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Magnetic and transport properties in (Ce, La)Cu_4Ga: evolution of the Kondo state

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Abstract. Measurements of the electrical resistivity, magnetization and susceptibility in an extended temperature range from 30 mK to 300 K on polycrystalline $(Ce_xLa_{1-x})Cu_4Ga$ samples ($0.0 \leq x \leq 1.0$) are presented. A crossover is observed from a spin frozen state with $T_K < T_{RKKY}$ for $x \leq 0.85$ to a heavy fermion state with $T_K > T_{RKKY}$ for $x \simeq 1$. The full formation of coherence at low temperatures seems to be prevented by lattice disorder probably caused by the arrangement of the Cu and Ga ions in the hexagonal unit cell.

1. Introduction

$CeCu_4Ga$ has been found to exhibit exciting and enormously enhanced low temperature properties [1, 2, 3, 4]. This compound crystallizes in the hexagonal $CaCu_5$ structure, and is built up from $CeCu_5$ when exchanging just one Cu by Ga, which causes an increase of the volume of the unit cell. Due to this substitution a common type of long range antiferromagnetic order found in $CeCu_5$ ($T_N \approx 4$ K) vanishes, while the electronic contribution to the specific heat c/T attains for $T \to 0$ a value of 1.9 J mol^{-1} K^{-2}, which exceeds the respective values of $CeAl_3$ or $CeCu_6$ [5]. Transport properties of $CeCu_4Ga$ indicate Kondo-like interaction; i.e. the magnetic contribution to the electrical resisitivity, ρ_{mag}, reveals a large temperature range where ρ_{mag} behaves like $(-\ln T)$. The thermopower, sensitive to energy derivatives at the Fermi surface, shows large values and a positive maximum, which accounts for the combined action of the Kondo effect and crystal field splitting [1]. Further hints towards the presence of a dominating Kondo interaction for this compound were deduced from the field dependence of the electronic contribution to the specific heat [4]. The substitution for Cu with Ga infers a large modification of the crystalline electric field energy level scheme. While $CeCu_5$ shows a single inelastic line at 17 meV, this line is lowered in $CeCu_4Ga$ down to 6 meV [6, 7], indicative too of a pronounced alteration of the electronic density of states near the Fermi level.

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The aim of this paper is to study the formation of a Kondo lattice state in $CeCu_4Ga$ when proceeding from a well known single-impurity Kondo regime in $(Ce_xLa_{1-x})Cu_4Ga$, $x \ll 1$, to the concentrated state near $x \simeq 1$.

2. Experimental details

Polycrystalline $(Ce_xLa_{1-x})Cu_4Ga$ samples were prepared by high frequency melting under argon atmosphere and subsequently annealed for seven days at 600 °C. Electrical resistivity data were taken by means of a conventional four-probe technique in the temperature range 1.5–300 K. Bulk magnetization measurements were performed using the extraction method, in magnetic fields up to 8 T and in the temperature range 1.5–300 K; low field susceptibility was then deduced from Arrott plots. A mutual inductance system was used to measure the low frequency (117 Hz) differential susceptibility $\chi = \partial M/\partial H$ of the samples in a magnetic field with $\approx$10 μT amplitude between 30 mK and 5 K in a standard demagnetization cryostat.

3. Results

Figure 1 shows the electrical resisitivity ρ of $(Ce_xLa_{1-x})Cu_4Ga$ in the concentration range $0.0 \leq x \leq 1.0$ and for temperatures ranging from 1.5 K up to room temperature. Beneath the steady increase of the overall resisitivity with increasing Ce concentration, $\rho(T)$ is characterized by a growing range where $d\rho/dT$ is negative. Since the increasing Ce content causes a regular sublattice of magnetic ions at least for concentrations near to $x \simeq 1.0$, a clear Kondo lattice behaviour should be observable, i.e. the resistivity should drop down to very low residual values for $T \rightarrow 0$. Such a behaviour was found e.g. for $(Ce_xLa_{1-x})Cu_6$ [8] or $(Ce_xLa_{1-x})Al_3$ [9] when the Ce concentration reaches a certain value close to $x = 1.0$. For the case of $(Ce_xLa_{1-x})Cu_4Ga$ this specific behaviour was not observed down to 1.5 K. The only sample which shows a maximum, followed by a reduction of $\rho(T)$ when the temperature is lowered, is the boundary compound $CeCu_4Ga$ [1]. However, the maximum in $\rho(T)$ is found at very low temperatures ($T_\rho^{max} \approx 1.7$ K) and the drop is only a few $\mu\Omega$ cm. Since Kondo lattices at very low temperatures obey a Fermi liquid behaviour, the resisitivity can be described by $\rho(T) = \rho_0 + AT^2$. For $x = 1.0$ we deduced ρ_0 as 132 $\mu\Omega$ cm and $A = 5.8$ $\mu\Omega$ cm K^{-2} [1].

