resistivity values at room temperature for different pieces of the same compound (e.g. 103, 109.5, 119.5 and $120.2 \mu\Omega \text{ cm}$ for $Ce_{0.5}Y_{0.5}Ni_{0.8}Pt_{0.2}$). However, the temperature dependence is always similar.

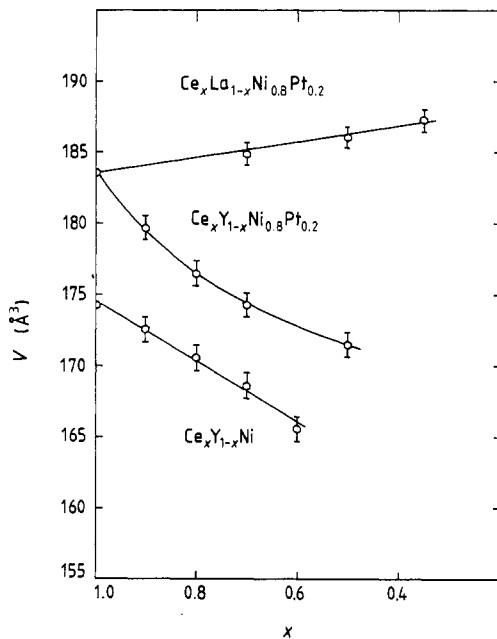


Figure 2. Crystallographic cell volume of $Ce_xLa_{1-x}Ni_{0.8}Pt_{0.2}$, $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ and $Ce_xY_{1-x}Ni$.

An unusual behaviour is obtained for Y-based samples when they were thermally cycled by cooling to 12 K and then warming to room temperature. As an example of such a behaviour we present, in figure 3, four thermal cycles performed on $Ce_{0.8}Y_{0.2}Ni_{0.8}Pt_{0.2}$. In the first cooling, an increase in the resistivity appears at around 100 K; this is certainly due to crack formation. This effect progressively disappears in successive cycles. The permanent increase in the resistivity at 300 K after each cycle shows a tendency to saturation; the number of cracks in the last few cycles does not increase significantly.

In order to check possible structural changes, we performed x-ray diffractograms at 300 K on samples before and after a full cycle but no crystallographic transformation was observed.

It is interesting to note that similar behaviour has been recently found for $CeSi_x$ [10], which is one of the few other ferromagnetic Kondo systems [10–13]. In [10] the results of thermal cycling experiments are presented, in particular for $CeSi_{1.855}$ near the localised–delocalised crossover point. An increase in ρ on cooling appears at about 120 K and the permanent change in ρ in successive cycles is also attributed to crack formation. In [10] this crack formation is associated with the hybridisation degree of the 4f wavefunction, i.e. with the change in the Ce valence.

In our study these anomalies have been observed in the Y-based compounds but neither $CeNi_yPt_{1-y}$ nor La-diluted compounds present such behaviour.

In figure 4 we compare the thermal variation in the electrical resistivity heating between 1.5 and 300 K for the studied compounds. These variations have been obtained as follows.

(i) For each sample we consider the lowest value of the resistivity at 300 K, before cooling, as the most reliable, because only initial metallurgical defects or cracks should be present.

