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The Kondo effect in $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$

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Abstract. We report the effect of diluting the magnetically ordered Kondo compound CeCu_2 ($T_N \approx 3.5$ K) by Y. This dilution shows that long-range magnetic order rapidly disappears. The deduced Kondo interaction, expressed by T_K , does not seem to increase as expected from the decrease in the unit-cell volume with increasing Ce content. The main effect is a substantial modification of the crystal-field level scheme associated with this dilution.

1. Introduction

Orthorhombic CeCu_2 belongs to a series of compounds showing simultaneously Kondo behaviour as well as antiferromagnetic ordering below 3.5 K (Gratz *et al* 1985, Onuki *et al* 1985). This compound is characterised by an electronic contribution to the specific heat c_P/T for $T \rightarrow 0$ of $80 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which up to 8 T is nearly unaffected by external magnetic fields (Bredl 1987). The low-temperature part of the specific heat agrees with an antiferromagnetic ground state. Antiferromagnetism with incommensurate spin structure was resolved from neutron diffraction measurements (Zemirli 1986).

The aim of this paper is to show a gradual crossover from the Kondo lattice behaviour in CeCu_2 to the single-impurity regime due to a substitution of Ce by Y which leaves the orthorhombic crystal structure (space group, Imma) unchanged. Owing to the smaller ionic radius of Y, chemical pressure effects may be anticipated, which in turn should enhance the Kondo behaviour with increasing Y content.

Samples of this pseudo-binary series were prepared from stoichiometric amounts of the constituents under an Ar atmosphere in a water-cooled Cu boat using high-frequency melting. Subsequently heat treatment at 700°C for 7 d was performed in evacuated quartz tubes. The phase purity was checked using Debye–Scherrer photographs (Cr $K\alpha$ radiation) as well as a standard Siemens diffractometer (Cu $K\alpha$ radiation). Both techniques confirmed the CeCu_2 structure for the whole concentration range of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

In this paper, we present measurements of the lattice constants, electrical resistivity, thermopower, specific heat, susceptibility and field-dependent magnetisation. The results will be discussed within the framework of the Kondo model. Details of the experimental equipment can be found elsewhere (see, e.g., Bauer *et al* 1987).

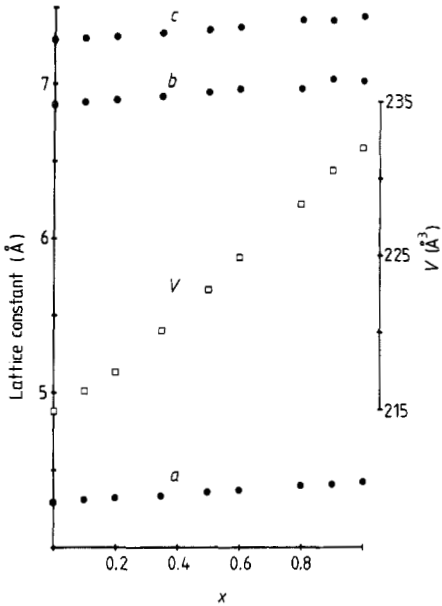


Figure 1. The lattice parameters a , b and c and the volume of the unit cell V for $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

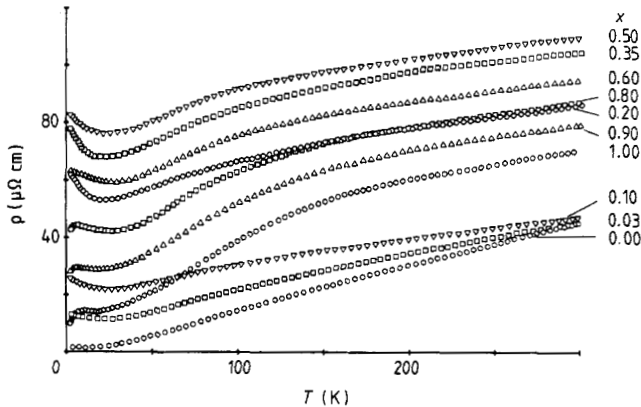


Figure 2. The temperature dependence of the electrical resistivity ρ of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

2. Results and discussion

Figure 1 shows the lattice constants a , b , c together with the volume V of the unit cell for different concentrations. Both the lattice parameters and the unit cell volume decrease smoothly when going from CeCu_2 to YCu_2 , which is referred to as the lanthanide contraction. The gentle variation in a , b , c as well as V indicates that there is no substantial change in the valency within this series. The reduction in V when proceeding from CeCu_2 to YCu_2 is about 7%. Within the RECu_2 compounds ($\text{RE} \equiv$ rare earth) the lattice parameters of CeCu_2 fit into those compounds of RE ions displaying the 3+ state (Gratz et al 1985).

