Thermal conductivity in $Ce(Cu,Al)_5$ compounds

1991 J. Phys.: Condens. Matter 3 7641

(http://iopscience.iop.org/0953-8984/3/39/010)

J. Phys.: Condens. Matter 3 (1991) 7641–7650. Printed in the UK

Thermal conductivity in $Ce(Cu,Al)_5$ compounds

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Received 12 April 1991

Abstract. Measurements of the temperature- and concentration-dependent thermal conductivity of $Ce(Cu_xAl_{1-x})_5$ and $La(Cu_xAl_{1-x})_5$ compounds ($0.8 \leqslant x \leqslant 1$) are presented. In both series, an increasing Al content causes an unusual growth of the portion of the lattice contribution to the total thermal conductivity. For the boundary compounds $CeCu_5$ and $LaCu_5$, the lattice thermal conductivity is practically negligible. A comparison of the experimental data of the isostructural magnetic and non-magnetic compounds reveals clear evidence of Kondo-type scattering processes in the Ce-based samples. A remarkable change of the crystal field splitting, caused by the Al substitution, is also observed from these measurements.

1. Introduction

Transport properties are usually an appropriate tool to study the Kondo effect in the presence of a strong crystal field. An interplay of both effects causes a very characteristic temperature dependence of transport coefficients. In particular, the spin-dependent contribution to the electrical resistivity shows two ($-\ln T$) regions which are usually separated by a broad maximum centred around the overall crystal field splitting temperature Δ_{CF} [1]. The ratio of the slope of both logarithmic branches is controlled by the degeneracy of the crystal field levels involved [1]. A very sensitive tool proving the Kondo interaction is the temperature-dependent thermopower $S(T)$. The Kondo interaction process causes a universal temperature dependence of $S(T)$ with unusually large absolute values which have maxima around the Kondo temperature T_K. However this universal behaviour is lost when crystal field splitting is taken into consideration [2, 3]. At low temperatures, the competition between the RKKY and the Kondo interaction determines the sign of the thermopower [4]. There is little theoretical information available concerning the temperature-dependence of the thermal conductivity when considering Kondo scattering in the presence of crystal field splitting [5]. Experimental investigations of the thermal conductivity are known e.g. for $CeAl_2$ [6, 7], $CeCu_2$ [8], $CeCu_5$ [9], $CeCu_6$ [10], $CeCu_2Si_2$ [11] or $CePt_2Si_2$ [12]. The overall shape of the temperature-dependent thermal conductivity of these compounds hardly points to anomalous behaviour associated with the Kondo effect.

The aim of this paper is to present a study of the temperature-dependent thermal conductivity of various $Ce(Cu_xAl_{1-x})_5$ intermetallics and to analyse it with respect to Kondo-type scattering processes. This will be done by applying a useful method which allows one to characterize the Kondo interaction in thermal conductivity data. It has been proven that the properties of the series $Ce(Cu_xAl_{1-x})_5$ with ($0.8 \leqslant x \leqslant 1.0$)

0953-8984/91/397641+10$03.50

are strongly influenced by the Al substitution; e.g. an increasing Al content causes the suppression of long-range magnetic order found for $CeCu_5$ ($T_N \approx 4$ K) [9, 13]. Simultaneously, the electronic contribution to the specific heat strongly increases and exhibits a value of 2800 mJ mol K^{-2} for $T \to 0$ and $x = 0.80$ [14].

2. Experimental procedure

Polycrystalline $Ce(Cu_xAl_{1-x})_5$ and $La(Cu_xAl_{1-x})_5$ samples were prepared by high frequency melting under a protective argon atmosphere and subsequently annealed for 3 weeks at 700 °C. The phase purity of the samples was verified from the x-ray pattern using a standard Siemens diffractometer and applying Cu K_α radiation. For thermal conductivity measurements a flow cryostat has been used. The temperature interval which can be covered ranges from about 3.5 K to 320 K. The shape of the samples is half-cylindrical with a diameter of 5 mm and a length of about 30 mm. One end of the sample is fixed to the heat exchanger of the cryostat. The temperature of the heat exchanger is controlled by means of a Ge or Pt resistor depending on the temperature range. On the free end of the sample a small electrical heater is mounted, which produces a constant heat flow through the sample and causes a temperature gradient. The gradient produced in this way is measured using a differential thermocouple. The magnitude of the gradient must be small compared with the absolute temperature and is in the range of about 0.2 K cm^{-1} to 3 K cm^{-1}. Such a method comes into use as the 'steady state longitudinal heat flow' method. In this case the thermal conductivity can be calculated as $\lambda(T) = l\dot{Q}/(A\Delta T)$, where $\dot{Q}$ is the heating power produced by the electrical heater, l and A are the length and the cross section of the sample, respectively, and ΔT is the temperature difference along the sample.

