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Transport Properties of Heavy Fermion Compounds: $YbIn_{1-x}Cu_{4+x}$ and $YbIn_{1-y}Ag_yCu_4$ [1]

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The intermetallic compounds of Yb with In and Cu ($YbIn_{1-x}Cu_{4+x}$) and Yb with In, Ag, and Cu ($YbIn_{1-y}Ag_yCu_4$) exhibit interesting magnetic and transport properties. Of the compounds of Yb with In and Cu the compound with $x = 0$, namely $YbInCu_4$, has attracted particular attention, because—while being a Curie–Weiss paramagnet—it undergoes a first-order isostructural phase transition at T_v = approx. 40 to 80 K and atmospheric pressure. Below T_v the ytterbium in this compound is in a mixed-valence state and the compound as a whole is sometimes called a light heavy-fermion system. Above T_v, the compound is known as a Curie–Weiss paramagnet of localized magnetic moments and, below T_v, a Pauli paramagnet in a nonmagnetic Fermi-liquid state. In the present paper the results of measurements of the thermal conductivity of polycrystalline samples, $YbIn_{1-x}Cu_{4+x}$ with $x = 0$,0.015, 0.095, and 0.17 and $YbIn_{1-y}Ag_yCu_4$ with $y = 0$, 0.3, 0.7, and 1.0, are reported. The thermal conductivity is separated into the phonon thermal conductivity (κ_{ph}) (i.e., related to the heat carried by phonons) and into the electronic thermal conductivity (κ_e) (related to the heat carried by electrons). The electrical resistivity of the compounds was measured to determine the temperature dependence of the Lorenz

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number. The results show that in the temperature interval 4.2 to 300 K the latter quantity behavior follows the theoretical predictions for heavy fermion materials.

KEY WORDS: electrical resistivity; heavy fermion compounds; Lorenz number; phase transition; thermal conductivity.

1. INTRODUCTION

Ytterbium compounds display a number of interesting properties being a corollary of the hybridization of the 4f localized electrons with the electrons of the conduction band. Good examples of such compounds are cubic $YbMCu_4$ of the structure AuB_5, where M = In, Ag, Cd, Mg, Tl, Zn, or Pb [1, 2]. Depending on the strength of the hybridization, the Yb ion in these compounds may adopt electronic configurations between trivalent $4f^{13}$ (Yb^{3+}) and divalent $4f^{14}$ (Yb^{2+}). Consider, for instance, the $YbMCu_4$ compound with In. Under atmospheric pressure it undergoes an isostructural phase transition at T_v = approx. 40 K. This transition is interrelated with a magnetic one, in which the compound transforms from one kind of a paramagnet to another. In the high-temperature phase ($T > T_v$) the number of the conduction electrons and their density of states is very low and, therefore, the $YbInCu_4$ is a Curie–Weiss paramagnet of localized magnetic moments; in the low temperature phase ($T < T_v$) the Yb ions are in the mixed valence state, the number of the conduction electrons and their density of states at the Fermi level increase considerably and thus the paramagnetism in the compound originates first of all from the conduction electrons. It is argued that the conduction electrons in the low temperature region are in a nonmagnetic state of a Fermi liquid, which is sometimes called the light heavy-fermion system [3–6]. As concerns the valence change at the phase transition, it is generally agreed that above T_v the Yb valence is 3 and it is 2.9 below T_v, although the L_3 x-ray absorption spectra [7, 8] and the x-ray K-line shifts [9] suggest that the Yb valence is 2.9 for $T > T_v$ and it is approximately 2.8 for $T < T_v$. Summarizing, we can say that in the high-temperature phase $YbInCu_4$ is a semimetal with a low hybridization and in the low-temperature phase it is a metal with features characteristic for heavy fermion and mixed-valence rare earth systems.

The second compound of the stoichiometric composition that we examine is $YbAgCu_4$. It represents a heavy-fermion system, which undergoes the transition from the high-temperature single-impurity regime ($T > T_K$; T_K is the Kondo temperature) to the coherent Kondo regime at low temperatures ($T < T_K$). The value of T_K estimated by using various physical effects is between 40 and 130 K [10, 11]. The properties of

$YbIn_{1-y}Ag_yCu_4$ vary in a continuous way between those characteristic of $YbInCu_4$ and those of $YbAgCu_4$ with changes in the value of y provided that y is neither too small nor too large. Thus, for y with values between 0.2 and 0.25 up to 0.5 the continuous phase transition between the Pauli paramagnet and the nonmagnetic Fermi liquid is possible to occur at a temperature T_v. The transition is accompanied by the change in the Yb ion valence from 2.80 below T_v to 2.91 above T_v [8, 12–16]. As concerns the magnetic state of the system, the Pauli paramagnetism of the conduction electrons prevails below T_v, whereas above T_v, it is the Curie–Weiss paramagnetism of the localized Yb ions.

