CROATICA CHEMICA ACTA
CCACAA, ISSN 0011-1643, e-ISSN 1334-417X
Croat. Chem. Acta **83** (1) (2010) 69–73.
CCA-3393

Original Scientific Paper

Transport Properties of $YbCu_{4.4}$ Giant-unit-cell Metallic Compound*

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RECEIVED MAY 11, 2009; REVISED SEPTEMBER 2, 2009; ACCEPTED SEPTEMBER 5, 2009

Abstract. The experimental results of the transport properties: electrical resistivity, ρ, thermopower, S, and thermal conductivity, κ, of a polycrystalline sample of $YbCu_{4.4}$, in the temperature range 2 to 300 K, are presented. In contrast to the divalent $YbCu_2$ compound, $YbCu_{4.4}$ has transport properties typical of an intermediate valence compound: relatively high electrical resistivity and large thermoelectric power. The electrical resistivity $\rho(T)$ exhibits a typical Kondo lattice systems' behaviour, with a room temperature value of $\rho_{\text{r.t.}} \approx 60$ μΩ cm, while thermoelectric power $S(T)$ is negative in the whole investigated temperature range. $S(T)$ shows a distinct temperature dependence, which is attributed to the Kondo interaction. The room temperature, r.t., value of the thermal conductivity is $\kappa_{\text{r.t.}} \approx 20$ W / m K. The pronounced maximum in $\kappa(T)$ at low temperatures, which is frequently found in simple nonmagnetic and rather pure samples, is absent. The thermal conductivity decreases monotonically in a whole temperature range with a change in the slope around 50 K. The absence of a maximum in $\kappa(T)$ could be related to the larger contribution of residual scattering processes and to the considerably weak coupling of electrons with phonons. The results are compared to the reported transport properties of similar Ce-Cu and Yb-Cu Kondo systems.

Keywords: complex metallic alloys, physical properties, electrical resistivity, thermopower, thermal conductivity

INTRODUCTION

While in metals and intermetallics periodicities of less than 1 nm usually occur and the corresponding unit cells host a few atoms only, a number of alloys (complex metallic alloys) contain more than several thousands of atoms per unit cell, with the length scale of the lattice periodicity up to several nanometres. In the focus of this work is the Yb-Cu system which for some phases has a large unit cell size. In this system several intermediate phases have been known up to now: YbCu, $YbCu_2$, $YbCu_{3.5}$, $YbCu_{4.5}$, $YbCu_5$ (which can be stabilized just under very high pressure) and $YbCu_{6.5}$. Existence of two phases which are very close in composition to the $YbCu_{4.5}$, *i.e.* $YbCu_{4.25}$ and $YbCu_{4.4}$ has been reported recently.[1] $YbCu_{4.4}$ is intermediate valence compound (IVC) with ytterbium close to trivalent state. Free trivalent Yb^{3+} state is characterized by total angular momentum $j = 7/2$, g = 8/7 and magnetic moment $m_{\text{eff}} = 4.54$ m_B (m_B – Bohr magneton). Magnetic susceptibility follows the Curie law down to 93 K[2] with a paramagnetic Curie temperature being about –25 K and magnetic moment $m = 4.39$ m_B, which is near free ion value for Yb^{3+}. Deviation from the Curie-Weiss law below 93 K is supposed to be due to the crystal field effect. $YbCu_{4.4}$ crystallizes in a monoclinically distorted 6 × 6 × 5.5 superstructure derived from cubic face-centred $AuBe_5$-type structure with 4570 atoms per unit cell which are distributed over 350 sites occupied by ytterbium and 1519 sites occupied by copper.[3] Cell parameters are about 5 nm (a = 41.(1) Å, b = 41.9(7) Å, c = 38.6(4) Å, β = 90.5(5)°). Three types of ytterbium sites occur in the structure and their relative abundances are 2:1:1. In previous investigation of $YbCu_{4.5}$ a significant variation in electrical resistivity[4–7] was observed due to sample preparation and measurement technique improvements. It is not certain if in previous researches always $YbCu_{4.5}$ has been investigated or it was some mixture of recently discovered phases that are very close in phase diagram. Our aim is to investigate the electrical resistivity and thermopower of $YbCu_{4.4}$ compound and to measure the thermal conductivity on the same specimen, all of that at low pressure (10^{-6} mbar) and in zero magnetic field and to compare our results with those in literature. To our best knowledge it is the first investigation of the thermal conductivity of $YbCu_{4.4}$.

