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Semimetallic behaviour of $YInCu_4$ and $LuInCu_4$

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Abstract. The electrical resistivity, the Hall coefficient, the transverse magnetoresistance and the thermal expansion have been measured for polycrystalline $YInCu_4$ and $LuInCu_4$ which form the cubic C15b crystal structure. The electrical resistivity of $YInCu_4$ shows an anomalous temperature dependence; it increases with increasing temperature, reaches a maximum at 270 K and decreases gradually at higher temperatures, while that of $LuInCu_4$ behaves as a normal metallic conductor. An analysis of experimental results indicates that both substances are semimetals with a small number of carriers, and that the number of carriers in the ground state plays a crucial role in the entire transport properties. The broad peak and the negative temperature dependence in the resistivity curve of $YInCu_4$ are explained as due to the increase in the number of excited carriers with increasing temperature. The possibility of mass enhancement associated with the strong electron–phonon coupling is discussed for $YInCu_4$.

1. Introduction

The intermetallic compounds $RTCu_4$, where R is a rare earth and T is a transition metal, have been investigated from various (especially magnetic) viewpoints. Their magnetic properties depend markedly not only on the R element but also on the T element. Some of them crystallize into the cubic C15b structure, in which R and T atoms are located at the face-centred positions and are in the zincblende-type arrangement. The C15b structure ($MgCu_4Sn$ type) is shown in figure 1. Compounds with the C15b structure have attracted considerable attention from a magnetic viewpoint because of the high crystallographic symmetry of the magnetic sublattice. Of them, the $RInCu_4$ system was recently found to show characteristic magnetic properties [1–15]. In particular, $YbInCu_4$ was studied in detail in connection with the Yb valence instability [1–13]. It shows a first-order phase transition of Yb valence at $T_v \simeq 40$ K from the local moment state at higher temperatures to the non-magnetic Fermi liquid state at lower temperatures. Since this is the only material that shows such a transition in the temperature, it has been extensively studied by many workers. However, in spite of numerous efforts, the origin of the first-order valence transition has not been completely elucidated. We studied $GdInCu_4$ in order to investigate the competition of an antiferromagnetic interaction in a high-symmetry lattice and found several anomalous properties [15, 16]. The Néel temperature, 6.9 K, is the lowest of the conducting materials containing gadolinium in spite of its relatively large antiferromagnetic interaction expected from the negatively large paramagnetic Curie temperature, −45 K. Furthermore, an unexpected temperature dependence of the electrical resistivity was found; it has a broad peak at around 80 K and shows a negative temperature dependence at higher temperatures.

In the study of $RInCu_4$, it was revealed that the system is in a delicate position from the viewpoint of the electric conduction. Therefore, it is very important to study the transport

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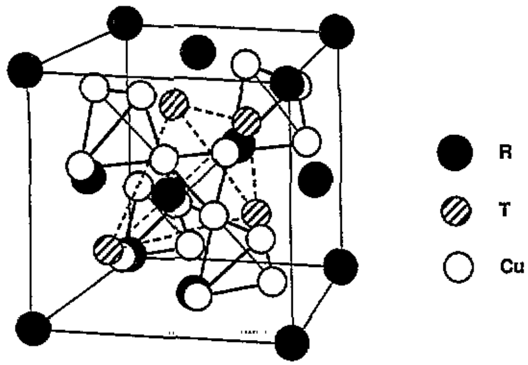

Figure 1. Crystal structure of $RTCu_4$ of the C15b type.

properties of non-magnetic materials. Thus, we started the study of $YInCu_4$ and $LuInCu_4$ and found that they show very interesting transport properties [17]. In particular, the electrical resistivity of $YInCu_4$ is anomalous similar to $GdInCu_4$; it shows a broad peak at 270 K and a negative temperature dependence at higher temperatures [15, 16]. In this paper, we shall report the results of the electrical resistivity, the Hall coefficient, the transverse magnetoresistance and the thermal expansion for $YInCu_4$ and $LuInCu_4$. The experimental results indicate that both $YInCu_4$ and $LuInCu_4$ belong to semimetals with a small number of carriers. The possibility of mass enhancement of carriers in $YInCu_4$ will be discussed in connection with the strong electron–phonon coupling of the system.