For some compositions of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ the electrical resistivity ρ as a function of temperature is depicted in figure 2. The shape of $\rho(T)$ for YCu_2 is simply given by the

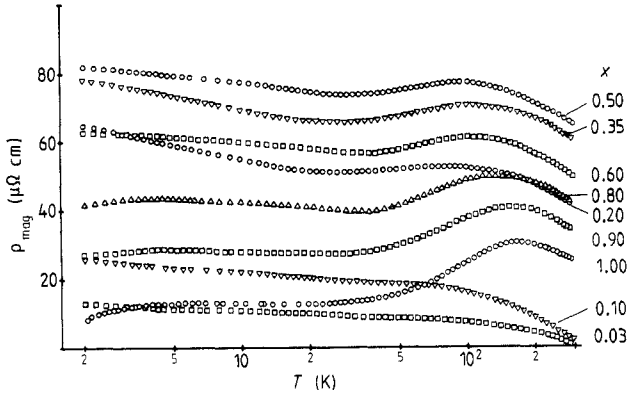


Figure 3. The magnetic contribution ρ_{mag} of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ against $\ln T$.

Table 1. The concentration-dependent unit cell volume V and the overall crystal-field splitting Δ_{CF} (deduced from resistivity measurements) of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

x	0.10	0.20	0.35	0.50	0.60	0.80	0.90	1.00
Parameter								
$V (\text{\AA}^3)$	216.1	217.8	219.2	222.6	224.8	228.2	230.6	231.9
$\Delta_{\text{CF}} (\text{K})$		70	85	95	110	140	160	180

sum of ρ_0 (residual resistivity) and $\rho_{\text{ph}}(T)$ (phonon contribution), where $\rho_{\text{ph}}(T)$ can satisfactorily be described by the well known Bloch–Grüneisen relation. The Debye temperature θ_{D} thus obtained is 170 K.

The introduction of Ce into the Y lattice sites changes $\rho(T)$ dramatically. As little as 3 at. % Ce leads to a pronounced minimum in $\rho(T)$, which in inter-metallic compounds is one of the signs of the existence of the Kondo interaction. The increase in lattice disorder due to the exchange of Ce with Y increases the absolute resistivity. At room temperature a maximum value of about $110 \mu\Omega \text{ cm}$ has been obtained for $x = 0.50$. Microscopically, the increase in $\rho(T)$ towards the middle of the concentration range is caused by the increasing amount of potential scattering, leading to an increase in ρ_0 . The minimum in the low-temperature region caused by the Kondo scattering in the crystal-field ground state becomes more pronounced in the middle of this series with a maximum depth of about $10 \mu\Omega \text{ cm}$ and for higher x -values decreases to lower values down to a few microhm centimetres. For compounds with x close to unity, a decrease in $\rho(T)$ below a few kelvins is observed. Although no clear anomaly appears at T_{N} , it is likely that this decrease is related to the onset of magnetic order. The concentration-dependent behaviour of the electrical resistivity therefore reflects the crossover from a single-impurity Kondo system ($x \ll 1$) to a Kondo lattice ($x \leq 1$).

