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Magnetic–non-magnetic crossover in $Ce(Pd_{1-x}Cu_x)_2Si_2$

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Abstract. Resistivity and static susceptibility measurements of $Ce(Pd_{1-x}Cu_x)_2Si_2$ indicate that the crossover from magnetic behaviour in antiferromagnetic $CePd_2Si_2$ to non-magnetic behaviour is very rapid on substituting copper for palladium. No antiferromagnetic transition is observed for $x = 0.2$. The static susceptibility is Curie–Weiss-like to the lowest temperatures measured ($\simeq 1.5$ K) for $x = 0.1$ and shows a broad maximum near 30 K for $x = 0.2$. The resistivity shows a continuous crossover with a rapid change in the behaviour at high temperatures near $x = 0.2$ which may correspond to changes in the crystal-field configuration. The temperature of the low-temperature peak in resistivity shows a significant change near $x = 0.4$ which may result from the interplay between the RKKY interaction and the 'Kondoesque' s–f exchange causing changes in the spin–spin correlation lengths.

1. Introduction

Most cerium-based compounds with the formula RM_2Si_2 (where R is the rare earth and M is a transition metal) have the $ThCr_2Si_2$-type tetragonal crystal structure. The cerium atom are in 'cages' formed by the metal and silicon atoms in a body-centred-tetragonal arrangement. If one starts with $CePd_2Si_2$ and substitutes for Pd with Cu, the environment of the cerium atoms—the cell volume and the relevant energy parameters—is changed while the tetragonal crystal structure of the system remains the same. This makes it possible to observe the crossover in behaviour that occurs without varying the cerium concentration, reducing the complexity of the problem. The original goal of this research was to measure the Néel temperatures T_N as a function of the concentration x. It was assumed that T_N goes continuously and (somewhat) gradually to zero as the copper concentration is increased. As shown below, this is not the case.

$CePd_2Si_2$ and $CeCu_2Si_2$ have a similar paramagnetic state at high temperature and are Kondo lattice systems. $CePd_2Si_2$ has an antiferromagnetic ground state with a Néel temperature of $T_N = 10$ K determined from neutron scattering [1] ($T_N = 9.2$ K from susceptibility measurements [2]), and its Curie–Weiss temperature is $\theta = 70$ K [2]. In contrast, $CeCu_2Si_2$ has a non-magnetic ground state with a superconducting transition temperature of 0.5 K [3]. Its Curie–Weiss temperature was determined by Sales and Viswanathan [4] to be 164 K and by Lieke and co-workers [5] to be 140 K. The effective moment of $CeCu_2Si_2$ was determined by Sales and Viswanathan [4] to be 2.68 μ_B and by Lieke and co-workers [5] to be 2.62 μ_B. The anisotropy of the susceptibility is also different: $CePd_2Si_2$ has the largest susceptibility along the [110] direction [6] while $CeCu_2Si_2$ has the largest susceptibility along [001] [7]. $CeCu_2Si_2$ is a heavy-fermion

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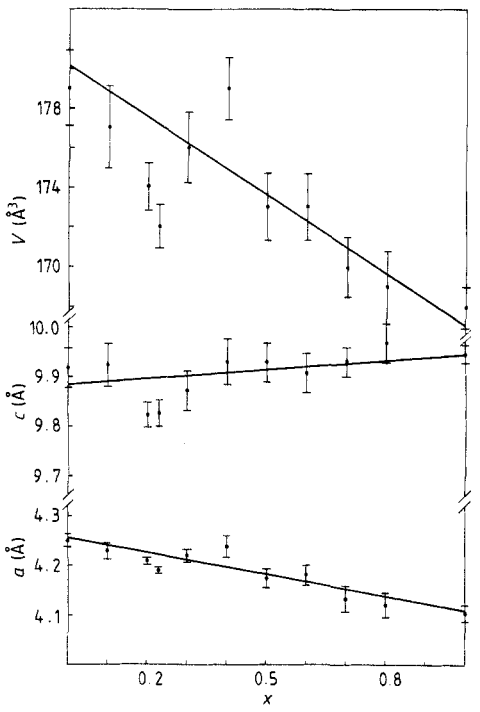

Figure 1. Lattice parameters, a and c, and unit-cell volume v as functions of x.

superconductor which is characterised by its large electronic specific heat at low temperature, very high density of states at the Fermi level and thus an effective mass of 200 times that of the free-electron mass as well as an enhanced Pauli susceptibility at low temperature [8]. We have investigated the behaviour of the system $Ce(Pd_{1-x}Cu_x)_2Si_2$ for the full range of x between 0 and 1 by measuring the resistivity as a function of temperature for different values of x. Static susceptibility measurements have been performed on samples with $x = 0, 0.1$ and 0.2.