3. Results

Figure 1 shows the thermal conductivity λ as a function of temperature of $Ce(Cu_xAl_{1-x})_5$ for various concentrations in the range $0.80 \leqslant x \leqslant 1.00$. While $CeCu_5$, on the one hand, is characterized by a maximum of $\lambda(T)$ at low temperatures, typically for metals and compounds with low scattering rates on static imperfections [15], $CeCu_4Al$ ($x = 0.80$), on the other hand, shows only a smooth increase of λ with temperature, hinting at strong interactions which result in short mean free paths of the conduction electrons. This change in the thermal conductivity across the $Ce(Cu_xAl_{1-x})_5$ series is partially caused by increasing scattering events of the conduction electrons on imperfections, inferred from the substitution, but is also due to a change of the spin-dependent scattering processes. Note that the reduction of the thermal conductvity is not at all linear with the concentration.

The overall temperature dependence of λ of $Ce(Cu, Al)_5$, as shown in figure 1, exhibits no anomalies associated with the Kondo effect in these samples. In contrast, this effect is clearly seen from measurements of the electrical resistivity, from the magnetoresistance and from the temperature dependence of the thermopower [14, 16]. It can be anticipated that in the case of the thermal conductivity the development of a characteristic Kondo behaviour is masked by additional scattering interactions of the conduction electrons as well as by the lattice contribution to the thermal conductivity. Therefore, a closer inspection of the experimental data seems to be necessary to figure

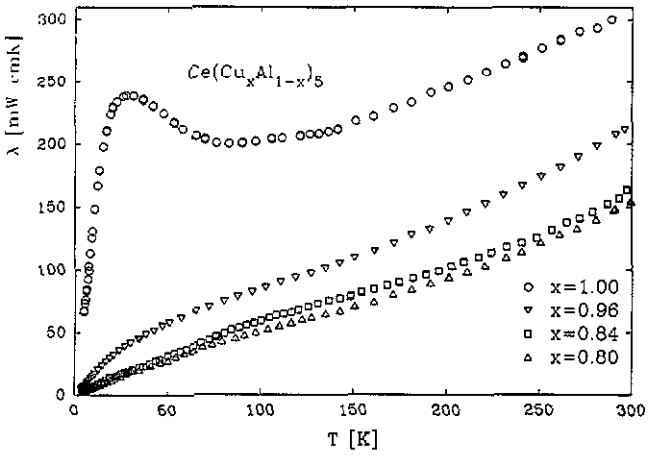

Figure 1. Temperature dependence of the thermal conductivity λ of $Ce(Cu_xAl_{1-x})_5$ compounds.

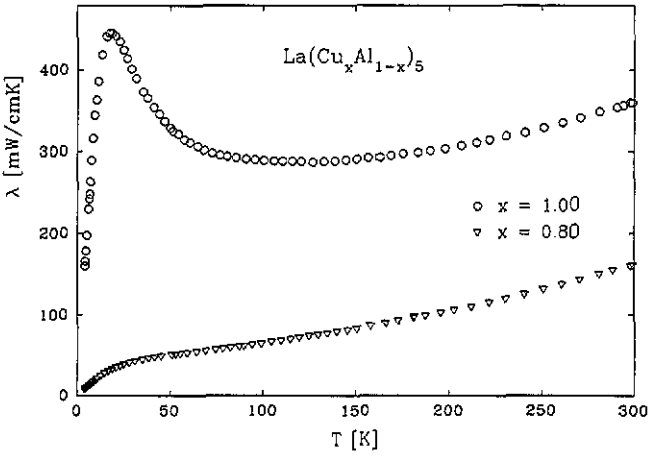

Figure 2. Temperature dependence of the thermal conductivity λ of $La(Cu_xAl_{1-x})_5$ compounds.

out the interaction process of the conduction electrons with the almost localized 4f moments of Ce. A commonly accepted way of doing this is a comparison with $\lambda(T)$ of isomorphous non-magnetic compounds, i.e. with $\lambda(T)$ of $La(Cu, Al)_5$.

