Heavy-Mass Behavior of Ordered Perovskites ACu$_3$Ru$_4$O$_{12}$ ($A = $ Na, Ca, La)

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We synthesized ACu$_3$Ru$_4$O$_{12}$ ($A = $ Na, Ca, La) and measured their DC magnetization, AC susceptibility, specific heat, and resistivity, in order to investigate the effects of the hetero-valent substitution. A broad peak in the DC magnetization around 200 K was observed only in CaCu$_3$Ru$_4$O$_{12}$, suggesting the Kondo effect due to localized Cu$^{2+}$ ions. However, the electronic specific heat coefficients γ exhibit large values not only for CaCu$_3$Ru$_4$O$_{12}$ but also for all the other samples. Moreover, the Wilson ratio and the Kadowaki-Woods ratio of our samples are all similar to the values of other heavy-fermion compounds. These results question the Kondo effect as the dominant origin of the mass enhancement, and rather indicate the importance of correlations among itinerant Ru electrons.

KEYWORDS: transition-metal oxide, ordered perovskite, ruthenium oxide, heavy fermion, electron correlation, Kondo effect

1. Introduction

A-site ordered perovskite oxides ACu$_3$Ru$_4$O$_{12}$ (where A is alkaline-earth metals, rare-earth metals or some other elements, and B is transition metals) have recently been extensively studied, because rich varieties of electronic and magnetic properties are realized by various combinations of A and B ions. For example, insulating CaCu$_3$Ru$_4$O$_{12}$ ($B = $ Ti, Ge, Sn) exhibit antiferromagnetism for $B = $ Ti and ferromagnetism for $B = $ Ge and Sn. Such variation is crucially decided by the d electrons in the B ion shells, rather than the ionic radii of the non-magnetic B ions. Semiconducting CaCu$_3$Ru$_4$O$_{12}$ ($B = $ Mn, Fe, Cr, Co) exhibit giant magnetoresistance originating from their ferrimagnetic ordered states. Metallic CaCu$_3$Ru$_4$O$_{12}$ ($B = $ V, Fe, Cr, Co, Ru) exhibit Pauli paramagnetic behavior. The crystal structure of ACu$_3$Ru$_4$O$_{12}$ is depicted in Fig. 1. The A and Cu ions order in the A-site of the perovskite ABO$_3$ in the ratio of one to three. The B and O ions form BO$_6$ octahedra that share the oxygen atoms at the corner and the octahedra are in many cases severely tilted.

Among these A-site ordered perovskite oxides, ACu$_3$Ru$_4$O$_{12}$ ($A = $ Na, Ca, La) has attracted much attention, because of its metallic conductivity with a heavy effective mass reported by Ramirez et al. and Kobayashi et al. These two groups disclosed the metal-insulator transition in ACu$_3$Ti$_{1−x}$Ru$_x$O$_{12}$ ($A = $ Na, Ca, La). Ramirez et al. additionally compared the resistivity and the specific heat of the A-site substituted systems. In CaCu$_3$Ru$_4$O$_{12}$, Kobayashi et al. found magnetic behavior ascribable to the lattice Kondo effect between the localized Cu$^{2+}$ ions with $s = 1/2$ spins and the itinerant electrons originating from the Ru 4d orbitals. They further argued that the mass enhancement is attributable to the Kondo effect. In contrast, on the basis of the band structure calculation using exchange correlation functional, Xiang et al. recently suggested that both the Ru 4d band itself and a mixed band where the Ru 4d band hybridizes with the nearly localized Cu 3d band might contribute to the heavy-mass behavior. Quite recently, Krimmel et al. reported the possibility of non-Fermi-liquid behavior below 2 K in CaCu$_3$Ru$_4$O$_{12}$ based on the specific heat and the spin-lattice relaxation rate.