$YbIn_{1-y}Ag_yCu_4$ with $y > 0.5$ has properties the same as the heavy-fermion compound $YbAgCu_4$ regardless of the value of T. Thermal conductivity measurements of $YbInCu_4$ and $YbAgCu_4$ have been reported in Refs. 17 and 18. According to our knowledge no such measurements have been made on either $YbIn_{1-y}Ag_yCu_4$ or $YbIn_{1-x}Cu_{4+x}$. Therefore, we have decided to choose $y = 0.3$ for the case of $YbIn_{1-y}Ag_yCu_4$ and $0.015 < x < 0.095$ for the case of $YbIn_{1-x}Cu_{4+x}$ to undertake measurements of the thermal conductivity.

Thus, the purposes of the present paper are the following:

– to prepare a set of samples within the homogeneity range, including the stoichiometric composition corresponding to $T_v = 40$ K;

– to measure $\kappa_{ph}(T)$ and $L(T)$ within the homogeneity range of $YbIn_{1-x}Cu_{4+x}$ and to study the variation of κ_{ph} as a function of x and the behavior $\kappa_{ph}(T)$ for $T > T_v$ and $L(T)$ for $T < T_v$ in the stoichiometric sample.

2. MEASUREMENTS

2.1. Specimens

It is known [5, 6] that the chemical composition of the obtained crystals may depend on the method of their preparation. Cast polycrystalline samples for the purposes of our measurements were produced from the melt with the original Cu concentration only slightly below the stoichiometry by using the directional vertical-Bridgman crystallization method. The melt started to solidify, forming the crystal which had the phase transition temperature T_v = approx. 70 K. The material that crystallized in later stages had T_v near 40 K. The material was melted in tantalum crucibles sealed in argon atmosphere [6]. $YbIn_{1-y}Ag_yCu_4$ was sintered from $YbInCu_4$ and $YbAgCu_4$ obtained from stoichiometric mixtures of pure metals [9]. The sample was analyzed on a DRONE-2 x-ray diffractometer with CuK_α

radiation. It was found to be of single phase and to have the $AuBe_5$ structure with the lattice constant 7.159 at 300 K. The samples were in the shape of parallelepipeds with dimensions of about 4 mm × 2 mm × 8 mm.

2.2. Measurement Procedure

The thermal conductivity was measured from 4.2 to 300 K by using the axial stationary heat flow method. The absolute temperature of the samples, as well as the temperature gradient along the sample, were determined with a manganin-constantan thermocouple. The average error of the total conductivity coefficient, κ_{tot}, was less than $\pm 2\%$ and the spurious error, estimated from the data scatter, did not exceed $\pm 0.3\%$. The experimental setup and the measurement procedure are described in detail in Ref. 19. The electrical resistivity of the samples was measured potentiometrically using the dc four–terminal method to within an uncertainty of $\pm 3\%$ [17, 18].

3. RESULTS

To illustrate the results of our measurements of the temperature dependences of κ_{tot} and ρ, we show in Fig. 1 representative results for samples 1 and 4. The measurements for these samples were made with the temperature decreasing from 300 to 4.2 K. We note that $\kappa_{tot}(T)$ of sample 4 was found to coincide well with that of the stoichiometric $YbInCu_4$ sample with $T_v \sim 40$ K which was reported in Ref. 16. We estimated the values of T_v for all five samples. For this purpose we first applied the diagram illustrating the dependence $T_v(x)$ in Ref. 20 for $YbIn_{1-x}Cu_{4+x}$ to find the values of x and thus the approximate comparison of the samples (Table I), and then we estimated T_v based also on the temperature dependence of the lattice constant, $a(T)$, the electrical resistivity, $\rho(T)$, and the total thermal conductivity, $\kappa_{tot}(T)$. The value of T_v for sample 4, being close in composition to the stoichiometric sample, was found to correspond well to that reported in Ref. 16 for $YbInCu_4$, being equal to approximately 40 K.