Figure 3 shows the magnetic contribution to the electrical resistivity ρ_{mag} as a function of temperature in a semi-logarithmic representation: $\rho_{\text{mag}}(T) = \rho[(\text{Ce}, \text{Y})\text{Cu}_2](T) - \rho[\text{YCu}_2](T)$. In this representation the behaviour of $\rho_{\text{mag}}(T)$ is characterised by two regions showing negative logarithmic slopes, separated by a broad maximum. The position of this maximum is shifted depending on concentration from approximately 180 K in CeCu_2 to about 70 K for $(\text{Ce}_{0.2}\text{Y}_{0.8})\text{Cu}_2$ (compare table 1). For

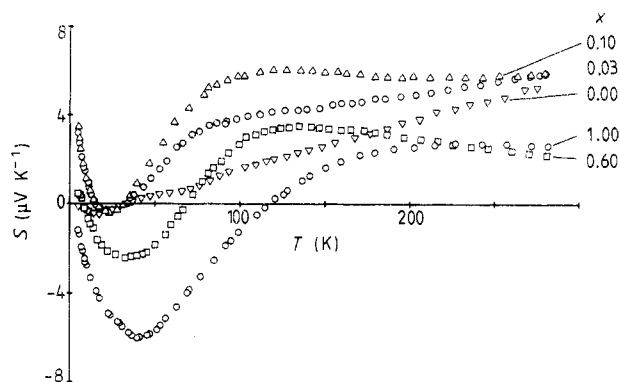


Figure 4. The temperature dependence of the thermopower S of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

smaller concentrations of Ce, e.g. $x = 0.10$ and 0.03 , no such pronounced behaviour is observable, although the general trend still exists. For low temperatures, ρ_{mag} deviates from the logarithmic behaviour. Following the ideas of Cornut and Coqblin (1972), the distinct behaviour mentioned above can be explained within the framework of a Kondo interaction in the presence of a strong crystal-field splitting. In this model the negative logarithmic temperature dependence of ρ_{mag} is referred to Kondo scattering processes of the conduction electrons with the localised $4f$ moments of the Ce ions. The position of the maximum in the ρ_{mag} against $\ln T$ plot, which separates these two linear regions, gives a measure of the overall crystal-field splitting Δ_{CF} . Furthermore, the ratio of the high- to the low-temperature $\ln T$ gradient reflects the degeneracy of the ground state of the compound under investigation, which should be $35/3$ or $7/3$ for a doublet and a quartet, respectively. The ratio r of the high- to the low-temperature linear gradient in CeCu_2 ($r \approx 12.2$) lies very close to the calculated value typical for a ground-state doublet well separated from excited states.

The shift and the broadening of the maxima as shown in figure 3 imply a change in the crystal-field level scheme with decreasing x . As already mentioned, the substitution of Ce by Y causes a decrease in the unit-cell volume and therefore chemical pressure may act on the Ce ions. This chemical pressure seems to be sufficiently large to modify the energy levels. The absolute position of the maximum in ρ_{mag} for this series, however, depends to some extent on how ρ_{ph} has been defined. Problems arising from the definition of ρ_{ph} were studied in detail by Wohlleben and Wittershagen (1985). The application of an external pressure to magnetically ordered Kondo compounds such as CeAl_2 (Nicolas-Francillion *et al* 1972) or CePt (Itoh *et al* 1987) reveals a similar decrease in Δ_{CF} in these compounds. Inelastic neutron scattering experiments performed on polycrystalline CeCu_2 indicate crystal-field levels around 110 and 280 K above the ground-state doublet (Loewenhaupt *et al* 1988). The broad maximum of $\rho_{\text{mag}}(T)$ observed for CeCu_2 is in agreement with the crystal-field level scheme. The evolution of the shape of ρ_{mag} with Y content seems to indicate an increase in the difference between the energy of the two excited doublets, as well as a decrease in the overall splitting (Cornut and Coqblin 1972).

In figure 4 the thermopower S as a function of temperature is displayed for different samples in this series. All the compounds containing Ce are characterised by a pronounced minimum at low temperatures followed by a crossover to positive thermopower values for more elevated temperatures. Above about 100 K a strong tendency towards saturation or even to a negative temperature coefficient of the thermopower is observed.

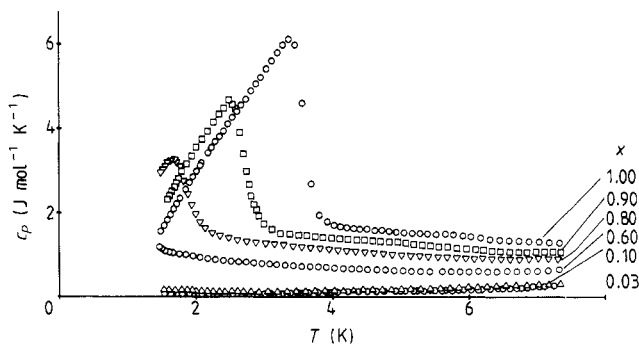


Figure 5. The temperature dependence of the specific heat c_p of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ below 8 K.