2. Experimental techniques

The samples were prepared by melting high-purity raw materials in an argon arc furnace several times. The compounds were then melted again and sucked into a mould in the copper hearth by a vacuum pump. The resulting sample has the shape of a rod with a length of over 1 cm and a cross section that is a square with an area of 1 mm^2. The resulting samle was then wrapped in tantalum foil and sealed in a vacuum in a Vycor tube for annealing. The samples were annealed for four to five days at 800 K.

An x-ray powder pattern was measured for each annealed sample using Cu Kα radiation. The powder patterns were used to check the samples for the correct crystal structure as well as to measure the lattice parameters of the samples. The lines in the x-ray powder patterns were analysed in terms of the $ThCr_2Si_2$ tetragonal structure. Figure 1 shows the lattice parameters a and c and the unit-cell volume as functions of the copper concentration, x. Our measurements are in good agreement with earlier measurements of the lattice parameters for $CePd_2Si_2$ ($a = 4.24$ Å and $c = 9.88$ Å [1]) and for $CeCu_2Si_2$ ($a = 4.110$ Å and $c = 9.942$ Å [9]).

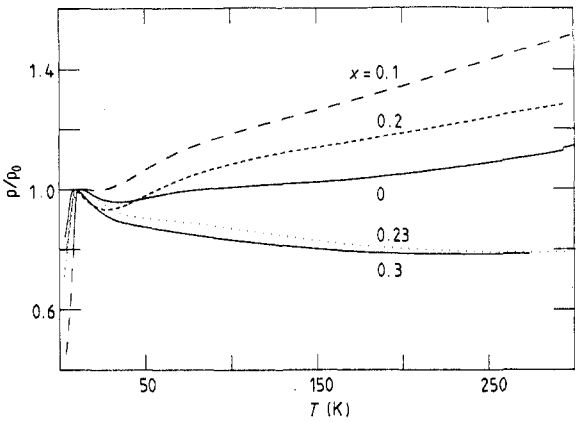

Figure 2. Scaled ρ versus T curves for $Ce(Pd_{1-x}Cu_x)_2Si_2$ for $x = 0, 0.1, 0.2, 0.23$ and 0.3.

The resistivity measurements were made by the standard four-probe DC method with the four copper wire leads attached to the sample by spot-welding. The distance between the two voltage leads on the sample was measured to get the length, and the cross sectional area was taken to be 1 mm^2 in the calculations of the resistivity. This gives only a rough measure of the absolute value of the resistivity of the samples because of voids in the sample where the sample did not completely fill the whole cross section of the mould. Microcracks may also form due to the tetragonal structure of the compound and the anisotropic lattice collapse upon cooling, changing the normalisation and causing the measured resistivity to change from one run to the next (the apparent resistivity increases). The deviation of the measured resistivity from the actual value may be 20% or more. Because of this, all data for a given sample were taken in the same temperature cycle on warming.

Static susceptibility measurements were made by the Faraday method using an electrobalance in a magnetic field $H \leq 2$ kOe. The temperature was measured using a 7% Fe–Au–chromel thermocouple, for which the limit of uncertainty in the temperature reading is ± 0.1 K above 5 K increasing to ± 0.5 K at 2 K.

3. Results and discussion

3.1. Resistivity

The resistivity curves for $CePd_2Si_2$ and $CeCu_2Si_2$ are quite similar. They have a similar shape with two rather broad maxima at roughly the same temperature. Both show a rapid decrease in ρ at low temperature. However, on close inspection some differences can be seen. The high-temperature behaviour is quite different. The resistivity of $CePd_2Si_2$ has a positive slope near room temperature while the resistivity of $CeCu_2Si_2$ has a negative slope. At low temperature the rapid drop in ρ on decreasing temperature occurs at about 20 K in $CeCu_2Si_2$ but at about 10 K in $CePd_2Si_2$. The cause of the low-temperature drop is also presumably different, being due to coherence effects in $CeCu_2Si_2$ and due to the antiferromagnetic ordering in $CePd_2Si_2$.