According to the data available in the literature, all the compositions of $YbIn_{1-x}Cu_{4+x}$ in its homogeneity range below and above T_v are metals and semimetals. Therefore, the measured coefficient of the thermal conductivity can be considered in the first approximation as the sum,

$$\kappa_{tot} = \kappa_e + \kappa_{ph}, \tag{1}$$

of the electronic and phonon components, meant as the sum of the components arising from the heat carried by the conduction electrons and

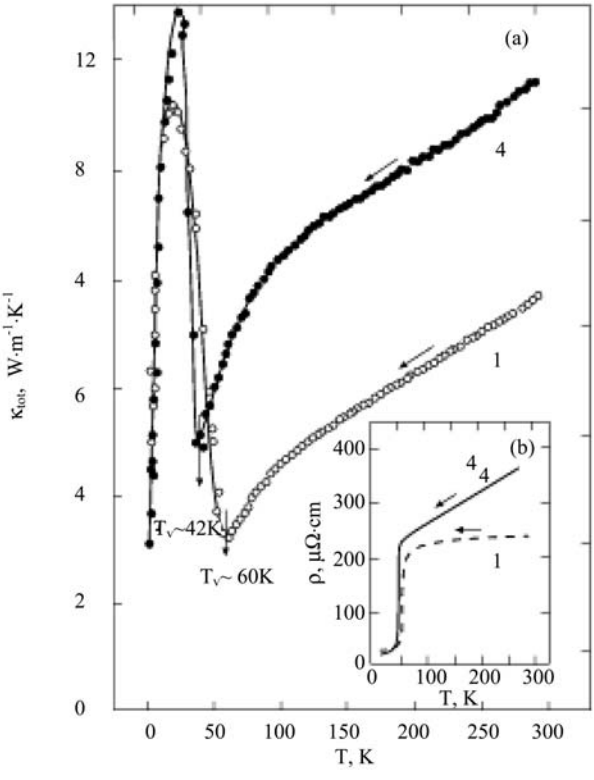

Fig. 1. Temperature dependence of (a) κ_{tot} and (b) ρ for samples 1 and 4.

Table I. Values of T_v Derived from Measurements of $a(T)$, $\rho(T)$, and κ_{tot} (T) on Samples 1 to 5, and Corresponding Values of x for the $YbIn_{1-x}Cu_{4+x}$ System Obtained from $T_v(x)$ Relation Obtained in Ref. 20.

Specimen number	T_v-transition temperature, obtained from measurements $a(T)$ (K)	$\rho(T)$ (K)	$\kappa_{tot}(T)$ (K)	Average value of T_v (K)	x	Sample composition
1	60	60	60	60	0.095	$YbIn_{0.905}Cu_{4.095}$
2	55	–	–	55	0.060	$YbIn_{0.94}Cu_{4.06}$
3	–	48	–	48	0.038	$YbIn_{0.962}Cu_{4.038}$
4	–	44	42	43	0.015	$YbIn_{0.985}Cu_{4.015}$
5	40	–	–	40	0	$YbInCu_4$

phonons, respectively. In the first approximation κ_e can be calculated using the Wiedemann–Franz law,

$$\kappa_e = LT/\rho \tag{2}$$

Since the studied samples are rather dirty metals and semimetals for which elastic impurity scattering contributes considerably, our assumption $L = L_0$ ($L_0 = 2.45 \times 10^{-8}\ \mathrm{W \cdot \Omega \cdot K^{-2}}$ is the Sommerfeld value of the Lorenz number) can hardly be questioned for $T > T_v$ [21]. Within this temperature region, the dependences $\kappa_{ph}(T)$ calculated from Eqs. (1) and (2) for samples 1 and 4 with $L = L_0$, as well as the ones for the $YbIn_{0.83}Cu_{4.17}$ samples 1P and 2F [22], can be represented by the power law $\kappa_{ph} \sim T^n$, where $n \sim 0.3$ to 0.38. These are the values close to those found for samples 1P and 2F [22] (Fig. 2), and all yield, of course, increasing functions of T. The