On the contrary, YCu_2 shows in its temperature variation an almost linear behaviour except a shallow minimum which may be attributed to phonon drag effects. Furthermore, the $S(T)$ data reveal a concentration-dependent shift of the broad high-temperature maximum towards lower temperatures as the Y concentration increases. It is generally known that the high-temperature maximum of $S(T)$ is related in a certain way to the crystal-field splitting Δ_{CF} (see, e.g., Maekawa *et al* 1986). The observed shift in $S(T)$ therefore seems to be in agreement with the modification of the crystal electric field splitting, previously deduced from the maximum in ρ_{mag} against $\ln T$.

Figure 5 shows the specific heat c_p for different x -values of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ in the temperature range from 1.45 to 8 K in a c_p against T representation. For Ce concentrations $x = 0.8, 0.9$ and 1.0 the specific heat data indicate magnetic ordering at 1.8 K, 2.7 K and 3.5 K, respectively. For smaller x -values we could not resolve any transition down to 1.45 K. For low temperatures ($T < 15$ K) the specific heat of the non-magnetic YCu_2 fits $c_p = 2T + 0.825T^3$ ($\text{mJ mol}^{-1} \text{K}^{-1}$) with a Debye temperature θ_D of about 190 K. The magnetic entropy S_m of the compounds containing Ce was deduced by subtracting the entropy data of YCu_2 . To avoid errors due to the magnetic entropy below 1.45 K, a temperature range which was not covered by our equipment, we have included the specific heat data down to 60 mK reported by Gratz *et al* (1985). Adding these data to the specific heat values shown above, the magnetic entropy per mole of Ce at T_N is found to be $3.83 \text{ J mol}^{-1} \text{K}^{-1}$, $2.94 \text{ J mol}^{-1} \text{K}^{-1}$ and $2.38 \text{ J mol}^{-1} \text{K}^{-1}$ for $x = 1.0, 0.9$ and 0.8 , respectively. These values have to be compared with a value of $5.76 \text{ J mol}^{-1} \text{K}^{-1}$, which can be expected when recovering the complete degeneracy of the doublet ground state in these orthorhombic compounds. The lack of entropy at T_N for the compounds with long-range magnetic order may partly be inferred by short-range order effects above T_N ; however, it seems more likely that the reduced S_m -values are caused by Kondo screening, which partially lifts the twofold spin degeneracy of the ground-state doublet, since the resistivity measurements clearly indicate Kondo-type interaction. Using a procedure developed by Mori *et al* (1985), which is based on a comparison of the magnetic entropy determined from experimental data with that of the calculated entropy of a single-impurity $s = \frac{1}{2}$ Kondo system, the Kondo temperature T_K can easily be deduced. Within this model, T_K is found to be 3.8 K, 4.7 K and 4.8 K for $x = 1.0, 0.9$ and 0.8 , respectively. It should be mentioned that for CeCu_2 the value of T_K is in excellent agreement with the half-width of the quasi-elastic Γ line deduced by inelastic neutron scattering for $T \rightarrow 0$ ($\Gamma/2 \approx 0.35 \text{ meV}$) (Loewenhaupt *et al* 1988).

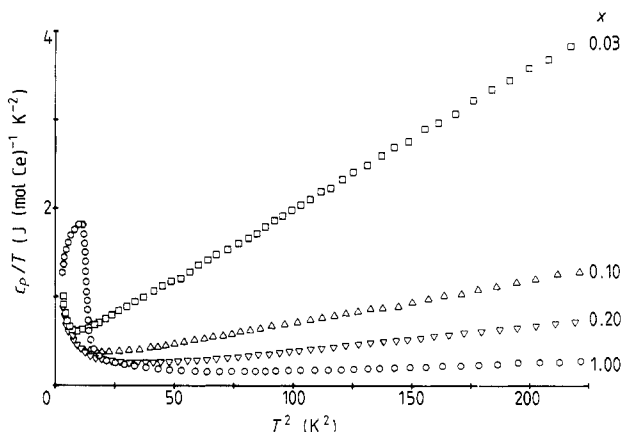


Figure 6. The specific heat c_p of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ as c_p/T against T^2 per mole of Ce.