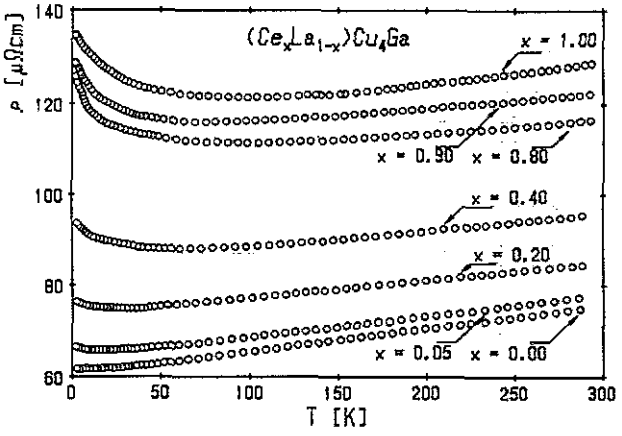

Figure 1. The temperature dependence of the resistivity ρ of $(Ce_xLa_{1-x})Cu_4Ga$.

Figure 2 displays the low temperature (T_{min} = 30 mK) a.c. susceptibility $\chi_{a.c.}(T)$ for different $(Ce_xLa_{1-x})Cu_4Ga$ compounds. A gradual change of $\chi_{a.c.}(T)$ is observed when proceeding from $x = 1.00$ to $x = 0.05$. While for the samples with concentrations near to $x \simeq 1.00$ only smooth maxima are observed, the absolute height in $\chi_{a.c.}(T)$ as well as the sharpness of the transition increases considerably for lower Ce concentrations. For $x = 0.05$ no well defined peak in $\chi_{a.c.}(T)$ is observed. The sharp maxima for $x = 0.2$ and $x = 0.4$ are reminiscent of a spin-glass-like transition. A similar trend towards a spin frozen state was found from susceptibility measurements in the well characterized series $(Ce, La)Cu_2Si_2$ [10] when the La content rises.

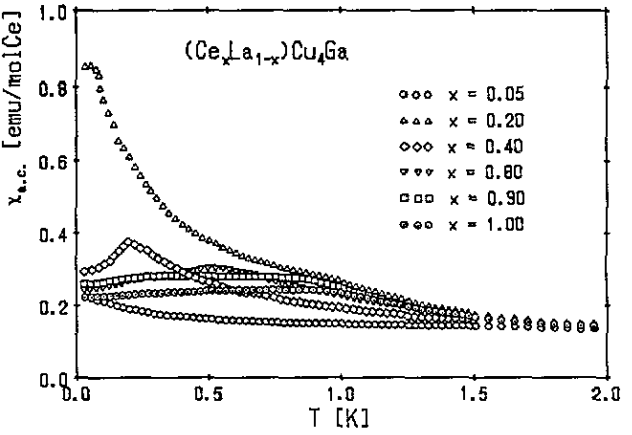

Figure 2. The temperature dependence of the a.c. susceptibility $\chi_{a.c.}$ of $(Ce_xLa_{1-x})Cu_4Ga$.

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

$$\chi(T) = \chi_0 + xC/(T - \theta_p).$$

χ_0 denotes the temperature independent Pauli susceptibility, C the Curie constant and θ_p the paramagnetic Curie temperature. The data drawn in figure 3 are obtained by subtracting χ_0 to show more clearly the behaviour of the Ce ions. The Pauli susceptibility χ_0 thus obtained increases with decreasing Ce content; this could arise from the 3d contribution of Cu (table 1). However, the anisotropy of the susceptibility in the main crystallographic directions can also give rise to a curvature of χ^{-1} of polycrystalline samples. After the correction by χ_0 above about 50 K all samples are characterized by a Curie–Weiss behaviour, with an effective magnetic moment very close to that of the free Ce^{3+} ion. The paramagnetic Curie temperatures are negative and do not vary strongly with concentration (see table 1).