The curves for $Ce(Pd_{1-x}Cu_x)_2Si_2$ also display these same features to some extent. The high-temperature maximum is reduced to a shoulder on a negatively sloping background for $0.2 < x \leq 0.8$, but the low-temperature maximum and the rapid decrease in

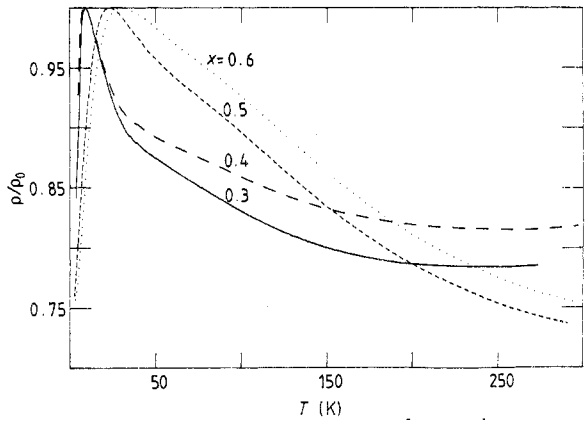

Figure 3. Scaled ρ versus T curves for $Ce(Pd_{1-x}Cu_x)_2Si_2$ for $x = 0.3, 0.4, 0.5$ and 0.6.

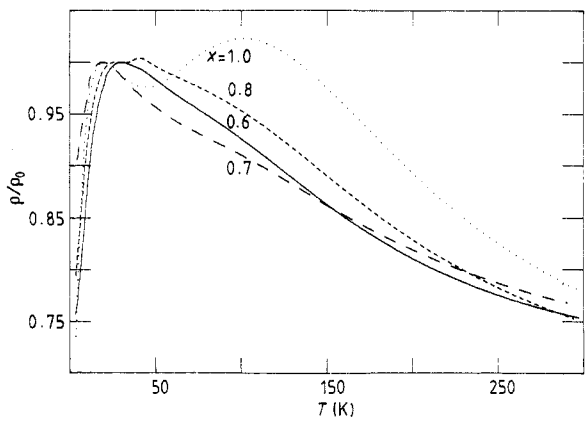

Figure 4. Scaled ρ versus T curves for $Ce(Pd_{1-x}Cu_x)_2Si_2$ for $x = 0.6, 0.7, 0.8$ and 1.

ρ below it is present for all x. Figures 2, 3 and 4 show the resistivity versus temperature curves for $Ce(Pd_{1-x}Cu_x)_2Si_2$ for various x normalised to the value at the low-temperature maximum.

3.2. Static susceptibility

The static susceptibility results for $CePd_2Si_2$ are consistent with those of other investigators [10]. We obtain a Curie–Weiss temperature of 62 K, a Néel temperature of 8 K, and an effective moment of 2.66 μ_B. These are consistent with [2]. The low-temperature static susceptibilities for $x = 0.1$ and $x = 0.2$ are shown in figures 5 and 6.

The susceptibility of the $x = 0.1$ sample is very large at low temperatures and suggests a phase transition with $T_N < 2$ K. Although it does show the sharp peak, which is supposed to locate the Néel temperature, with only one data point available below it, it can be taken as weak evidence for magnetic ordering only. The susceptibility of the $x = 0.2$ sample shows no sign of ordering and displays a broad maximum near $T = 30$ K.

3.3. Discussion

The changes in the resistivity that occur at high temperature appear to be related to the crystal-field configuration changes on going from $CeCu_2Si_2$ to $CePd_2Si_2$. The high-temperature resistivity of $CeCu_2Si_2$ is fitted reasonably well by a theory derived by

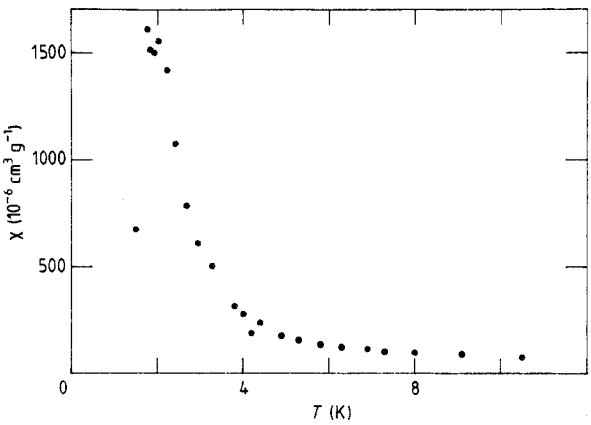

Figure 5. The low-temperature static susceptibility of $Ce(Pd_{0.9}Cu_{0.1})_2Si_2$.

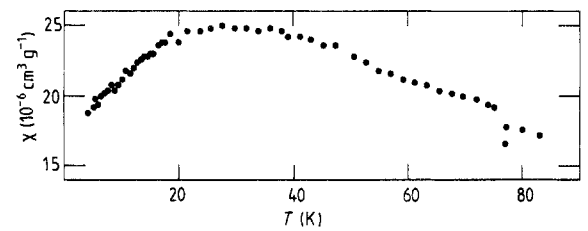

Figure 6. The low-temperature static susceptibility of $Ce(Pd_{0.8}Cu_{0.2})_2Si_2$.