* Presented at the EU Workshop "Frontiers in Complex Metallic Alloys", Zagreb, October 2008.
Dedicated to Professor Boran Leontić on the occasion of his 80th birthday.
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EXPERIMENTAL

The polycrystalline $YbCu_{4.4}$ sample used in our investigation was grown by Bridgman method in tantalum crucible. Sample was bar shaped with dimensions approximately $0.6 \times 2.5 \times 5.5$ mm^3. Thermal conductivity was measured along the long axes using an absolute steady-state heat-flow method.[8] The thermal flux through the samples was generated by a 1 kΩ RuO_2 chip-resistor, glued to one end of the sample, while the other end was attached to a copper heat sink. The temperature gradient across the sample was monitored by a chromel-gold with 0.07 % Fe differential thermocouple with 25 μm wires to minimize heat flow through wires.

The electrical conductivity and the thermopower were measured simultaneously.[9] The thermopower was measured using differential method which gives thermopower of the sample without the need to calculate thermal gradient across the sample. For the thermopower measurement two chromel-gold with 0.07 % Fe thermocouples with 50 μm wires were used. Thermal gradient was achieved with two 1 kΩ RuO_2 chip-resistors – one on each side of the sample (they were switched off and on alternately to produce thermal gradients in both directions of the sample). Gold wires of the thermocouples for the thermopower measurements were used as the voltage terminals in the electrical resistivity measurement.[10] All measurements were performed in the temperature interval from 2 to 300 K. The results are compared to the data of the $CeCu_6$ compound.[7]

RESULTS AND ANALYSIS

Figures 1, 2 and 3 present our experimental data of the total thermal conductivity $\kappa_{tot}(T)$, electrical resistivity $\rho(T)$ and thermopower $S(T)$ of the $YbCu_{4.4}$ sample, respectively.

Temperature behaviour of the electrical resistivity of the $YbCu_{4.4}$ (Figure 4) is similar to that of the electrical resistivity of the Kondo lattice system $CeCu_6$, which shows a logarithmic behaviour at high temperatures and T^2 behaviour only at very low temperatures[7, 11] (low and high temperatures with respect to the Kondo temperature T_K). Our measurements were not performed at low enough temperatures to observe the low temperature T^2 dependence, but this has been established in earlier investigations.[6] If we assume that the phonon-derived contribution to the electrical resistivity rises continuously with temperature, then the magnetic part of the resistivity decreases, at least in the high-temperature limit. To obtain the magnetic part of the resistivity one has to subtract the phonon part using resistivity data of some reference nonmagnetic compound that has similar structure. Splender *et al.*[6] used $LuCu_5$ data because it has $AuBe_5$ structure. We have used our original data,

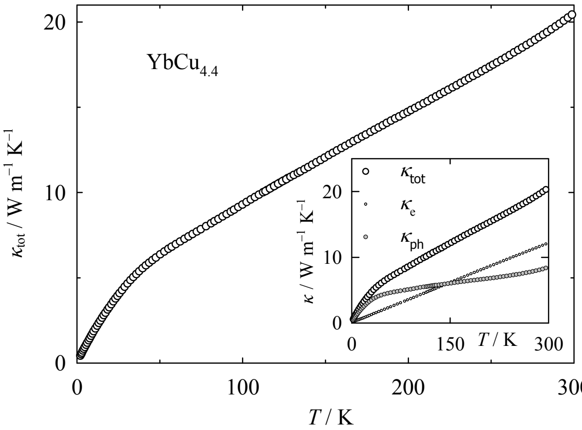

Figure 1. Temperature dependence of the total thermal conductivity, $\kappa_{tot}(T)$, of the $YbCu_{4.4}$ sample. The inset shows the dependence of the electronic, $\kappa_e(T)$, and phononic, $\kappa_{ph}(T)$, contribution to the total thermal conductivity.

and supposed that phonon contribution is not too large at intermediate temperatures to obtain logarithmic behaviour as seen in Figure 4. The data for the $YbCu_{4.4}$ above the Kondo temperature are fitted to formula $\rho(T) = a \ln(T) + b$ (Figure 4). The insets to Figure 4 show, as a comparison, the fits of $YbCu_{4.5}$ data of Ref. 6 and of $CeCu_6$ data of Ref. 7. The fitting parameters are shown in Table 1. It may be seen from Table 1 that the slope of our data, in logarithmic scale, is almost four times smaller in absolute value than that of Splender *et al.*[6] It means that magnetic part of the electrical resistivity is screened with that of the phonon-derived contribution.