Figure 2 shows $\lambda(T)$ for two compounds of $La(Cu_xAl_{1-x})_5$. Again, the substitution of Cu by Al causes a remarkable change of the $\lambda(T)$ behaviour and an enormous decrease in the absolute values of $\lambda(T)$. Compared with the thermal conductivity of the respective Ce compounds, the absolute $\lambda(T)$ values of the La-based samples are larger. This unambigiously reflects the absence of an additional thermal resistivity due to the interaction of the conduction electrons with the Ce 4f moments.

4. Discussion

In metallic solids the thermal conductivity λ originates from two different contributions

$$\lambda = \lambda_e + \lambda_l \tag{1}$$

where λ_e refers to the heat transport by electrons and λ_l to that of the lattice system.

The heat transport due to the conduction electron system is limited by different scattering processes. Based on Matthiessen's rule the thermal resistivity W_e can be expressed by

$$1/\lambda_e \equiv W_e = W_{e,o} + W_{e,ph} + W_{e,mag}. \tag{2}$$

The subscripts (e,o), (e,ph) and (e,mag) denote scattering processes of conduction electrons with impurities, with thermally excited phonons and with magnetic moments, respectively. The temperature dependence of $W_{e,o}$ and $W_{e,ph}$ is well-known and demonstrated in many textbooks [15, 17]. While $W_{e,o} = \alpha/T$ in the whole temperature range, the contribution $W_{e,ph}$ follows Wilson's law which predicts, at low temperatures, that $W_{e,ph} = \beta T^2$ and $W_{e,ph} = \text{const}$ for high temperatures (α and β are simple constants). The contribution due to scattering of conduction electrons with almost localized magnetic moments has been calculated for the paramagnetic temperature range [18]. Using the first Born approximation for the transition probability and neglecting crystal field effects, $W_{e,mag}$ is given by

$$W_{e,mag} = DJ^2(g-1)^2 j(j+1)1/T \tag{3}$$

where J is the s–f coupling constant, g is the Landé factor, j the total angular momentum of the magnetic moments and D is a constant.

Very recently, Bhattacharjee and Coqblin [5] have calculated the thermal resistivity due to Kondo-type interaction in the presence of strong crystal field splitting. Based on a third-order perturbation calculation which accounts for the interaction of the conduction electrons with the magnetic ions when the final state of the scattering process is developed via an intermediate state, it follows that

$$1/W_{e,mag}(T) = \lambda_{e,mag}(T) = C(2j+1)\frac{T}{R}(1-Y) \tag{4}$$

where C is again a constant. The function Y expresses the ratio of third- and second-order perturbation contributions ($Y < 1$), giving therefore the proportions of Kondo-like interaction and direct scattering processes with the almost localized 4f moments, respectively. The function R contains parameters like the coupling constant J, the degeneracy of each crystal field level, their energy separation and their average thermal population. Numerical solutions of equation (4) yield a broad spectrum of possible $\lambda_{e,mag}(T)$ dependencies, mainly controlled by the parameters incorporated in the function R. Some of the solutions are shown in the original paper by Bhattacharjee and Coqblin [5].

As with the electronic thermal conductivity, the lattice thermal conductivity λ_l is bounded by interaction processes of the phonons on various scatterers. Assuming the Matthiessen rule, λ_l can be expressed as

$$1/\lambda_l \equiv W_l = W_{l,o} + W_{l,e} + W_{l,ph} + \cdots. \tag{5}$$

The subscripts (l, o), (l, e) and (l, ph) characterize scattering processes of lattice vibrations on static imperfections, the conduction electron system and the phonon–phonon interaction (i.e. normal and Umklapp processes), respectively. Makinson [19] pointed out that there are two main processes limiting the phonon mean free path: U-processes and phonon–electron scattering. The former dominate at ordinary temperatures, the latter at low temperatures. Both processes yield a characteristic temperature dependence: $W_{l,g} = \gamma T$ and $W_{l,e} = 1/(\delta T^2)$ [21].

The knowledge of the temperature dependence of a particular process allows one to discuss in detail the measured thermal conductivity for both the magnetic and the non-magnetic compounds.