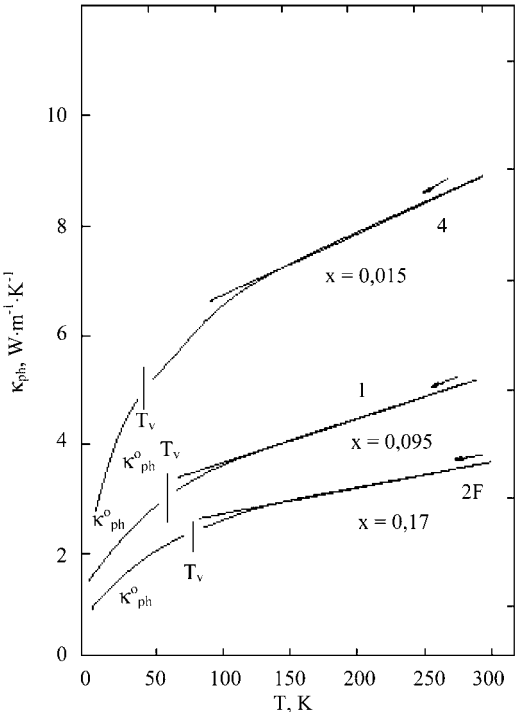

Fig. 2. Dependence of κ_{ph} on temperature for samples 1, 4, and 2F [22] of the $YbIn_{1-x}Cu_{4+x}$ system. See the text and Ref. 22 for the explanation of κ^0_{ph}.

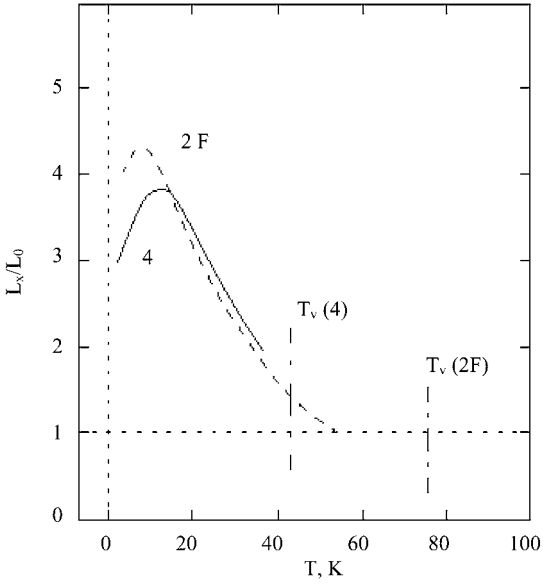

Fig. 3. Temperature dependence of L_x/L_0 for samples 4 ($YbIn_{0.985}Cu_{4.015}$) and 2F ($YbIn_{0.83}Cu_{4.17}$).

behavior of $\kappa_{ph}(T)$ at high temperatures for sample 4 ($T_v \sim 43$ K), being close to the stoichiometric one, is exactly like that for $YbIn_{0.83}Cu_{4.17}$. The dependence $\kappa_{ph}(T)$ estimated earlier in this way for $YbInCu_4$ can be found in Ref. 22 (Fig. 3).

When analyzing the data of $YbIn_{0.7}Ag_{0.3}Cu_4$ in the present paper (Fig. 6), we also find similar dependence, in which for $T < T_v$ there is a high maximum, being apparently an artifact of the applied approximation. According to our knowledge, there is no experimental evidence for such abnormal behavior. Therefore, in Ref. 22 and in the consideration of the present paper, too, a better approximation for $T < T_v$ was applied. Namely, the temperature dependence κ_{ph} below T_v was approximated by the power law T^n. We denote it as κ^0_{ph} in Fig. 2. The exponent n was chosen in such a way to fit well to the dependence $\kappa_{ph}(T)$ above T_v (see Fig. 4 of Ref. 22), and it probably depends on the amount of the impurities in a sample. It should be mentioned here that the value of n appeared to depend on the method of the sample preparation; one of the samples of $YbInCu_4$, which was analyzed in Ref. 22, was prepared in Saint Petersburg, the second in Frankfurt am Mainz. The same concerns the samples of different composition, which we consider in the present paper. In Fig. 2 we show how