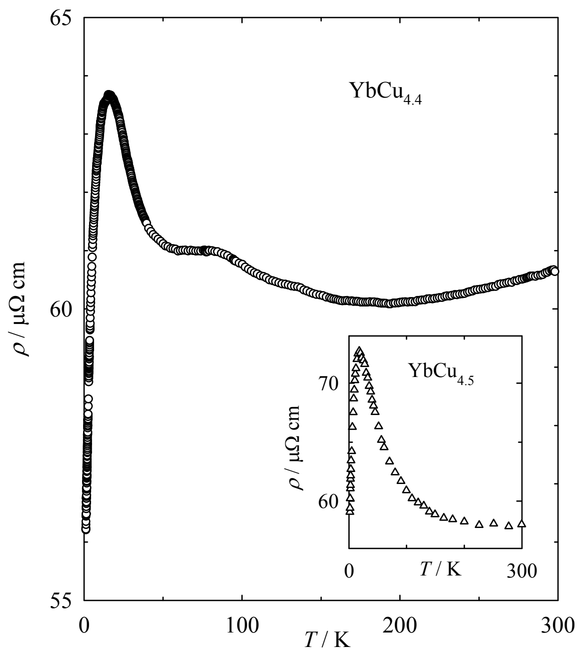

Figure 2. Temperature dependence of the electrical resistivity, $\rho(T)$, of the $YbCu_{4.4}$ sample. The inset shows electrical resistivity data of the $YbCu_{4.5}$ taken from Ref. 6.

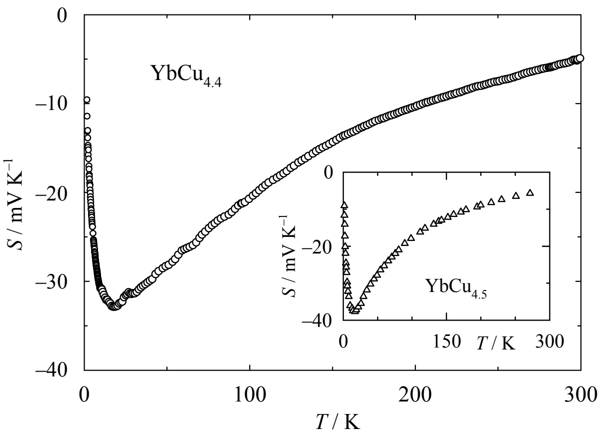

Figure 3. Temperature dependence of the thermopower, $S(T)$, of the $YbCu_{4.4}$ sample. The inset shows the thermopower data of the $YbCu_{4.5}$ taken from Ref. 6.

At higher temperatures the screening becomes even more pronounced and is seen in the high temperature upturn of the resistivity. The same behaviour is obtained for our data as well as for the $CeCu_6$ data. The origin of the shoulder observed at 80 K is unclear at present. In comparison with earlier results our sample has lower maximum electrical resistivity with approximately the same high and low temperature values. Splender *et al.* have reported data for two types of samples. One of them has had low and the other large saturation value at low temperatures. The origin of the difference is unclear at present and high purity single crystal measurements are required for clarification of this point.

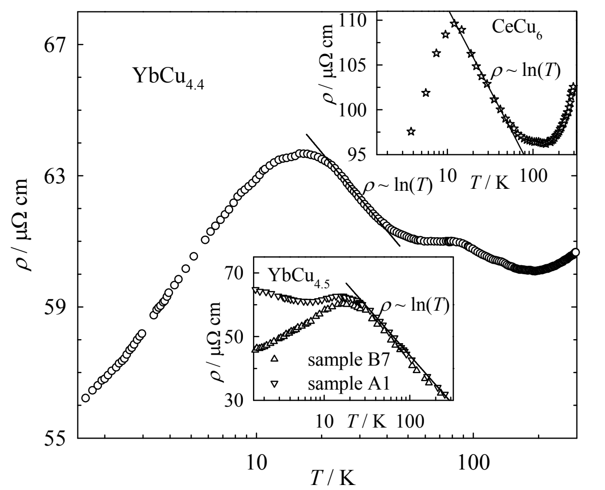

Figure 4. The electrical resistivity, $\rho(T)$, of $YbCu_{4.4}$. Upper inset: magnetic contribution to the electrical resistivity of the $YbCu_{4.5}$ for two different samples; taken from Ref. 6. Lower inset: the electrical resistivity of $CeCu_6$; taken from Ref. 7.

Table 1. Fitting parameters for electrical resistivity

Sample	a / μΩ cm	b / μΩ cm
$YbCu_{4.4}$ [(a)]	−7.9	74.0
$YbCu_{4.5}$ [(b)]	−30.6	104.6
$CeCu_6$ [(c)]	−18.33	129.7

[(a)] This work. [(b)] Ref. 6. [(c)] Ref. 7.