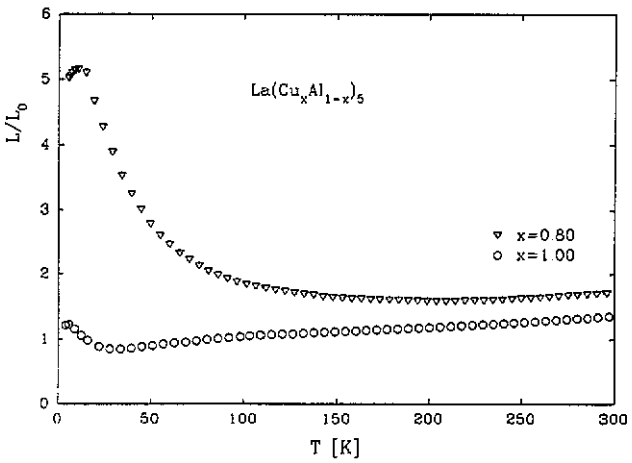

Figure 3. Temperature dependence of the normalized Lorentz number L/L_0 of $La(Cu_xAl_{1-x})_5$ compounds.

Figure 3 displays the temperature dependence of the normalized Lorentz number L/L_0 for $La(Cu_xAl_{1-x})_5$, $x = 1.00$ and $x = 0.80$; ($L(T) = \lambda(T)\rho(T)/T$, $L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}). The Lorentz numbers of $LaCu_5$ show only slight deviations from the theoretical value L_0 in the whole temperature range. The conditions, for which $L(T) \approx L_0$ are derived from the Wiedemann–Franz law: λ_l is negligible and the relaxation time approximation is valid. The latter condition indicates that the conduction electrons contribute with a similar weight to both the electrical and the thermal resistivity. Since $L(T) \approx L_0$ for $LaCu_5$, the heat conductivity due to lattice vibrations seems to be of minor importance and can therefore be neglected.

These arguments do not hold in the case of $LaCu_4Al$ ($x = 0.80$). Especially at low temperatures, where the Lorentz number L deviates considerably from the theoretical value L_0. Because electronic processes yield $L(T)$-values of the order of L_0 [15], the L-excess over the theoretical value L_0 for the compound $x = 0.80$, is most likely caused by a remarkably large lattice contribution to the thermal conductivity.

For the low temperature regime, the thermal conductivity of the La-based compounds can be described considering the most dominant interaction processes

$$\lambda = \lambda_e + \lambda_l = \frac{1}{W_{e,0} + W_{e,ph}} + \lambda_{l,e} = \frac{1}{\alpha/T + \beta T^2} + \delta T^2. \tag{6}$$

A least squares fit to the data according equation (6) is presented in figure 4 for $LaCu_5$ and $LaCu_4Al$. The coefficients α, β and δ are given in table 1. As inferred

too from the analysis of the Lorentz numbers, the lattice contribution to the thermal conductivity is negligible for $LaCu_5$, at least at low temperatures; $\lambda(T)$ is satisfactorily accounted for by the electronic part λ_e. Concerning $LaCu_4Al$ ($x = 0.80$) it is found that λ_l is of comparable magnitude with λ_e. This obvious alteration of the importance of the lattice contribution may be understood from the following argument: it can be seen that for temperatures around 10 K, $\lambda(T)$ of $LaCu_5$ is approximately twenty times larger than $\lambda(T)$ of $LaCu_4Al$. If one assumes that the lattice contribution λ_l in both compounds is of about the same size, then λ_l is of the order of λ_e in $LaCu_4Al$, while it is just 1% in the case of $LaCu_5$. The coefficient α which describes the strength of the interaction of conduction electrons with static imperfections rises with rising Al content. This is also seen from the strong increase of the electrical residual resistivity of these compounds [14].

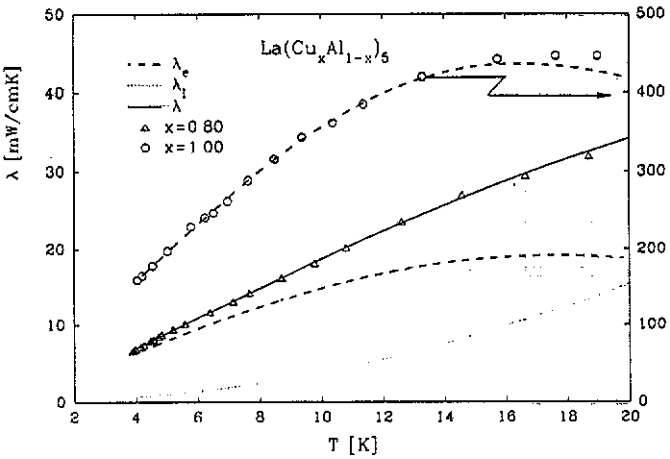

Figure 4. The low temperature thermal conductivity of $La(Cu_xAl_{1-x})_5$ ($x = 1.00, 0.80$). The dashed and the dotted curves are the electronic (λ_e) and the lattice components (λ_l) of the total thermal conductivity according equation (6), respectively. The full curve is the sum of λ_e and λ_l. See also table 1.