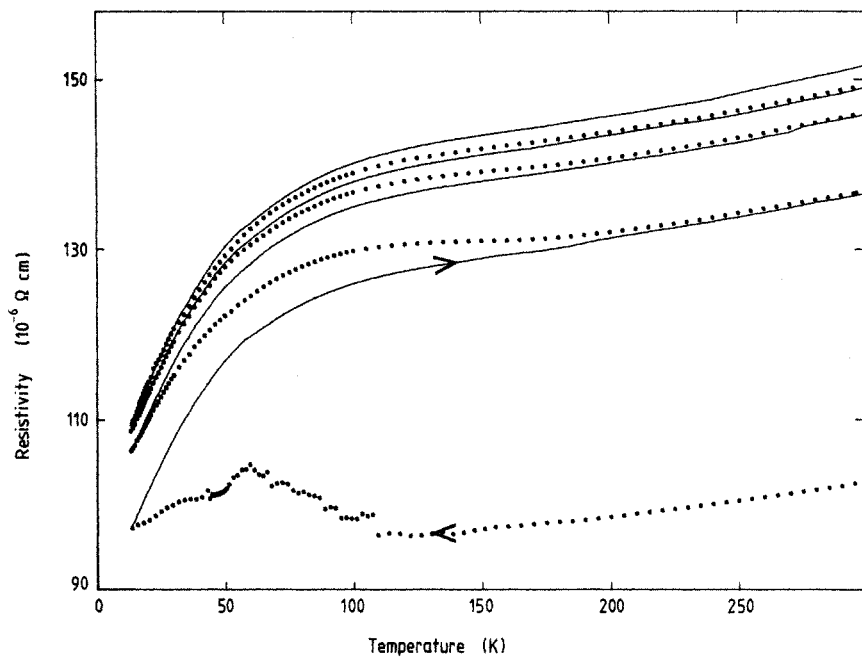


Figure 3. Thermal cycling electrical resistivity of $Ce_{0.8}Pt_{0.2}Ni_{0.8}Pt_{0.2}$: ●, data obtained on cooling; —, data obtained on warming.

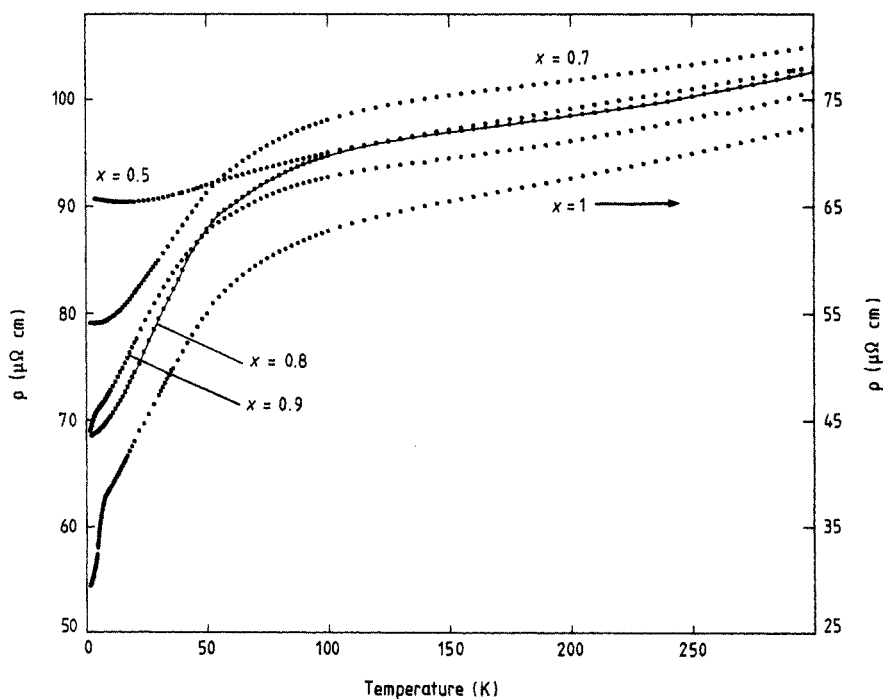


Figure 4. Thermal dependence of the electrical resistivity of $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$, obtained as explained in the text.