2. Experimental procedures

The samples were prepared in an arc furnace under an argon atmosphere. The purities of the parent metals Y, Lu, In and Cu were 99.9%, 99.9%, 99.99% and 99.999%, respectively. In melting, the samples were turned upside down and remelted several times to improve homogeneity. After the melting, each sample was wrapped in a tantalum foil and annealed in an evacuated silica tube for 1 week at 750 °C. After the anneal, powder x-ray diffraction measurements were carried out at room temperature in order to identify the crystal structure and to estimate the lattice parameter. The Bragg reflections indexed to (200) and (420), which do not exist for the C15-type cubic Laves phase and are evidence of the C15b structure, were observed in the x-ray powder diffraction patterns. No phase other than the C15b phase was observed in the patterns.

The electrical resistivity was measured using a four-probe method between 2.8 and 800 K. The temperature dependence of the Hall coefficient was measured in a field of 15 kOe with an electric current of 70 mA between 4.2 and 300 K. A five-probe method was used to adjust to zero voltage in zero field. The magnetoresistance was measured in fields up to 16 kOe between 4.2 and 300 K. The thermal expansion was measured from 4.2 to 300 K with a conventional differential-transformer-type dilatometer.

3. Experimental results

3.1. Lattice parameter

The lattice parameter of $YInCu_4$ at room temperature is 7.201 Å which is larger than that of $LuInCu_4$, 7.193 Å by 0.1%.

3.2. Electrical resistivity

The temperature dependences of the electrical resistivity for $YInCu_4$ and $LuInCu_4$ are shown in figures 2 and 3, respectively. The resistivity of $YInCu_4$ decreases rapidly below 6 K. This may indicate the transition to superconductivity, but no anomaly was observed in the temperature dependence of the specific heat [17]. Therefore, it may be ascribed to a small amount of indium-rich impurity phases such as indium alloys although T_c for pure indium is much lower at 3.4 K. The anomaly at low temperatures will not be discussed here. The most interesting characteristic of $YInCu_4$ is that the resistivity exhibits a broad maximum around 270 K and decreases monotonically above the temperature. A similar temperature dependence has already been observed for $GdInCu_4$, for which the temperature of the maximum is 80 K [15, 16]. On the other hand, the resistivity of $LuInCu_4$ increases monotonically with increasing temperature like a normal metallic conductor. It is very interesting that these two compounds, which are expected to have similar electronic structures, show considerably different temperature dependences. The residual resistivity of $YInCu_4$ is larger than that of $LuInCu_4$ by a factor of 5. It seems that both compounds show a quadratic temperature dependence below about 60 K.

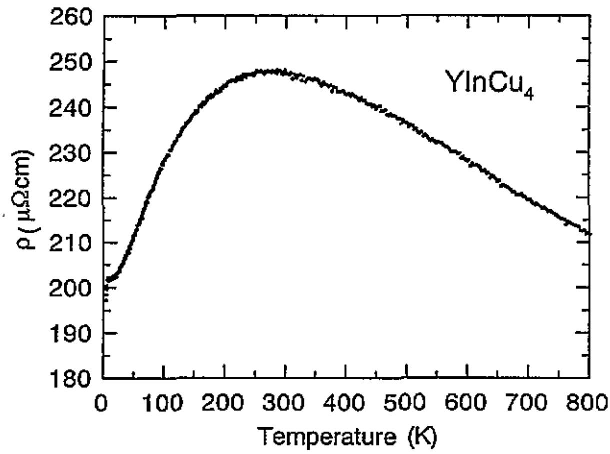

Figure 2. Temperature dependence of the electrical resistivity of $YInCu_4$.

3.3. Hall coefficient

The temperature dependence of the Hall coefficient R_H of $YInCu_4$ and $LuInCu_4$ are shown in figure 4. Both compounds show (positive) large values in the entire temperature range, indicating that these substances are low-carrier systems. The values for $YInCu_4$ are twice to three times those for $LuInCu_4$. This suggests that the number of carriers is smaller for $YInCu_4$ than for $LuInCu_4$. The carrier concentrations assuming a single carrier are of the order of 10^{20} cm^{-3} and 10^{21} cm^{-3} for $YInCu_4$ and $LuInCu_4$, respectively. The Hall coefficient decreases gradually with increasing temperature, suggesting a gradual increase in the carrier concentration.