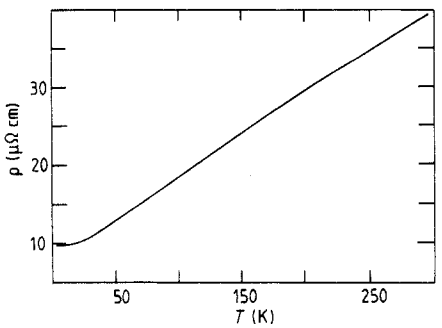

Figure 7. The ρ versus T curve for $LaPd_2Si_2$.

Kashiba and co-workers [11] where the broad maximum results from the crystal-field splitting and the peak occurs at roughly a third of the splitting if the Kondo temperature T_K is small compared with the crystal-field splitting (This was shown to hold for the $Ce_{1-x}La_xPb_3$ series in [12]). The temperature dependence of the magnetic resistivity for the two end compounds obtained by subtracting the resistivity of $LaPd_2Si_2$ (which serves as the non-magnetic background in our measurement as shown in figure 7, which shows the same behaviour as the 'metallic-like' resistivity of $LaCu_2Si_2$ [13]) from the total resistivity is shown in figure 8. The peak position, 68 K in $CePd_2Si_2$ and 100 K in $CeCu_2Si_2$, scales roughly with the crystal-field splitting. This was determined to be 19 meV (220 K) in $CePd_2Si_2$ [14] and 31 meV (360 K) in $CeCu_2Si_2$ [15]. No evidence is observed in the resistivity for the crystal-field level observed at 14 meV in $CeCu_2Si_2$ which should produce a feature at about 45 K in the resistivity. This was also pointed out in [11].

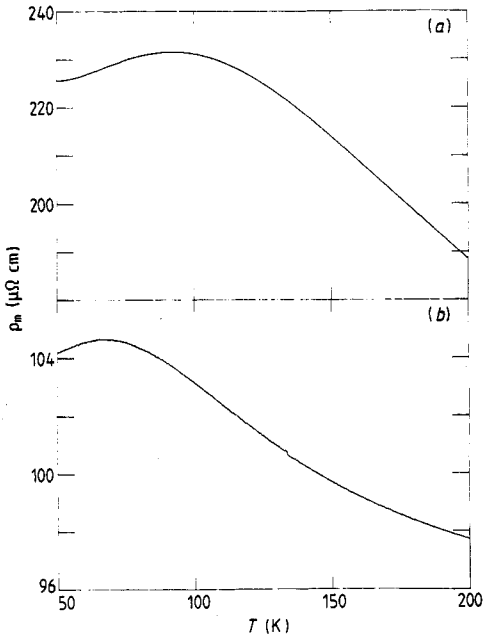

Figure 8. Magnetic resistivity versus temperature curves for (*a*) $CeCu_2Si_2$ and (*b*) $CePd_2Si_2$.

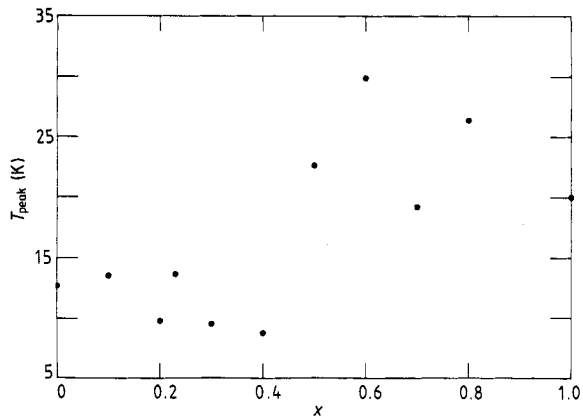

Figure 9. The low-temperature peak position versus x for $Ce(Pd_{1-x}Cu_x)_2Si_2$.

Between $x = 0.2$ and $x = 0.3$ the resistivity curves change significantly: the slope at high temperature changes from positive to negative. To investigate this change a sample with $x = 0.23$ was made and measurements made on it. Its curve shows a maximum at low temperature like the other curves do; however, it has a shoulder between 50 and 100 K and then decreases with increasing temperature, looking more like the resistivity for $x = 0.3$ than that for $x = 0.2$. A second sample with $x = 0.2$ was prepared and measured with the same results. There is a significant change in the high-temperature ($T > 50$ K) resistivity between $x = 0.2$ and $x = 0.23$. We believe that this large change is a result of changes in the crystal-field parameters which result from changes in the anisotropy of the system.