At present, it is not conclusive whether or not the Kondo effect is dominant or ever effective for the observed mass enhancement. Thus, it is useful to examine compounds in which the formal valence of Cu is shifted from 2+ in order to weaken the Kondo effect. This can be done by substituting Ca$^{2+}$ ions in order not to introduce direct disorder at the Cu or Ru site. We compare the physical properties of CaCu$_3$Ru$_4$O$_{12}$ with those of NaCu$_3$Ru$_4$O$_{12}$ and LaCu$_3$Ru$_4$O$_{12}$ to examine the

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Fig. 1. (Color online) Crystal structure of ACu$_3$Ru$_4$O$_{12}$. Each of the octahedra is BO$_6$, in which the B ion is located at the center and the O ions occupy the corners. Each O ion is shared by two octahedra. The small red spheres represent Cu atoms and the large blue spheres represent A atoms. The figure is generated using the program "VESTA."
Kondo scenario. (Note that the formal valence of Cu would be equal to 2+ for Ca2+ and deviate from 2+ as the valence of A-site varies from 2+.) Kobayashi et al. controlled the heavy-mass behavior by substituting Mn for the Cu site or Ti for the Ru site, but these substitutions introduce much disorder at the Cu or Ru site, which are considered responsible for the electric conductivity. Because the Cu and Ru sites are directly involved in the Kondo mechanism, the A-site substitution without disorder at the Cu and Ru sites may be more useful to examine the origin of the mass enhancement of CaCu3Ru4O12.

The main discussion in this paper is on the dominant origin of the mass enhancement of ACu3Ru4O12 (A = Na, Ca, La), based on the measurements of the susceptibility, specific heat, and resistivity. The electronic specific heat coefficients γ of all our samples are relatively large compared with those of transition-metal oxides without strong correlations but comparable to the ruthenate superconductor Sr2RuO4 with strong correlations. Moreover the effective mass of LaCu3Ru4O12 is even heavier than that of CaCu3Ru4O12. This result indicates that the Kondo effect does not play a dominant role for the mass enhancement of CaCu3Ru4O12. Otherwise, γ of CaCu3Ru4O12 would be the largest. For all our samples, the Wilson ratio and the Kadowaki-Woods ratio correspond well to other heavy-fermion compounds. These ratios provide additional evidence that the Kondo effect is not the dominant origin. Nevertheless, the susceptibility-maximum in CaCu3Ru4O12 implies the presence of the Kondo effect. We propose that the correlations among itinerant Ru electrons are dominant for the mass enhancement and the Kondo effect provides a minor contribution to the mass enhancement.

2. Experimental

Samples of ACu3Ru4O12 were synthesized with a conventional solid state reaction. Well ground stoichiometric mixtures of powders of Na2CO3, CaCO3, La2O3, CuO, and RuO2 were pressed into pellets, placed in alumina crucibles, and heated and kept at 1000°C for about 1 day. Only for NaCu3Ru4O12, we used 5% less RuO2 since unreacted RuO2 was detected when we used a stoichiometric mixture. Then they were reground, pelletized, and heated, and kept at 1000°C for about 1 day. By repeating this procedure for 1–3 times, we obtained the polycrystalline samples of Na0.5Ca0.5Cu3Ru4O12, CaCu3Ru4O12, Ca0.5La0.5Cu3Ru4O12, and LaCu3Ru4O12. It is difficult to synthesize NaCu3Ru4O12 because of its lower melting point 851°C. We first heated the ground mixture at 750°C, and the reground mixture was pelletized and heated at 900°C. Then, the sample consisting of fine single crystals shown in Fig. 2 was obtained. To characterize these samples, we used powder X-ray diffractometry with the CuKα1 radiation. As shown in Fig. 3, we confirmed that the impurity peaks of CuO and RuO2 are estimated less than 4% from the X-ray diffraction patterns, indicating almost single-phase samples. The cubic lattice parameter a systematically increases from 0.739 nm for A = Na to 0.748 nm for A = La (See Table I).

The DC susceptibility was measured from 1.8 K to 350 K with a commercial SQUID magnetometer (Quantum Design, model MPMS), and the specific heat from 2 K to 300 K with a commercial calorimeter (Quantum Design, model PPMS). The resistivity was measured from 2 K to 350 K using a standard four-probe method with DC or AC current. We measured the resistivity on at least three samples from each batch and confirmed their reproducibility. The AC susceptibility is measured by a mutual inductance method down to 20 mK using a 3He-4He dilution refrigerator (Cryoconcept, model DR-JT-S-100-10).