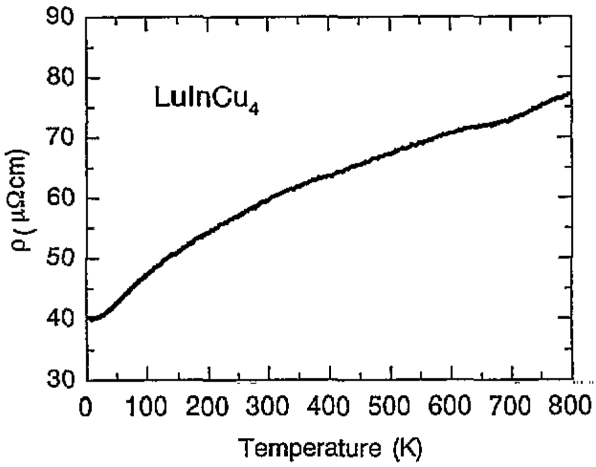

Figure 3. Temperature dependence of the electrical resistivity of $LuInCu_4$.

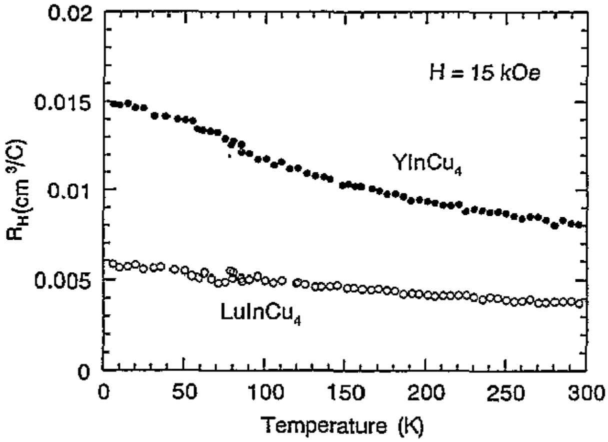

Figure 4. Temperature dependences of the Hall coefficients for $YInCu_4$ and $LuInCu_4$.

3.4. Magnetoresistance

If the current is carried by both electrons and holes, the magnetoresistance will be correspondingly large. We measured the low-field transverse magnetoresistance for $YInCu_4$ and $LuInCu_4$. The magnetoresistance was substantially proportional to H^2 at all temperatures within the experimental uncertainty. The temperature dependences of the magnetoresistance measured under a field of 16 kOe are shown in figure 5. The magnetoresistances of both substances decrease monotonically with increasing temperature. The values for $LuInCu_4$ are much smaller than those for $YInCu_4$.

3.5. Thermal expansion

To discuss the effect of the unit-cell volume on the transport properties, we measured thermal expansion curves for $YInCu_4$ and $LuInCu_4$, which are shown in figure 6 by small

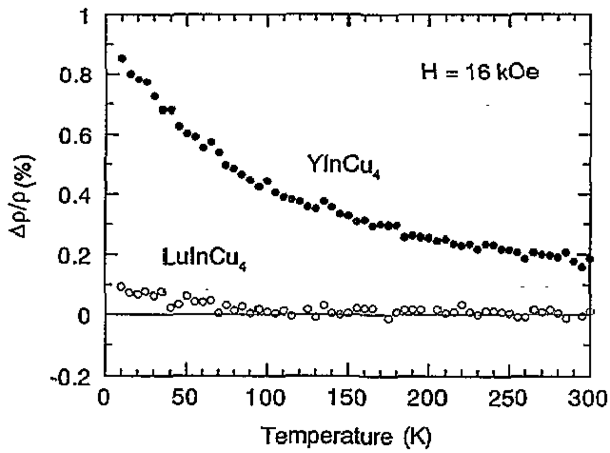

Figure 5. Temperature dependences of the magnetoresistance measured under a field of 16 kOe for $YInCu_4$ and $LuInCu_4$.

full circles. We obtained almost the same curves for both materials. The thermal expansion coefficient estimated from a linear part above 150 K is 1.47×10^{-5} K^{-1}, which is a normal value for metallic materials.

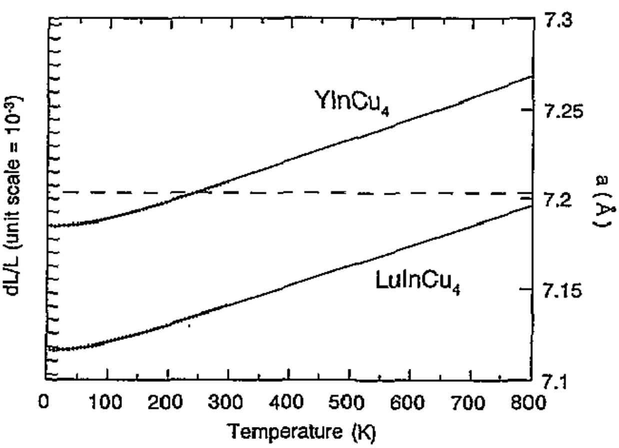

Figure 6. Thermal expansion curves (●) and the temperature dependences of the calculated lattice parameter (——) for $YInCu_4$ and $LuInCu_4$: – – –, the lattice parameter at which the resistivity reaches a maximum.