Table 1. The coefficients α, β and δ for $La(Cu_xAl_{1-x})_5$($x = 1.00$, 0.80), compare with equation (6).

	$x = 1.00$	$x = 0.80$
α (cm mW^{-1})	0.0252	0.618
β (cm K^3 mW^{-1})	2.84×10^{-6}	5.58×10^{-5}
δ (mW cm^{-1} K^{-3})	$\approx 1 \times 10^{-6}$	0.0386

The temperature dependence of L/L_0 for various $Ce(Cu_xAl_{1-x})_5$ compounds is displayed in figure 5. The main feature of this figure is an increase of L/L_0 with an increasing Al content which resembles the concentration-dependent behaviour of the respective La compounds. Therefore, the conclusions which may be drawn are similar to those in the case of the non-magentic compounds: (i) the thermal conductivity of $CeCu_5$ is dominated by electronic heat transport; (ii) the substituted Ce compounds

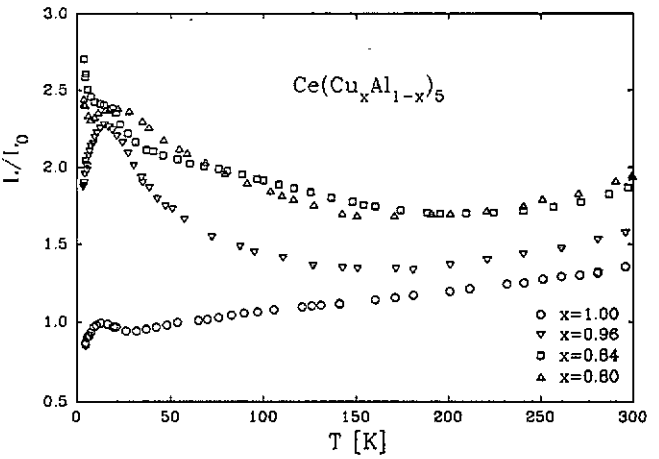

Figure 5. Temperature dependence of the normalized Lorentz number of Ce(Cu$_x$Al$_{1-x}$)$_5$.

are characterized by a growing importance of the lattice thermal conductivity since the electronic contribution becomes strongly depressed.

Following these arguments, it is not unreasonable to assume that the lattice contribution λ_l for compounds with the same nominal Al concentration is of equal magnitude in the respective Ce- and La-based compounds. This fact will help to isolate the particular contribution due to the Kondo effect in a simple way. To extract $W_{e,mag}$ from the measured data the following procedure is applied, and is valid for those cases where λ_l is negligible or at least of equal magnitude in the Ce- and the La-based compounds

$$\lambda^m = \lambda_e^m + \lambda_l^m \tag{7a}$$

$$\lambda^{nm} = \lambda_e^{nm} + \lambda_l^{nm}. \tag{7b}$$

The superscripts (m) and (nm) refer to magnetic and non-magnetic compounds, respectively. For $\lambda_l^m \approx \lambda_l^{nm}$ the difference of equations (7*a*) and (7*b*) reads

$$\begin{aligned} 1/\lambda^m - 1/\lambda^{nm} \equiv \Delta W &\approx W_e^m - W_e^{nm} \\ &= (W_{e,0}^m - W_{e,0}^{nm}) + (W_{e,ph}^m - W_{e,ph}^{nm}) + W_{e,mag}. \end{aligned} \tag{8}$$

Assuming that for the isomorphous Ce and La compounds $W_{e,0}$ and $W_{e,ph}$ are equal, equation (8) simply yields $\Delta W \approx W_{e,mag}$.