Magnetization curves taken at 1.5 K in fields up to 8 T are displayed in figure 4. The magnetization at 8 T shows values below 1 μ_B/Ce, which is not very different from those expected from a $|\pm 1/2\rangle$ or a $|\pm 5/2\rangle$ crystal field ground state for polycrystalline hexagonal compounds. The field dependent magnetization curves, however, indicate a $|\pm 1/2\rangle$ state, since for degeneracies $N \geq 4$ an upturn in the M–H curves should be observable [11] ($N = 2j + 1$ where j is the total angular momentum). The slight decrease of the magnetization when the Ce content increases may be inferred from a progressive Kondo screening of the magnetic moment.

Table 1. Pauli susceptibility χ_0 and the paramagnetic Curie temperature $|\theta_p^H|$ for $(Ce_xLa_{1-x})Cu_4Ga$.

x	χ_0 (10^{-4} emu/mol Ce)	θ_p^H (K)
0.05	3.2	−13.7
0.20	3.1	−16.1
0.40	2.7	−16.9
0.80	1.9	−17.2
0.90	1.9	−16.4

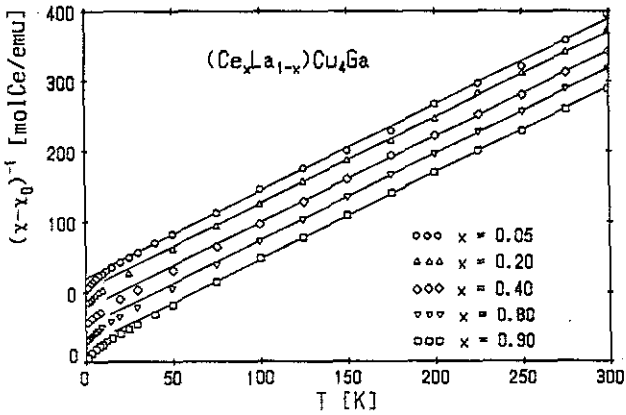

Figure 3. The d.c. susceptibility χ as χ^{-1} versus T for $(Ce_xLa_{1-x})Cu_4Ga$. The curves are subsequently shifted by 25 mol Ce emu^{-1}.

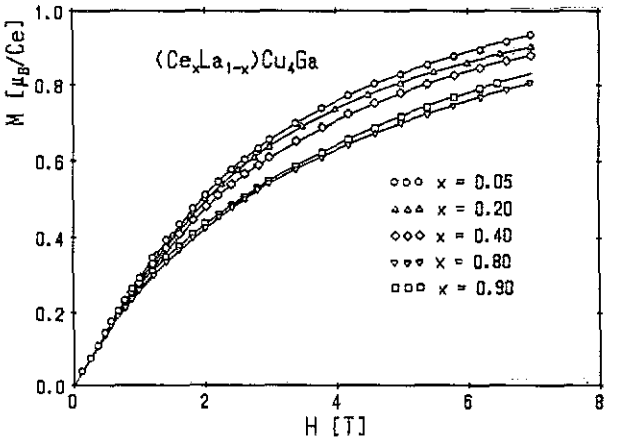

Figure 4. Isothermal magnetization curves (T = 1.5 K) of $(Ce_xLa_{1-x})Cu_4Ga$. The full curves are guides to the eye.

4. Discussion

The magnetic contribution to the electrical resistivity, ρ_{mag}, is shown in figure 5 in a semilogarithmic representation as ρ_{mag} versus T ($\rho_{mag} = \rho\{(Ce,La)Cu_4Ga\} - \rho\{LaCu_4Ga\}$). All the compounds investigated reflect a behaviour where ρ_{mag} is proportional to $(-\ln T)$ over an large temperature range. At low temperatures and

for samples with $x < 1$, ρ_{mag} reaches a constant value. Though there is not a very distinct change of ρ_{mag} when proceeding from $x \ll 1$ to $x \simeq 1$, a comparison of $\rho(T)$ as well as of ρ_{mag} normalized to the room temperature data shows that the largest temperature variation arises for the sample with $x = 0.80$. Below and above this concentration these normalized quantities exhibit smaller changes. We interpret this dependence of x as a border between a single-impurity Kondo regime for $x < 0.8$ and a Kondo lattice regime for $x > 0.8$. As mentioned above, a characteristic drop of $\rho(T)$ at low temperatures (usually below about 10 K) is found only for $x = 1.0$. The absence of such a large drop in $\rho(T)$ for samples $x \simeq 1$ indicates that the coherent state may not be well developed. Thus, at least partly, destruction of the coherence between the Ce $4f^1$ moments is probably caused by the chemical environment of the Ce ions, since the $CaCu_5$ structure possesses two inequivalent Cu sites. Therefore it seems likely that structural disorder induced by the Ga substitution prevents the full development of a coherent ground state.