4. Discussion

4.1. Semimetallic behaviour

The Hall coefficient indicates that the carrier concentration of $LuInCu_4$ is much smaller than that of normal metals although the electrical resistivity behaves as a metallic conductor.

However, the nuclear spin–lattice relaxation time T_1 of $LuInCu_4$ obeys the Korringa law, i.e. T_1T = constant, between 4.2 and 300 K [18]. This indicates a finite density of states at the Fermi level. Therefore, it is reasonable to recognize $LuInCu_4$ as a semimetal with a small number of carriers in accordance with the theoretical prediction that $LuInCu_4$ can be classified as a compensated semimetal [12]. Other experimental results such as the large residual resistivity, the diamagnetic susceptibility [19] and the small nuclear spin–lattice relaxation rate [18] are also consistent with this interpretation.

On the other hand, a broad peak and a negative temperature dependence were observed in the resistivity curve of $YInCu_4$. This is markedly different from $LuInCu_4$ in spite of the fact that the electronic structures are expected to be similar to each other. To determine the scattering process of carriers, we introduce the Hall mobility μ_H which is defined as

$$\mu_H = \frac{R_H}{\rho} \tag{1}$$

where ρ is the resistivity and R_H the Hall coefficient. This is shown as a function of temperature in figure 7 for both $YInCu_4$ and $LuInCu_4$. It should be noted that the temperature dependences are similar to each other, i.e. a monotonic decrease with increasing temperature, except for the difference in absolute values by a factor of 2. This suggests that the scattering mechanisms of the carriers are the same, and that the resistivity curve of $YInCu_4$ should also be explained within the framework of a semimetal as for $LuInCu_4$. Therefore, the semiconductor-like behaviour of $YInCu_4$ at high temperatures would be ascribed to the increase in the carrier concentration.

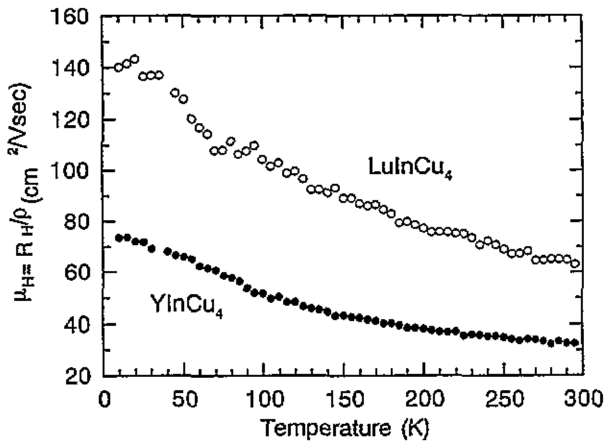

Figure 7. Temperature dependences of the Hall mobility for $YInCu_4$ and $LuInCu_4$.

According to the band calculation for $LuInCu_4$ [12], the simplified band structure near the Fermi level is schematically shown in figure 8. The Fermi surface of $LuInCu_4$ consists of very small hole and electron pockets with $\epsilon_F^h = 0.192$ eV and $\epsilon_F^e = 0.592$ eV around the W and X symmetry points, respectively. In addition to these bands, other energy levels exist just below the Fermi level, which may behave as electron donors at high temperatures. The band structure of $YInCu_4$ is expected to be similar, but an analysis of the Hall coefficient indicates that the carrier concentration is much smaller than that of $LuInCu_4$. The difference between $YInCu_4$ and $LuInCu_4$ may be explained by assuming that, with increasing unit-cell volume, the band overlap decreases and, as a result, the Fermi energies ϵ_F^h and ϵ_F^e decrease and the ground-state carrier number becomes extremely small. Therefore, at high temperatures, namely $k_B T \geqslant \epsilon_F$, the conductivity is dominated by thermally excited carriers, giving rise to a semiconductor-like dependence. In addition, when $k_B T$ becomes comparable with ϵ_g (see figure 8), indirect excitations are expected to occur from the lower bands, and additional carriers may contribute to the transport properties. This is the case for $YInCu_4$. On the other hand, the much larger band overlap and the Fermi energy greater than $k_B T$ of the present experiments need fully degenerate statistics, which cause the metallic behaviour of $LuInCu_4$.