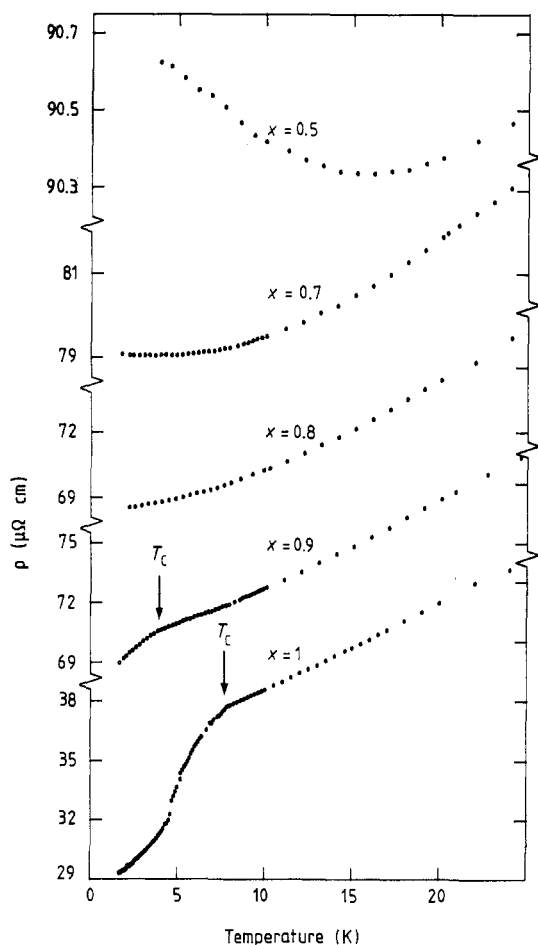


Figure 5. Low-temperature dependence of the electrical resistivity of $\text{Ce}_x\text{Y}_{1-x}\text{Ni}_{0.8}\text{Pt}_{0.2}$.

(ii) The variation which represents the best intrinsic behaviour of the resistivity is that obtained when the induced cracks seem to be saturated; this is the heating curve of the last cycle.

(iii) This curve has been divided by a constant in order to obtain the most reliable value of ρ (300 K) as explained in (i).

The only Y-based compound showing a slope change at $T_C = 3.1$ K is $\text{Ce}_{0.9}\text{Y}_{0.1}\text{Ni}_{0.8}\text{Pt}_{0.2}$. For $x < 0.9$ the compounds do not present any magnetic order. In figure 5, we present the low-temperature resistivities. A tendency for a minimum to appear at low temperatures is observed with increasing Y content. This minimum is observed at around 3 K for $x = 0.7$ and becomes deeper and shifted to 15 K for $x = 0.5$.

The magnetic contribution ρ_m to the resistivity cannot be determined with accuracy because of the absence of a reliable estimation of the phonon contribution and of the intrinsic residual resistivities, owing to the metallurgical problems quoted above. Nevertheless it can be appreciated from figure 4 that the magnetic contribution ρ_m clearly decreases when the Y content increases. From the general shape of the ρ against T

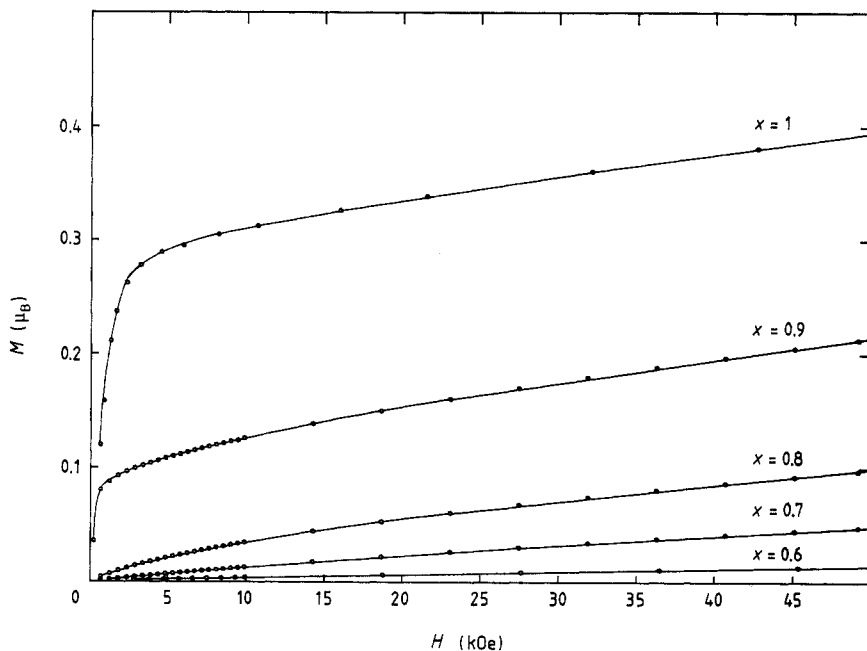


Figure 6. Magnetisation as a function of the applied magnetic field at 1.5 K for $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$.

curves in the non-ordered compounds, we can reasonably foresee a ρ_m behaviour with a broad maximum at high temperatures (about 100 K), characteristic of a Fermi liquid regime.