The temperature behaviour of the thermopower is typical for intermediate valence compounds. The $YbCu_{4.4}$ has large, broad minimum around 20 K as may be seen in Figure 2. At higher temperatures the absolute value of the thermopower decreases logarithmically as temperature increases. This behaviour is ascribed to the Kondo interaction. $CeCu_6$ thermopower data show very similar behaviour at high temperatures (inset of Figure 5). The difference of the $CeCu_6$ and $YbCu_{4.4}$ thermopower data is their sign. This can be understood from the electron-hole symmetry of Ce^{3+} $4f^1$ compared to Yb^{3+} $4f^{13}$. In the framework of Bhattacharjee and Coqblin theory[12] the temperature dependence of $S(T)$ hints at a crystal-field splitting.

The total thermal conductivity, κ_{tot}, may be represented as a sum of phonon, κ_{ph}, and electronic, κ_e, components

$$\kappa_{tot} = \kappa_{ph} + \kappa_e \quad (1)$$

Assuming the validity of the Wiedemann-Franz law, the electronic thermal conductivity κ_e may be written in the form

$$\kappa_e = L_0 T / \rho \quad (2)$$

where L_0 is the Sommerfeld value of the Lorentz number ($L_0 = 2.45 \times 10^{-8}$ W Ω K^{-2}).

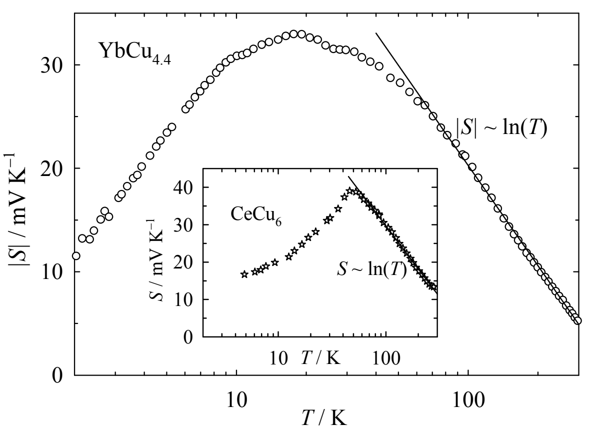

Figure 5. Temperature dependence of the absolute value of the thermopower $|S(T)|$ in $YbCu_{4.4}$. The inset shows temperature dependence of the $CeCu_6$; taken from Ref. 7.

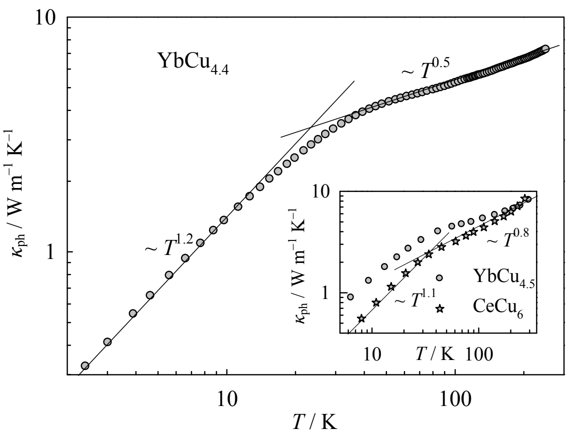

Figure 6. Temperature dependence of the phonon thermal conductivity, $\kappa_{ph}(T)$, of the $YbCu_{4.4}$. The inset shows, for comparison, the temperature dependence of the phonon thermal conductivity of $YbCu_{4.4}$ and $CeCu_6$[6] compounds.

The circles in Figure 6 represent the temperature dependence of the phonon thermal conductivity $\kappa_{ph}(T)$ calculated by making use of Eqs. (1) and (2). We may readily see from this figure that the temperature dependence $\kappa_{ph}(T)$ of the $YbCu_{4.4}$ exhibits an amorphous-like behaviour. This dependence is similar to the temperature dependence of the phonon thermal conductivity $\kappa_{ph}(T)$ of classical amorphous solids. The observed effect is most likely caused by the presence of Yb ions with a homogeneous mixed valence in these compounds.