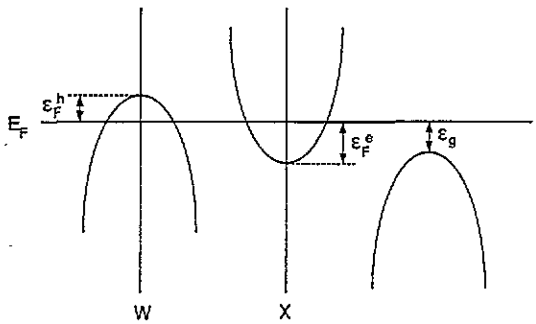

Figure 8. The simplified band structure near the Fermi level for $LuInCu_4$.

An intimate correlation between the resistivity and the unit-cell volume was confirmed in the study of the pseudo-ternary (Gd–Lu)$InCu_4$ system [16]. In this system, the temperature when the resistivity reaches a maximum shifts to a higher temperature with increasing Lu concentration, i.e. with decreasing unit-cell volume. A study of $(Gd_{1-x}Lu_x)InCu_4$ compounds with various x revealed that the resistivity attains a maximum at the temperature where the lattice parameter becomes about 7.205 Å for all the compounds. The lattice parameter up to 800 K, which is shown in figure 6 by solid lines, was calculated with the lattice parameter at room temperature and the thermal expansion curves assuming a constant thermal expansion coefficient above 200 K. The lattice parameter of $YInCu_4$ attains the critical value, 7.205 Å (the broken line in the figure), at about 270 K, which is just the temperature of the resistivity maximum. The lattice parameter of $LuInCu_4$ is smaller than 7.205 Å in the entire temperature range of measurement. This is consistent with no maximum in the resistivity curve.

4.2. *Possibility of mass enhancement*

A quadratic temperature dependence of the resistivity was suggested for both $YInCu_4$ and $LuInCu_4$. Generally, the magnitude of the coefficient A of the T^2-term is discussed within the same context as the mass enhancement of carriers. Tentatively estimated values of A are 3.9×10^{-3} $\mu\Omega$ and 1.1×10^{-3} $\mu\Omega$ cm K^2 for $YInCu_4$ and $LuInCu_4$, respectively, which are comparable with those of high-T_c A15 superconductors [20–23], in which the strong electron–phonon coupling was claimed to be responsible for the large A- and γ-values, where γ is the electronic specific heat coefficient [24]. It was suggested that the electron–phonon coupling may be large in the C15b compound [25]. On the other hand, on the assumption of a compensated semimetal, the resistivity is formally written, by introducing the effective scattering rate τ^{-1} of carriers,

$$\rho = \frac{\tau^{-1}}{ne(m_e^{-1} + m_h^{-1})} \tag{2}$$

where m_e and m_h are the effective masses of electrons and holes, respectively. If τ^{-1} has a T^2-dependence, regardless of the mechanism, a small concentration and/or large effective masses of carriers also give rise to a large value of A. For a typical semimetal bismuth, large values, $A = 8 \times 10^{-3}$ $\mu\Omega$ cm K^2 [26] and $(1.4\text{–}1.5)\times 10^{-2}$ $\mu\Omega$ cm K^2 [27] were reported. The large A-values of $YInCu_4$ and $LuInCu_4$ may be interpreted by this context. No matter what the scattering mechanism, one needs a precise argument about both the concentration and the masses of the carriers in order to discuss the origin of the T^2-dependence and the magnitude of the coefficient A.

In order to discuss the mass enhancement, we need knowledge of the carrier concentration. For $YInCu_4$ and $LuInCu_4$, the large magnetoresistance as well as the band calculation of $LuInCu_4$ [12] suggest that the assumption of the single carrier is irrelevant. Therefore, we attempt to make a crude estimation of the number of carriers assuming a two-carrier system with equal numbers of electrons and holes. For compensated semimetals, the conductivity σ, the Hall coefficient R_H and the magnetoresistance $\Delta\rho/\rho$ are given by

$$\begin{aligned} \sigma &= ne(\mu_e + \mu_h) \\ R_H &= \frac{1}{ne}\frac{\mu_e - \mu_h}{\mu_e + \mu_h} \\ \frac{\Delta\rho}{\rho} &= \mu_e\mu_h H^2 \end{aligned} \tag{3}$$