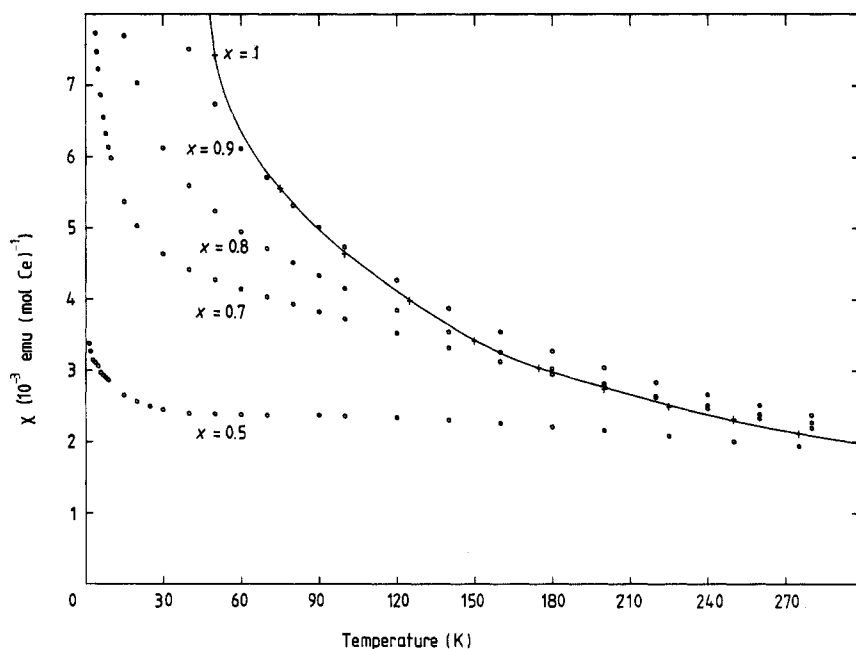
5. Magnetic measurements

Magnetic measurements confirm that, among the studied compounds with $x \neq 1$, only $Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$ shows ferromagnetic behaviour. The Curie temperature obtained from Arrott plots is 3.1 K in agreement with that found by electrical resistivity measurements. Figure 6 shows the field dependence of the magnetisation at 1.5 K for all the studied compounds. In a 50 kOe applied field the magnetisation per Ce atom strongly decreases when the Y content increases. For $x = 0.9$, this reduction is about 40% with regard to magnetisation for $x = 1$. For $x = 0.7$ and $x = 0.5$ the magnetisation is extremely low. The thermal dependence of the reciprocal susceptibility for $Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$ follows a Curie–Weiss law above 50 K, giving an effective moment of $2.60\mu_B$ per Ce atom close to the Ce^{3+} free-ion value and a paramagnetic Curie temperature θ_p of -81 K.

For the other compounds, deviations from the Curie–Weiss law are observed, and the linearity seems to appear only above 200 K. Correcting for temperature-independent contribution to the susceptibility χ_0 , a Curie–Weiss law with effective moments close to the Ce^{3+} free-ion value is found down to temperatures smaller than 100 K. The θ_p

Table 2. Magnetic characteristics of $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$ compounds.

Compound	T_C (K)	M at 50 kOe (μ_B/Ce atom)	θ_p (K)	χ_0 (emu mol $^{-1}$)
$CeNi_{0.8}Pt_{0.2}$	8.6	0.3960	-49	0
$Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$	3.1	0.2359	-81	0
$Ce_{0.8}Y_{0.2}Ni_{0.8}Pt_{0.2}$	—	0.1220	-89	1.1×10^{-5}
$Ce_{0.7}Y_{0.3}Ni_{0.8}Pt_{0.2}$	—	0.0689	-123	1.7×10^{-4}
$Ce_{0.5}Y_{0.5}Ni_{0.8}Pt_{0.2}$	—	0.0306	-296	2.5×10^{-4}

**Figure 7.** Thermal variation in susceptibility of $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$.

absolute values obtained after these corrections increase roughly with increasing Y content. The magnetic characteristics of these compounds are presented in table 2.