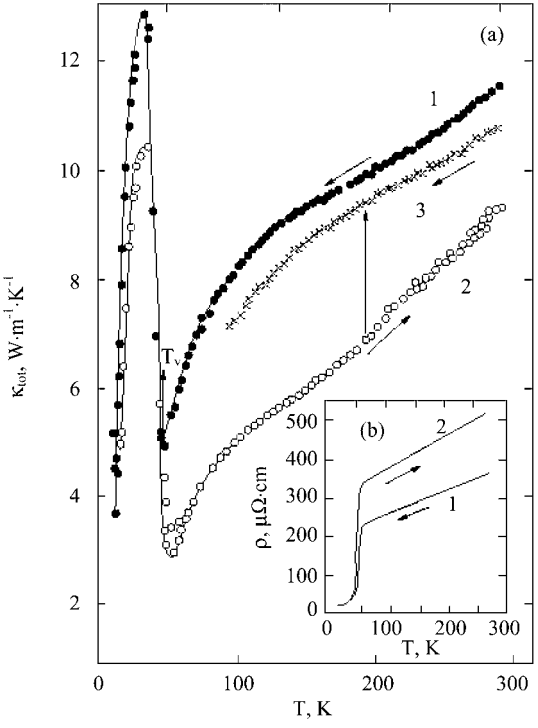

Fig. 4. Temperature dependence of (a) κ_{tot} and (b) ρ for sample 4; (a) (1) direct run (300 to 4.2 K), (2) reverse run (4.2 to 300 K), and (3) direct run (300 to 80 K), measurement after the sample was stored for 30 days at room temperature (after having been measured in cycle 2); and (b) (1) direct run (300 to 4.2 K), measurement on the sample corresponding to curve 3 in Fig. 4a and (2) reverse run (4.2 to 300 K), measurement on the sample corresponding to curve 2 in Fig. 4a. (Part of the $\rho(T)$ data obtained on sample 4 are omitted).

$\kappa_{ph}(T)$ for $YbIn_{1-x}Cu_{4+x}$ is extrapolated to temperatures below T_v for different values of x. The physical origin of different values of x for different samples is less important as the fact that any value of x less then unity found or simply assumed in such considerations leads to the temperature-dependent Wiedemann–Franz ratio, $L_x(T)$, which below T_v is greater than the Sommerfeld value of the Lorenz number $L_x(T)/L_0 > 1$ and, moreover, exhibits the maximum. In Fig. 3 we show the dependences of $L_x(T)/L_0$ obtained in this way for samples 4 and 2F presented in Ref. 22. It means

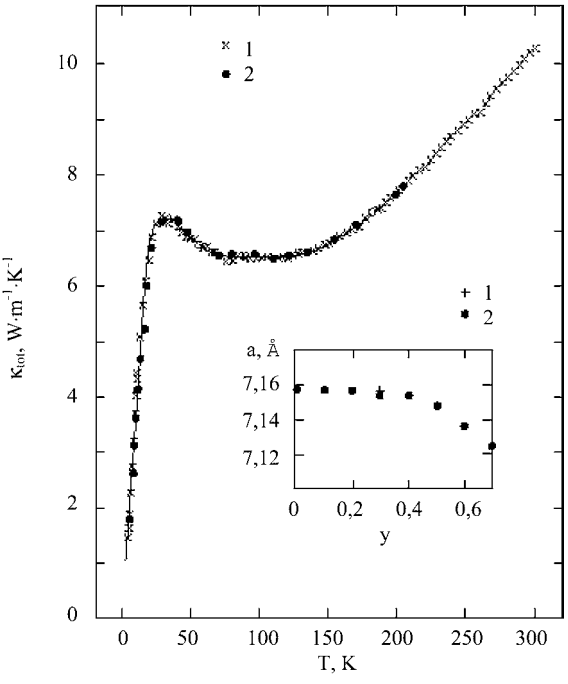

Fig. 5. Temperature dependence of κ_{tot} for an $YbIn_{0.7}Ag_{0.3}Cu_4$ sample; (1) measurements from 300 to 4.2 K and (2) reverse run (4.2 to 200 K). The inset shows the dependence of the lattice constant of $YbIn_{0.7}Ag_{0.3}Cu_4$ on y; (1) our data and (2) data from Ref. 13.

we assume $\kappa_e = L_x T/\rho = \kappa_{tot} - \kappa_{ph}^0$ and calculate $L_x(T)/L_0 = \kappa_e \rho / TL_0$. This is the dependence characteristic for heavy-fermion materials.

Our earlier measurements of the temperature dependence of the electrical resistivity in $YbInCu_4$ revealed an interesting phenomenon [17]. Namely, in the course of thermal cycling made through T_v, ρ was found to decrease both above and below T_v. We interpret [22] this phenomenon as an effect of the generation of a stress in the lattice, which is caused by the change of Yb valence from 3 to 2.9. The thermal conductivity is sensitive to the formation of various defects in a material [23]. Therefore, we also studied how the defects formed during the cycling in $YbIn_{1-x}Cu_{4+x}$ influence the thermal conductivity. Most of the measurements were made on sample 4 (Fig. 4). The total thermal conductivity, κ_{tot}, was found to decrease substantially (curve 2, Fig. 4a) after thermal cycling. The defects that had formed in the sample after thermal cycling disappeared almost