3. Results

Figure 4(a) displays the measured DC susceptibility χ = M/H at 10 kOe from 2 K to 350 K. The susceptibility of CaCu3Ru4O12 has a distinct broad maximum at around 200 K. In contrast, such a distinct peak is absent in the other samples. We note that the susceptibility of our samples contain smaller Curie tails at low temperatures than those reported by
Fig. 4. (Color online) Temperature dependence of (a) the susceptibility \( \chi = M/H \) under 10 kOe, (b) the specific heat \( C_P \), and (c) the resistivity \( \rho \) of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \).

Fig. 5. (Color online) Variation of the specific heat of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \) divided by temperature, \( C_P/T \), as a function of \( T^2 \). The lines are obtained by fitting the equation \( C_P/T = \gamma + \beta T^2 \) to the data from 5 K to 15 K.

Labeau et al.\(^{18} \) and Krimmel et al.\(^{26} \) Among our samples of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \), there is a systematic tendency of an increase in the susceptibility at the broad peak at 200 K as the Curie tail becomes smaller. In search of possible superconductivity of these metallic compounds, we measured the AC susceptibility of all the samples down to 20 mK, but found no evidence for any magnetic transitions.

Figure 4(b) shows the specific heat \( C_P \). There are no indications of magnetic transitions. The \( C_P/T \) curves of all the samples are similar and \( C_P \) seem to approach around 400 J/f. u. mol K at 300 K (f. u.: formula unit). These values correspond to 80% of the value estimated from the Dulong-Petit law \( C_V = 3NR \approx 499 \) J/f. u. mol K, where \( N = 20 \) is the number of atoms per formula unit, and \( R \) is the gas constant.

\[ C_P/T = \gamma + \beta T^2 \]

The values of \( \gamma \) of the other samples are also large and in particular \( \text{LaCu}_3\text{Ru}_4\text{O}_{12} \) has the largest \( \gamma \). In fact, as the \( A \)-site ions vary from \( \text{Na}^+ \) to \( \text{La}^{3+} \), \( \gamma \) exhibits a systematic increase. The Debye temperatures \( \theta_D \) of all these samples are evaluated to be about 500 K using the relation \( \theta_D = (12\pi^4 NR/5\beta)^{1/3} \).

Fig. 4(c) represents the resistivity \( \rho \) of all the samples. In order to characterize the temperature dependence at low temperatures, we fit the relation \( \rho(T) = \rho_0 + A'T^2 \) to the data using \( \rho_0, A' \), and \( \alpha \) as the fitting parameters. The resulting exponents \( \alpha \) for all members lies within 2.0 ± 0.2 below 25 K, demonstrating the \( T^2 \) behavior. This quadratic temperature dependence is also evident in Fig. 6, where \( \rho - \rho_0 \) is plotted against \( T^2 \). The coefficients \( A \) of the \( T^2 \) term listed in Table I are eval-
Table I. Parameters characterizing the physical properties of ACu$_3$Ru$_4$O$_{12}$. The $\chi_{10\text{K}}$ values are extracted from the raw data of $M/H$, $\gamma$, $\beta$, $A$, and $\rho_0$ are obtained by fitting $C_p/T = \gamma + \beta T^2$ from 5 K to 15 K and $\rho = \rho_0 + AT^2$ up to 25 K. Using these parameters, we evaluate: Debye temperature $\Theta_D$, Wilson ratio $R_W$, Kadowaki-Woods ratio $ak_W \equiv A/\gamma^2$, volumetric electronic specific heat coefficient $\gamma$, Hussey’s Kadowaki-Woods ratio $ak_{WH} \equiv A/\gamma^2$ with $b_0 = 1 \mu\Omega$ cm K$^{-2}$ cm$^3$ mol$^{-1}$, and Jacko’s Kadowaki-Woods ratio in three-dimensional systems $ak_{WJ}$.