Low thermal conductivity and the absence of a maximum imply a short electron mean-free-path.[11] This is expected from the electrical resistivity data as well. Furthermore, the absence of a maximum is related to the larger contribution of residual scattering processes and to the significant weak coupling of electrons with phonons. If we suppose that the whole contribution to the thermal conductivity is of the electronic type, then we obtain large (a few times larger than standard Sommerfeld value L_0) Lorentz number: $L(T) = \kappa\rho/T$ especially at very low temperatures where the scattering of the electrons on the magnetic ions is enhanced. This means that at low temperatures the phonon mediated thermal conductivity dominates, while at high temperatures the electronic thermal conductivity is larger (see inset to Figure 1), and hence the change in slope of the thermal conductivity above 50 K. At intermediate temperatures, where a Kondo-like logarithmic behaviour of the electrical resistivity is obtained, electron scattering on magnetic Yb^{3+} ions is enhanced. This leads to the electron thermal conductivity reduction with lowering temperature. Similar situation is observed in the $CeCu_6$, as seen from Figure 6, and the difference is the lower electronic thermal conductivity of $CeCu_6$, due to higher electrical resistivity, so that the phonon contribution to the thermal conductivity dominates in the whole temperature range. Above 1 K and up to 20 K thermal conductivity of the $YbCu_{4.4}$ is almost linear in temperature, as observed in other Kondo systems $CeCu_6$, $CeAl_3$ and $CeCu_2Si_2$.

DISCUSSION AND CONCLUSION

The investigated polycrystalline $YbCu_{4.4}$ sample displays similar temperature behaviour of electrical resistivity and thermopower as reported earlier for the $YbCu_{4.5}$.[6,7] The thermal conductivity shows an anomalous behaviour: a pronounced maximum in the thermal conductivity at low temperatures, which is frequently found in simple nonmagnetic and rather pure samples, is absent here and the total thermal conductivity increases monotonically with temperature above 50 K. Recent NMR study of the $YbCu_{4.4}$ sample from the same source shows an anomalous behaviour around 4 K, probably originating from the presence of a tantalum grains in the sample indicated by the SEM analysis.[13] SEM analysis of our specimen also verified a presence of a few tantalum grains. Less pronounced maximums in the electrical resistivity and thermopower of our $YbCu_{4.4}$ and of the electrical resistivity shoulder around 80 K are most probably related to the presence of small tantalum grains in the specimen. In general, transport properties of the $YbCu_{4.4}$ are similar to those of the $CeCu_6$. Two new phases in the vicinity of the $YbCu_{4.5}$ composition were reported recently. Thus it is possible that a phase admixture in previously[6] measured samples created such variety in the low temperature behaviour of the electrical resistivity. Separate growth of the super structural phases $YbCu_{4.5}$, $YbCu_{4.4}$ and $YbCu_{4.25}$ is difficult because melting temperatures and compositions are very close. In order to solve the mystery of existence of two types of $YbCu_{4.5}$ samples that have been reported,[6] measurements on monocrystals of all three super structural phases are required.

Acknowledgements. This work has been done within the activities of the 6th Framework EU Network of Excellence "Complex Metallic Alloys" (Contract No. NMP3-CT-2005-500140), and has been supported in part by the Ministry of Science, Education and Sports of the Republic of Croatia through the Research Project No. 035-0352826-2848. We thank T. Weber for SC-XRD measurements.

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SAŽETAK

Transportna svojstva YbCu$_{4.4}$ kompleksne metalne slitine

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Prikazani su eksperimentalni rezultati transportnih svojstava: električne otpornosti, ρ, termostruje, S, i toplinske vodljivosti, κ, polikristalnog uzorka YbCu$_{4.4}$ u temperaturnom području od 2 do 300 K. Za razliku od dvovalentne YbCu$_2$ slitine, YbCu$_{4.4}$ pokazuje svojstva tipična za spojeve necjelobrojne valencije: relativno veliku električnu otpornost i veliku termostruju. Električna otpornost, $\rho(T)$, ima ovisnost tipičnu za guste Kondo sustave s vrijednošću na sobnoj temperaturi $\rho_{\text{r.t.}} \approx 60\ \mu\Omega\,\text{cm}$, dok je termostruja negativna u cijelom mjerenom temperaturnom području. $S(T)$ ima izraziti minimum koji se pripisuje Kondo interakciji. Vrijednost toplinske vodljivosti na sobnoj temperaturi je $\kappa_{\text{r.t.}} \approx 20\ \text{W/m K}$. Maksimum u $\kappa(T)$ na niskim temperaturama, koji se uobičajeno pojavljuje u jednostavnim nemagnetičnim i vrlo čistim uzorcima, nije uočen. Toplinska vodljivost monotono raste u cijelom mjerenom rasponu temperatura s promjenom nagiba na temperaturi od oko 50 K. Odsutnost maksimuma u $\kappa(T)$ vjerojatno je povezana s velikim doprinosom rezidualnih procesa raspršenja i prilično slabim elektron-fonon vezanjem. Rezultati su uspoređeni s transportnim svojstvima sličnih Ce-Cu i Yb-Cu Kondo sustava.