To achieve an appropriate representation of the $W_{e,mag}$ data, figure 6 shows ΔWT versus $\ln T$ for Ce(Cu$_x$Al$_{1-x}$)$_5$, $x = 1.00$ and 0.80. This representation relates the electrical resistivity to the thermal resistivity by the Wiedemann–Franz law ($\Delta WT \approx W_{e,mag}T \approx \rho_{mag}$). The experimental ΔWT data for $CeCu_5$ show a behaviour which is characterized by two negative logarithmic ranges, separated by a broad maximum around 190 K. Considering the proportionality of this quantity with ρ_{mag}, the Kondo effect in the crystal field ground state and in the full $j = 5/2$ multiplet seems to be made evident. The maximum around 190 K can therefore be attributed to the overall crystal field splitting. To prove these findings, $\rho_{mag}(T)$ of Ce(Cu$_x$Al$_{1-x}$)$_5$ with $x = 1.00$ and $x = 0.80$ is shown in figure 7 for comparison. As expected for a Kondo-lattice compound, ρ_{mag} of $CeCu_5$ shows a negative logarithmic dependence

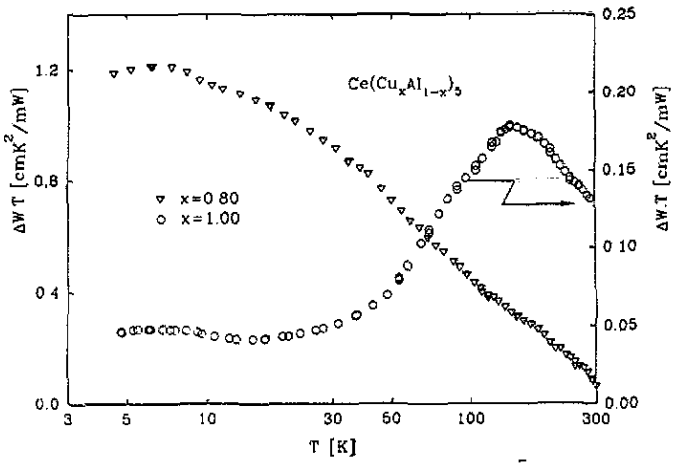

Figure 6. Magnetic contribution to the thermal conductivity of $Ce(Cu_xAl_{1-x})_5$(x = 1.00,0.80) as ΔWT versus ln(T).

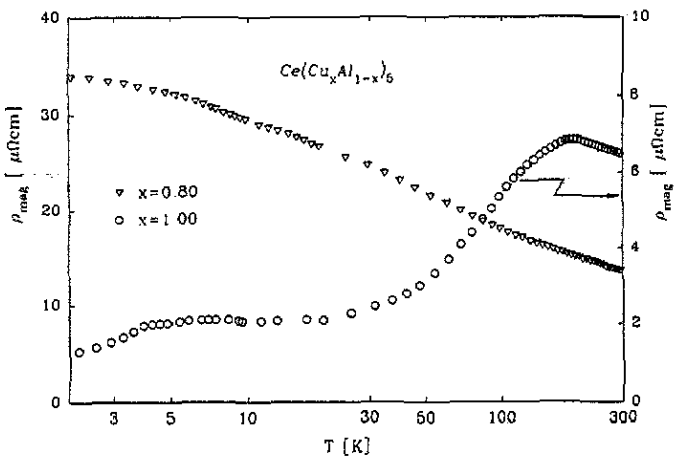

Figure 7. Magnetic contribution to the electrical resistivity of $Ce(Cu_xAl_{1-x})_5$(x = 1.00,0.80) as ρ_{mag} versus ln(T).

at low and at high temperatures as well as a maximum close to 200 K. Crystal field effects in the hexagonal $CeCu_5$ compound cause a lifting of the six-fold degenerate $j = 5/2$ state into 3 doublets with eigenstates $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$. Inelastic neutron scattering experiments on $CeCu_5$ have revealed a strong inelastic line at $\approx$ 16.9 meV which is caused by a transition from the ground state doublet to the first excited doublet. This transition can be identified with the maximum in ρ_{mag} and ΔWT. The behaviour of the compound $x = 0.80$ in figure 6 and figure 7 is different from that of $CeCu_5$. In spite of the fact that for both quantities (ρ_{mag} and ΔWT) a large interval with a negative logarithmic temperature dependence is observed, a pronounced maximum reflecting the crystal field splitting is absent. This observation is attributed to the fact that the substitution of Cu by Al also causes a large alteration of the crystal field level scheme. A detailed investigation by means of inelastic neutron scattering shows that the strong transition from the ground state to the first excited level moves from 16.9 meV ($x = 1.00$) to about 5.5 meV ($x = 0.80$) [21]. For those

cases where the Kondo temperature of the full multiplet (T_K^H) is comparable to the crystal field splitting energy, i.e. $k_B T_K^H \approx \Delta_{CF}$ the very distinct behaviour described by the model of Cornut and Coqblin [1] should not be observable. A more sophisticated theory by Guessous [22] predicts that the maximum due to crystal field splitting vanishes. Instead a maximum at low temperatures appears, inferred from correlation effects. In this scope, the behaviour of ρ_{mag} and ΔWT of $CeCu_4Al$ ($x = 0.80$) proves the breakdown of Cornut and Coqblin's theory because T_K^H becomes comparable to Δ_{CF}.