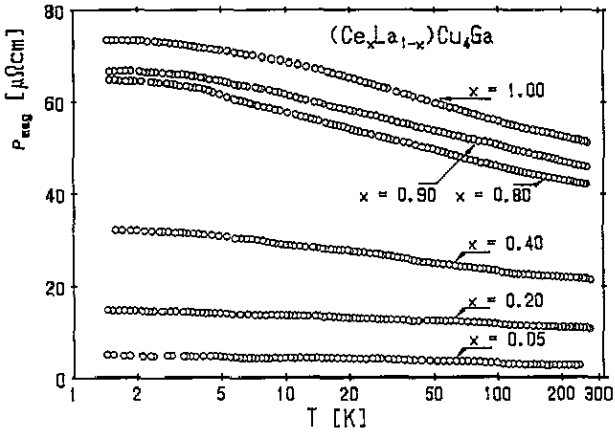

Figure 5. The magnetic contribution to the electrical resistivity, ρ_{mag}, as a function of ln T for $(Ce_xLa_{1-x})Cu_4Ga$

A comparison of the ρ_{mag} data, scaled by the Ce concentration shows, that for T $\geq$ 10 K ρ_{mag}/x behaves almost independently of concentration. This behaviour shows that ρ_{mag} is purely a single-ion effect and correlations are absent at elevated temperatures.

Cornut and Coqblin [12] have demonstrated that the combined interaction of the Kondo effect and crystal field splitting leads to a very distinct behaviour of ρ_{mag}. Within their model, $\rho_{mag}(T)$ is characterized by two $(-\ln T)$ ranges which are separated by a maximum at $T \simeq \Delta$ (Δ temperature of the overall crystal field splitting). However, this pronounced behaviour appears only for the case when the Kondo temperature T_K is much smaller than the crystal field splitting temperature. Hanzawa *et al* [13] have shown that in the presence of the crystal field splitting the Kondo temperature of the highest level, T_K^H, can be calculated from $T_K^H = (T_K\Delta_1\Delta_2)^{1/3}$, where T_K is the Kondo temperature of the crystal field ground state and Δ_1, Δ_2 the splitting energies of the first and second excited level, respectively. This equation accounts e.g. for the case of Ce where the $j = 5/2$ multiplet is split by the crystal field into three doublets. Neutron scattering measurements on $CeCu_4Ga$ revealed the first excited level at 65 K [7]. The second one could not be resolved clearly. However, a fit to the

magnetic part of the specific heat data yields $\Delta_1 \simeq 65$ K and $\Delta_2 \simeq 85$ K [14]. Since the electronic contribution to the specific heat, γ, of $CeCu_4Ga$ approaches at $T = 0$ a value of 1.9 J mol^{-1} K^{-2} [1] T_K is found to be ~ 3 K ($T_K = 0.68R/\gamma$; R is the gas constant). Using these data T_K^H is calculated for $CeCu_4Ga$ to be 25 K. This value agrees well with the paramagnetic Curie temperature $|\theta_p^H| = 26$ K. In the case where T_K^H is of the order of Δ, the Cornut–Coqblin theory does not predict the correct ρ_{mag} versus T behaviour. Guessous [15] has extended this theory. He proved that for $T_K^H \approx \Delta$, there is no clear resolvable peak in ρ_{mag} versus T, which accounts for the overall crystal field splitting temperature as in the Cornut–Coqblin theory. We think that the ρ_{mag} versus T curves of $(Ce, La)Cu_4Ga$ which show hardly any structure are just indicating the fact that T_K^H and Δ are of comparable magnitude.

Using the low temperature a.c. susceptibility data of figure 2, we have determined an effective paramagnetic Curie temperature θ_p^L for the samples $0.05 \leq x \leq 1.0$ in the crystal field ground state by extrapolating $\chi_{a.c.}^{-1}$ versus T towards zero. $|\theta_p^L|$ as a function of the Ce concentration is given in figure 6, together with the temperature of the maximum in $\chi_{a.c.}$ versus T. In spite of some uncertainties in the extrapolation procedure, $|\theta_p^L|$ shows a regular rise with increasing Ce content. Taking into account the model of Grüner and Zawadowsky [16] $|\theta_p^L|$ is a measure for the Kondo temperature T_K of the system; i.e. $T_K = m|\theta_p^L|$, where m is of the order of one. According to figure 6 the Kondo temperature therefore decreases with rising La content. This dependence of T_K on the concentration x can be understood from the volume dependence of the exchange constant J since T_K is given by: $T_K = 1/N(E_F)\exp(-1/|J|N(E_F))$. $N(E_F)$ is the conduction electron density of states at the Fermi energy E_F.