Table 2. The concentration dependence of the electronic contribution to the specific heat γ (per formula unit) and γ (per mol Ce) of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

Parameter \ x	0.03	0.10	0.20	0.60	0.80	0.90	1.00
γ (mJ mol ⁻¹ K ⁻²)	12	20	27	61	84	91	105
γ (mJ (mol Ce) ⁻¹ K ⁻²)	400	200	135	102	105	102	105

In figure 6 we give a plot of c_p/T against T^2 for those compounds which are expected to be in a non-magnetic ground state ($x = 0.03, 0.10$ and 0.20) together with the data of the boundary CeCu_2 . From a high-temperature extrapolation ($8 \text{ K} < T < 15 \text{ K}$) towards zero, strongly enhanced γ -values, compared with that of YCu_2 (about $2 \text{ mJ mol}^{-1} \text{ K}^{-2}$), have been found (table 2). These large γ -values are thought to be inferred from the mixing of the Ce 4f electrons with the conduction electrons. Below a few kelvins, c_p/T against T^2 deviates from linear behaviour and shows a strong upturn, typically for single-impurity Kondo systems. For different thermodynamic quantities such as the specific heat or the susceptibility, the single-impurity Kondo problem has been solved exactly without any approximation. Using the model of Andrei *et al* (1983), the Kondo temperature T_K of such compounds can be related to the electronic contribution to the specific heat for $T \rightarrow 0$ by $T_K \approx 0.68 R/\gamma$, where R denotes the gas constant. Using the experimental values of c_p/T at our lowest temperature available ($T \approx 1.45 \text{ K}$), we can estimate an upper limit for T_K yielding $T_K \approx 6 \text{ K}$, 7 K and 6.6 K for $x = 0.03, 0.10$ and 0.20 , respectively. When comparing the values of T_K deduced from specific heat data in both regimes (magnetic ordered and paramagnetic), only a tiny increase with increasing Y content seems to occur, although the T_K -values are obtained using two different methods. This weak enlargement of T_K may be inferred from chemical pressure due to the reduction in the size of the unit cell.

The susceptibility χ of these compounds has been measured in the temperature range 1.5–300 K. The results have been analysed assuming that

$$\chi = \chi_0 + C/(T - \theta_p). \quad (1)$$

The data drawn in figure 7 are obtained by subtracting χ_0 to show more clearly the

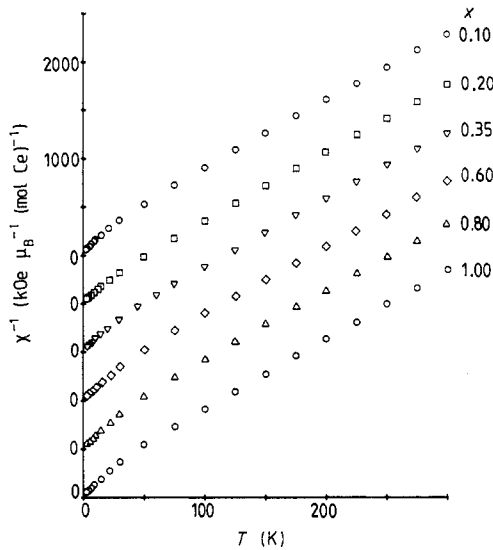


Figure 7. The temperature dependence of the reciprocal susceptibility χ^{-1} of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ per mole of Ce.

Table 3. The concentration dependence of the paramagnetic Curie temperature θ_p and the Pauli susceptibility χ_0 of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$.