where μ_e and μ_h are electron and hole mobilities, n is the number of electrons or holes, e is the electron charge and H is the applied field [28]. Although the last equation is obtained in the high-field limit, we use this as the first approximation. Using these equations, we calculated the temperature dependence of μ_e, μ_h and n for both $YInCu_4$ and $LuInCu_4$. The mobilities are of the order of 100 cm^2 V^{-1} s^{-1} for both compounds, which are smaller than those of conventional semimetals [29]. The number n of carriers is of the order of 10^{19} cm^{-3} and 10^{20} cm^{-3} for $YInCu_4$ and $LuInCu_4$, respectively. These values are roughly comparable with the carrier concentrations of typical semimetals, antimony [30] and arsenic [31], respectively. The numbers of carriers per formula unit at 10 K are listed in table 1. On the assumption of the same scattering ratios for electrons and holes, the ratio m_e/m_h of effective masses is estimated from μ_e/μ_h to be about 1.1 and 2 for $YInCu_4$ and $LuInCu_4$, respectively.

Table 1. Numbers of electrons or holes at 10 K and experimental and calculated electronic specific heat coefficients.

	n at 10 K (formula unit)$^{-1}$	γ_{exp} (mJ mol^{-1} K^{-2})	γ_{calc} (mJ mol^{-1} K^{-2})	γ_{band} (mJ mol^{-1} K^{-2})	$\gamma_{exp}/\gamma_{calc}$
$YInCu_4$	0.0024	3–4 [16]	0.53	—	~ 7
$LuInCu_4$	0.03	0.8 [3]	1.17	1.77 [12]	0.7
		3 [32]			2.6

Next, we try to estimate the mass enhancement of carriers. The electronic specific heat coefficient for the free electron is given by $\gamma_0 = \pi^2 N k_B / 2E_F$ where N is the number of electrons. The Fermi energy E_F depends only on the carrier density n as $E_F = (\hbar^2/2m_0)(3\pi^2 n)^{2/3}$, where m_0 is the mass of the free electron. Because of the existence of two Fermi surfaces, the calculated γ-values for $YInCu_4$ and $LuInCu_4$, should be multiplied by a factor of 2: $\gamma_{calc} = 2\gamma_0$. The results are listed in table 1 together with experimental values [3, 17, 32]. For $LuInCu_4$, $D(E_F)$ estimated by the band calculation leads to $\gamma_{band} = 1.77$ mJ mol^{-1} K^{-2} [12], which is about twice our estimated value. This is not surprising because the actual band structure near the Fermi level is far from a free-electron type but the small Fermi surface may have specific curvature. For $LuInCu_4$, two experiments were reported [3, 32]. An earlier result gives a very close value to our calculation, although it may involve large ambiguity because it was measured for a non-stoichiometric sample. Nevertheless, the difference between the experiment and the calculations is not so large. On the other hand, the experimental value for $YInCu_4$ is as large as that for $LuInCu_4$ in spite of the smaller concentration of carriers. This leads to a large factor: $\gamma_{exp}/\gamma_{calc} \simeq 7$. This discussion is, of course, highly speculative because of the ambiguous estimation of the number of carriers. However, the fact that γ_{exp} for $YInCu_4$ is even larger than that for $LuInCu_4$ indicates qualitatively a large mass enhancement in $YInCu_4$, which would be too large to be explained by conventional effects. Contrary to discussion in a previous letter [17], we conclude that the γ-value for $YInCu_4$ is enhanced if we take into account the small number of carriers. A mechanism such as the strong electron–phonon coupling may be responsible for the enhancement.

5. Concluding remarks

The electrical resistivity of $YInCu_4$ has a broad hump at around 270 K and shows a negative temperature dependence above the temperature. This feature was not observed for isostructural $LuInCu_4$, which behaves as a metallic conductor. It was found that both materials belong to semimetals with the small number of carriers, and that the transport properties can be roughly explained within the category. The carrier concentration is much smaller for $YInCu_4$ than for $LuInCu_4$, which is probably related to the unit-cell volume. By comparing the carrier concentration with an experimental electronic specific heat coefficient, the enhancement of carrier masses was suggested for $YInCu_4$. Finally, we would like to comment that the $RInCu_4$ system may provide a unique stage for investigating rare-earth magnetism in a low-carrier system. It behaves as a narrow-gap semiconductor at high temperatures. The carrier concentration can be controlled by changing the unit-cell volume.

Acknowledgments

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