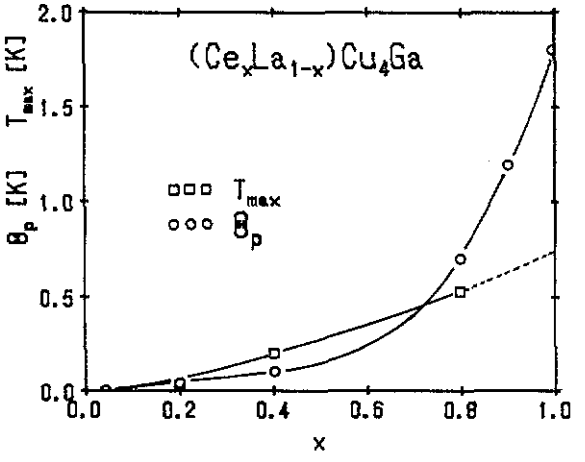

Figure 6. The concentration dependent variation of $|\theta_p^L|$ and of T_{max}, deduced from $\chi_{a.c.}(T)$, for $(Ce_xLa_{1-x})Cu_4Ga$. The full curves are guides to the eye.

It is well known that pressure applied to the crystal enhances the coupling constant J (for a review see e.g. Schilling [17]). The exchange of Ce for La in $CeCu_4Ga$ reveals a steady increase of the volume of the unit cell; this causes a reduction of J and therefore T_K is diminished upon the La substitution. In the following we assume that T_{max} accounts for the RKKY interaction. The interaction strength depends on J as $T_{RKKY} \sim J^2N(E_F)$. Therefore, the different functional dependence of T_K and T_{RKKY} on J divides figure 6 into two regions:

(a) $T_{RKKY} > T_K$ ($x < 0.80$): the ground state of the compound is a magnetic one and probably of spin frozen nature;
(b) $T_K > T_{RKKY}$ ($x > 0.80$): magnetic ordering seems to be quenched by the Kondo interaction; a heavy fermion behaviour with a high γ state evolves.

The concentration dependence of T_K and T_{RKKY} in $(Ce_xLa_{1-x})Cu_4Ga$ shown in figure 6 resembles the behaviour of these quantities in $(Ce_xLa_{1-x})Cu_2Si_2$ [10]. While for $(Ce_xLa_{1-x})Cu_2Si_2$ and $(Ce_xLa_{1-x})Cu_4Ga$ a crossover takes place from a high γ heavy fermion state for $x \simeq 1$ to a spin frozen state for $x \leq 0.95$ and $x \leq 0.85$, respectively, for $(Ce_xLa_{1-x})Ru_2Si_2$ a crossover is observed to long range magnetic order for $0.10 \leq x \leq 0.90$ [18].

5. Summary

In $(Ce_xLa_{1-x})Cu_4Ga$ the temperature dependence of the electrical resistivity is evidence for the Kondo effect dominating low temperature interaction. The independence of the magnetic contribution to the electical resistivity, ρ_{mag}, of the Ce concentration shows that ρ_{mag} is purely a single-ion effect and correlation between the Ce ions absent at elevated temperatures. Due to the arrangement of the Cu and Ga atoms within the hexagonal unit cell a full development of coherence seems to be prevented. A total destruction of coherence has been observed for $(Ce, La)Cu_3Ga_2$ [19]. At low temperatures a crossover is observed from a heavy fermion state for $x \simeq 1$ to a spin frozen state for $x \leq 0.85$. However a certain type of magnetic order with very small magnetic moments also cannot be ruled out for the heavy fermion compounds $x \simeq 1$. Such unusual magnetic order has been observed in most of the heavy fermion systems even in compounds with superconducting ground states [20]. From measurements of the specific heat in $CeCu_4Ga$ we estimate that due to the Kondo interaction a reduction of the magnetic moments by about 80% takes place. This can result either in a diminished number of 4f moments which are involved in magnetic order, or in a reduction of the full moments. This is analogous to the situation for $Ce(Cu_xAl_{1-x})_5$ [21].

Acknowledgments

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