The curves for $x = 0.3$ and $x = 0.4$ are very similar, but another change occurs between $x = 0.4$ and $x = 0.5$. The temperature T_{peak} of the low-temperature resistivity peak has been plotted as a function of x in figure 9. A rapid change in T_{peak} occurs near

$x = 0.4$. Originally we interpreted this change as resulting from the crossover from a magnetically ordered ground state for $x \leqslant 0.4$ to a heavy-fermion ground state for $x \geqslant 0.5$ since the low-temperature peak originates from the magnetic ordering in $CePd_2Si_2$ and from the coherent fluctuations in $CeCu_2Si_2$. The susceptibility measurements indicate that this is not the case. We believe that the magnetic crossover happens around $x = 0.1$. This means that the jump in the peak position between $x = 0.4$ and $x = 0.5$ must result from changes in the temperature at which coherence effects become important. This may result from the interplay between the Kondo interaction and the RKKY interaction strengths. Since the Kondo temperatures of the two end compounds, as measured from the neutron quasi-elastic linewidth, are comparable, this must result from changes in the RKKY interaction strength.

We see changes in the resistivity curves as x is increased from 0 to 1: the high-temperature slope changes from positive to negative near $x = 0.2$ and the low-temperature peak position changes abruptly near $x = 0.4$. We think that these changes can be interpreted as follows. Because copper has one more valence electron than palladium, substituting copper for palladium in the system $CePd_2Si_2$ changes the band structure, resulting in a change in anisotropy: the direction of largest susceptibility changes from the [110] direction for $CePd_2Si_2$ to the [001] direction for $CeCu_2Si_2$. The crystal-field configuration also changes, causing changes in the high-temperature resistivity. The change in the high-temperature resistivity slope near $x = 0.2$ which we have observed may correspond to this change in crystal-field configuration. The changes in the band structure and in the ground-state wavefunction due to the change in the crystal field change the symmetry of the hybridisation and the RKKY interaction strength while the Kondo temperature T_K remains relatively constant. For $CePd_2Si_2$, the RKKY interaction is much stronger than the Kondo interaction, the moment is frozen, and spin fluctuations are suppressed, leading to antiferromagnetic ordering. Upon substituting copper for palladium, the RKKY interaction strength is lowered, and for $CeCu_2Si_2$ the situation is the opposite: the Kondo interaction dominates and the magnetic moment is quenched, resulting in a non-magnetic ground state. The low-temperature peaks for various values of x shown in figure 9 are related to 'Kondo lattice' scattering. The peak temperatures are low for $x < 0.4$ when the RKKY interaction is relatively large. For $x > 0.4$, the peak temperatures are higher and the Kondo interaction dominates. The changes in band structure and hybridisation give rise to the lattice parameter anomalies and anomalous changes in unit-cell size near $x = 0.2$ and $x = 0.4$ shown in figure 1.

In summary, we have performed resistivity, static susceptibility, and x-ray diffraction measurements on the pseudo-ternary alloy system $Ce(Pd_{1-x}Cu_x)_2Si_2$ and have observed qualitative and quantitative changes in the resistivity as well as anomalies in the lattice parameters and unit-cell volume as functions of x. The susceptibility shows weak evidence of magnetic order for $x = 0.1$ and displays a broad maximum for $x = 0.2$, evidence of a crossover from magnetic (at $x \leqslant 0.1$) to non-magnetic behaviour. We believe that the magnetic crossover occurs near $x = 0.1$, since T_N falls from 8 K at $x = 0$ to the apparent value $T_N \simeq 2$ K at $x = 0.1$ suggesting crossover at $x \geqslant 0.1$. The high-temperature resistivity changes dramatically on going from $CePd_2Si_2$ to $CeCu_2Si_2$, possibly reflecting the changes in crystal-field configuration resulting from the observed changes in anisotropy (direction of largest susceptibility) which accompany changes in band structure. A peak in the resistivity that appears at low temperature also shifts with x. We believe this reflects variations in the strength of the RKKY interaction. Because both of these changes are accompanied by anomalies in the lattice parameters and unit-cell volume which may result from the changes in energy band hybridisation as the palladium

concentration is decreased, we believe that the macroscopic anomalies (in ρ and χ) may be due to changes in the band structure and anisotropy upon varying the Pd concentration in the system. This may also be the mechanism responsible for the absence of magnetic order in $CeCu_2Si_2$, i.e. the changes in hybridisation and anisotropy could combine to reduce the RKKY interaction strength whereupon the Kondo interaction would dominate and the ground state would become non-magnetic. Additional measurements will be necessary to confirm this hypothesis.

Acknowledgments

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