5. Summary

Both $Ce(Cu_xAl_{1-x})_5$ as well as $La(Cu_xAl_{1-x})_5$ compounds exhibit a very impressive change of behaviour in transport properties caused by a change of the Al content. In particular, the thermal conductivity of these compounds is characterized by a crossover from an electronic dominated conductivity in case of $CeCu_5$ and $LaCu_5$ towards the case where the lattice thermal conductivity is essential ($CeCu_4Al$ and $LaCu_4Al$). A very efficient way to study this alteration originates from the concentration- and temperature-dependent Lorentz number. Since the lattice thermal conductivity is of equal importance for both the La- and the Ce-based compounds (with the same Al concentrations), a comparison of the magnetic and the non-magnetic compounds allows one to extract the magnetic scattering contribution due to the interaction of the conduction electrons with the almost localized Ce 4f moments. As a result, the Kondo interaction in the presence of crystal field splitting is deduced from the total measured effect. Typically, the thermal resistivity caused by the combined influence of the latter processes shows logarithmic dependencies in ΔWT, which of course can be expected from the relationship of this quantity with ρ_{mag}.

References

[1] Cornut B and Coqblin B 1972 *Phys. Rev.* B **5** 4541
[2] Bhattacharjee A K and Coqblin J 1976 *Phys. Rev.* B **13** 3441
[3] Maekawa S, Kashiba S, Tachiki M and Takahashi S 1986 *J. Phys. Soc. Japan* **55** 3194
[4] Fischer K H 1989 *Z. Phys.* B **76** 315
[5] Bhattacharjee A K and Coqblin J 1988 *Phys. Rev.* B **38** 338
[6] Bauer E, Gratz E, Mikovits W, Sassik H and Kirchmayr H 1982 *J. Magn. Magn. Mater.* **29** 192
Bauer E, Gratz E and Adam G 1986 *J. Phys. F: Met. Phys.* **16** 493
[7] Peysson Y 1986 *PhD Thesis* University of Grenoble
[8] Gratz E, Bauer E, Barbara B, Zemirli S, Steglich F, Bredl C D and Lieke W 1985 *J. Phys.* **15** 1975
[9] Bauer E, Gratz E and Schmitzer C 1987 *J. Magn. Magn. Mater.* **63–64** 37
[10] Peysson Y, Salce B, Ayache C and Bauer E 1986 *J. Magn. Magn. Mater.* **54–57** 423
[11] Franz W, Griessel A, Steglich F and Wohlleben Z 1978 *Z. Phys.* B **31** 17
[12] Raki M, Forro L, Ayache C, Schmitt D, Bhattacharjee A K and Coqblin B 1990 *Physica* B **163** 93
[13] Willis J O, Aiken R H, Fisk Z, Zirngibl E, Thompson J D, Ott H R and Battlog B 1987 *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions* ed L C Gupta and S K Malik (New York: Plenum) p 57
[14] Bauer E, Gratz E, Kohlmann J, Winzer K, Gignoux D and Schmitt D 1990 *Z. Phys.* **80** 263
[15] Wilson A H 1958 *The Theory of Metals* 2nd edn (Cambridge: Cambridge University Press)
[16] Bauer E 1991 *Adv. Phys.* at press
[17] Ziman J M 1960 *Electrons and Phonons* 4th edn (Oxford: Clarendon)
[18] Bauer E, Gratz E and Kirchmayr H 1987 *Z. Phys.* **68** 63
[19] Makinson R E B 1938 *Proc. Camb. Phil. Soc.* **34** 474

[20] Klemens P G 1969 *Thermal Conductivity* vol 1, ed R P Tye (London: Academic)
[21] Gignoux D, Schmitt D, Bauer E and Murani A P 1990 *J. Magn. Magn. Mater.* **88** 63
[22] Guessous A 1987 *PhD Thesis* University of Grenoble