Parameter	x	0.10	0.20	0.35	0.50	0.80	1.00
θ_p (K)		-32	-27	-29	-29	-34	-30
χ_0 ($10^{-4} \mu_B \text{ kOe}^{-1} (\text{mol Ce})^{-1}$)		2.0	1.15	0.68	0.18	0.15	0.05

behaviour of the Ce ions. χ_0 denotes the temperature-independent Pauli susceptibility and θ_p the paramagnetic Curie temperature. The Pauli susceptibility χ_0 thus obtained increases with decreasing Ce content; this could arise from the 3d contribution of Cu (table 3). Considering the Curie-Weiss term, it follows that the values of the effective magnetic moment μ_{eff} for the $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ series is almost constant, and very close to the moment of the Ce^{3+} ion ($\mu_{\text{eff}} \approx 2.54 \mu_B$). This seems to support the results obtained for the lattice constants and justify a 3+ state for the whole series, independent of the Ce concentration. The paramagnetic Curie temperature θ_p for this series is again concentration independent, amounting to roughly -30 K. When both the Kondo effect and the interaction of the Ce ions are taken into account, θ_p can be approximated by

$$\theta_p = \theta_p^K + \theta_p^{\text{RKKY}} \quad (2)$$

with the temperature θ_p^{RKKY} being a measure of the RKKY interaction. Considering the weakness of T_N in these compounds, the observed magnitude of θ_p must be attributed to a large extent to the Kondo-type interaction. On the basis of the single-impurity Kondo model, $|\theta_p^K|$ serves as a measure for the Kondo temperature T_K by $T_K \sim m|\theta_p^K|$ (Gruener and Zawadowsky 1974), where m ranges from 0.25 to 1.0, depending on different calculations. In any case this quantity indicates a Kondo temperature which

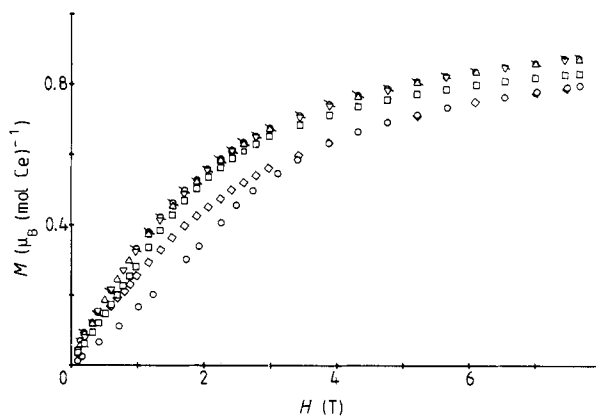


Figure 8. Isothermal magnetisation curves of $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ at $T = 1.5$ K: \circ , $x = 1.00$; \square , $x = 0.80$; \odot , $x = 0.60$; ∇ , $x = 0.35$; \triangle , $x = 0.20$; \diamond , $x = 0.10$.

stays almost constant for all the different Ce contents and matches the behaviour deduced from specific heat data.

Figure 8 displays the isothermal magnetisation curves obtained at $T = 1.5$ K in external magnetic fields up to 8 T for several concentrations in this series. CeCu_2 is characterised by a metamagnetic transition around 2 T in agreement with the anti-ferromagnetic spin structure (Zemirli 1986). The magnetic moment per mole of Ce obtained at 8 T ($T = 1.5$ K) appears to be approximately constant. The metamagnetic transition, however, becomes less pronounced for $x = 0.8$ and vanishes for those samples which does not show long-range magnetic order above 1.5 K.

3. Conclusion

The physical properties of the orthorhombic isostructural $(\text{Ce}_x\text{Y}_{1-x})\text{Cu}_2$ series are obviously influenced by the Kondo-type interaction. For Ce contents near CeCu_2 the Ce–Ce interaction of RKKY type overcomes the Kondo effect; therefore, long-range magnetic order is established. The large reduction in T_N with increasing Y content emphasises the importance of the Kondo effect. The exchange of Ce with Y is accompanied by a regular reduction in the crystallographic unit cell, leading to chemical pressure effects on the Ce ions. Since pressure enhances the coupling constant J (Schilling 1979), the Kondo temperature $T_K \sim \exp[-(1/JN(E_F))]$ should also increase (here, J is the coupling constant between the 4f shell and the conduction band ($J < 0$) and $N(E_F)$ is the electronic density of states at the Fermi edge). However, the observed T_K -values for this series remain almost constant. The only effect which is attributed to chemical pressure is the modification of the crystal-field splitting found from resistivity measurements. Furthermore, this type of measurement indicates that there is a systematic change from a single-impurity regime ($x \ll 1$) to a Kondo lattice behaviour at least for $x \geq 0.8$.

Acknowledgments

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