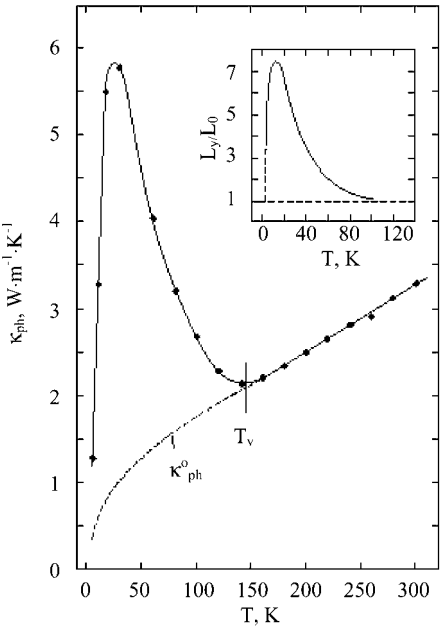

Fig. 6. Temperature dependence of κ_{ph} for $YbIn_{0.7}Ag_{0.3}Cu_4$. The solid curve is the calculation of κ_{ph} using Eqs. (1) and (2) with $L = L_0$. The points were obtained through calculations from the averaged values of κ_{tot} and ρ. The dashed line plots the lattice thermal conductivity obtained by extrapolation of the experimental data for κ_{ph} from the high-temperature region. The inset is the temperature dependence of L_y/L_0 for our $YbIn_{0.7}Ag_{0.3}Cu_4$ sample.

completely after the soft anneal, i.e., after the sample was kept at room temperature for a month (curve 3, Fig. 4a). Although it would be possible and perhaps also interesting to estimate the influence of the defects created during the cycling on the phonon part of the conductivity, $\kappa_{ph}(T)$, the analysis of the behavior of this quantity can hardly help to determine the nature of defects. It is possible that the phase transition at T_v, which changes the valence state of Yb, also generates the stress in the lattice [24]. One cannot also exclude the possibility that thermal cycling induces small displacements of Cu from their equilibrium positions. Besides the compounds with indium, we also investigated ones with indium and silver. One of them was a cast polycrystalline sample of $YbIn_{0.7}Ag_{0.3}Cu_4$ for which we measured the thermal conductivity and the electrical resistivity in the

temperature range 4.2 to 300 K. Figure 5 presents the experimental data for the thermal conductivity denoted as in previous cases as κ_{tot}. Figure 6 shows the plots resulting from the latter figure under the assumption of Eqs. (1) and (2) with $L = L_0$. When one uses the procedure described above while discussing Fig. 3, the Wiedemann–Franz ratio behaves as shown in the inset. The dashed line below T_v in this figure shows the assumed extrapolation described by the power law $\kappa_{ph} \sim T^n$ with $n = 0.6$, the value following from the straight-line extrapolation in the semilogarithmic plot (see, Fig. 4 of Ref. 22). Thus, also for this compound, the estimated behavior of the Wiedemann–Franz ratio indicates that this compound is also a heavy-fermion system.

4. CONCLUSIONS

In the paper we present the results of our investigations on the thermal conductivity, electrical conductivity, and the Wiedemann–Franz ratio of $YbIn_{1-x}Cu_{4+x}$ and $YbIn_{1-y}Ag_yCu_4$ in the temperature range 4.2 to 300 K. Our analysis of the measured quantities (thermal conductivity, electrical resistivity) indicates that the Wiedemann–Franz ratio (temperature-dependent Lorenz number) behaves in the region of low temperatures in a way typical for a heavy-fermion system. We also analyze the nature of the defects in $YbIn_{1-x}Cu_{4+x}$. They are probably formed by thermal cycling (lowering and raising the temperature) during the process of measuring the thermal conductivity. The electrical conductivity $\sigma = 1/\rho$ decreases to a greater extent than the phonon thermal conductivity, κ_{ph}, meant as that following from the heat carried by phonons. A prolonged soft annealing of the samples at room temperature suppresses this effect in $\rho(T)$, $\kappa_{tot}(T)$, and $\kappa_{ph}(T)$. The $YbIn_{0.7}Ag_{0.3}Cu_4$ composition transfers to a state corresponding to a light heavy-fermion system. The Lorenz number behaves in accordance with the above theoretical pattern for the Lorenz number behavior in a heavy-fermion system.

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