The susceptibilities of the compounds are presented in figure 7. This figure shows quite well the evolution from the ferromagnetic behaviour for $x = 1$ and $x = 0.9$ to a Fermi liquid state for $x = 0.5$. In this last compound a small and broad maximum at around 90 K characteristic of a Fermi liquid with spin fluctuations [14] is observed.

6. Discussion

The experimental results reported above clearly show that the substitution of Ce by Y atoms in $CeNi_{0.8}Pt_{0.2}$ has, as expected, an effect opposite to that of La substitution.

The important decrease in T_C from 8.6 K in $CeNi_{0.8}Pt_{0.2}$ to 3.1 K in $Ce_{0.9}Y_{0.1}Ni_{0.8}Pt_{0.2}$, as well as the decreases in the magnetisation and magnetic resistivity, cannot be attributed only to the dilution effects as for La substitution for which these decreases are much smaller [7]. The introduction of Y, which decreases the cell volume, enhances the hybridisation of the 4f wavefunctions, leading to an increasingly delocalised behaviour. For $x = 0.9$, the Kondo interactions are increased as can be evaluated from the increase in $|\theta_p|$ and the huge reduction in the Ce moment estimated from the magnetisation measurements. For $x \leq 0.8$ the magnetic order disappears, and the intermediate-valence character is enhanced with increasing Y content as was observed in $Ce_xY_{1-x}Ni$ [6].

As noticed in the crystallographic analysis (figure 2) the largest initial decrease in $\Delta V/V$ is observed in $Ce_xY_{1-x}Ni_{0.8}Pt_{0.2}$. This can be interpreted as an indication of the evolution from a 3+ valence state for $x = 1$ to the intermediate valence for $x < 0.8$.

These results are consistent with the theoretical model of the Kondo lattice, as can be seen from figure 1. As we have discussed, the introduction of Y leads to an increase in $|\Gamma N(E_F)|$ and then we expect the same effect as an increase in y in the diagram of figure 1. Because of the situation of $CeNi_{0.8}Pt_{0.2}$ in the diagram, a small y increase leads to a steep decrease in T_C and an increase in Kondo interactions, according to our results.

It is interesting to note the existence of a minimum in the resistivity of $Ce_{0.5}Y_{0.5}Ni_{0.8}Pt_{0.2}$. This can be attributed to the growing of the importance of a Kondo impurity effect in these diluted non-magnetic compounds.

The last comment is about the anomalous behaviour in the resistivity. It is noticeable that these anomalies appear in two ferromagnetic Kondo systems [1, 10], and near the composition of crossover from the localised to delocalised state. The interpretation given in $CeSi_x$ [10] is that the changes in the Ce valence, associated with anisotropic changes in cell parameters give rise to large internal stress which could be relieved by crack formation in polycrystalline samples and brittle materials as $CeSi_{1.85}$. The open question, in our study, is whether crack formation is induced by the increase in hybridisation 4f wavefunctions when lowering the temperature or whether it is independent of the magnetic effects and only related to metallurgical problems. In fact, changes in the Ce valence state with the temperature have been observed in CeNi and other intermediate-valence compounds [15]. Furthermore, CeNi presents a large and anisotropic thermal expansion and the γ -to- α transition [5] is also strongly anisotropic. Then it is reasonable to think about the same crack formation in $CeSi_{1.85}$ and our compounds. In La-based compounds the anomaly could not be observed because the localisation of the 4f electron is not modified or only very weakly modified. Thermal expansion and temperature-dependent x-ray diagrams have been undertaken in order to ascertain the origin of this anomalous behaviour.

In conclusion the present work allows us to obtain a better insight into the dilution effects in the ferromagnetic Kondo system $CeNi_xPt_{1-x}$, which can be interpreted in the framework of the theory of competition between the Kondo effect and RKKY exchange interactions.

Acknowledgments

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