| A-site ions | lattice parameter $a$ (nm) | $\chi_{10\text{K}}$ (10$^{-3}$ cmu/f. u. mol) | $\gamma$ (mJ/f. u. mol K$^2$) | $\beta$ (mJ/f. u. mol K$^4$) | $A$ (mJ cm$^2$/K$^2$) | $\rho_0$ ($\mu\Omega$ cm) |
|-------------|-----------------------------|-----------------------------------------------|-----------------------------|-----------------------------|-----------------|---------------------|
| La          | 0.7477 ± 0.0001             | 6.17                                          | 136                         | 352                         | 10.2            | 231                 |
| Ca$_{1-x}$La$_x$ | 0.7460 ± 0.0001             | 4.72                                          | 113                         | 303                         | 10.8            | 135                 |
| Ca           | 0.7421 ± 0.0001             | 4.72                                          | 85                          | 277                         | 8.5             | 36                  |
| Na$_{1-x}$Ca$_x$ | 0.7407 ± 0.0002             | 3.56                                          | 84                          | 243                         | 10.2            | 78                  |
| Na           | 0.7386 ± 0.0001             | 3.14                                          | 75                          | 262                         | 6.1             | 8                   |

| A-site ions | $\Theta_D$ (K) | $R_W$ (mJ cm$^{-2}$/mol K$^{-2}$) | $\gamma$ (mJ cm$^{-2}$/mol K$^{-2}$) | $\rho_0$ (mJ cm$^{-2}$/mol K$^{-2}$) | $ak_W$ (mJ cm$^{-2}$/mol K$^{-2}$) | $ak_{WH}$ (mJ cm$^{-2}$/mol K$^{-2}$) |
|-------------|----------------|-------------------------------|---------------------------------|----------------------------------|---------------------------------|-------------------------------------|
| La          | 480            | 3.3                           | $0.9 \times 10^{-5}$           | 1.08                            | 0.009$b_0$                     | 450                                 |
| Ca$_{1-x}$La$_x$ | 505            | 3.1                           | $1.3 \times 10^{-5}$           | 0.90                            | 0.013$b_0$                     | 662                                 |
| Ca           | 519            | 4.0                           | $1.8 \times 10^{-5}$           | 0.69                            | 0.018$b_0$                     | 845                                 |
| Na$_{1-x}$Ca$_x$ | 543            | 3.1                           | $2.1 \times 10^{-5}$           | 0.69                            | 0.021$b_0$                     | 963                                 |
| Na           | 529            | 3.1                           | $1.7 \times 10^{-5}$           | 0.62                            | 0.016$b_0$                     | 684                                 |

Fig. 6. (Color online) Temperature-dependent part of the resistivity $\rho - \rho_0$ plotted against $T^2$ for ACu$_3$Ru$_4$O$_{12}$.

4. Discussion

In this section we examine the origin of the mass enhancement in ACu$_3$Ru$_4$O$_{12}$ from the relations among electronic specific heat coefficients $\gamma$, the susceptibility values $\chi_{10\text{K}}$, and the coefficients $A$ of the $T^2$ term in the resistivity.

We evaluate the Wilson ratio $R_W \equiv \pi^2k_B^2\chi_{10\text{K}}/(3\mu_B^2)$, using $\chi_0 = \chi_{10\text{K}}$ obtained at 10 K. Theoretically the value of $R_W$ equals 1 for a free electron gas, whereas it approaches 2 in the strong correlation limit for local Fermi liquids. It may become greater than 2 if ferromagnetic fluctuations are present. The size of the deviation from unity is regarded as a measure of the strength of many-body electron correlations. $R_W$ of the present compounds are all above 3 and comparable to that of some other heavy-fermion compounds.

The relation between $\gamma$ and $A$ is described by the Kadowaki-Woods ratio $ak_W \equiv A/\gamma^2$, which is $1 \times 10^{-5}$ ($\mu\Omega$ cm K$^{-2}$)/(mJ/mol K$^2$) for some typical heavy-fermion metals. If $\gamma$ is expressed in terms of mJ/Ru mol K$^2$, $ak_W$ of ACu$_3$Ru$_4$O$_{12}$ ($A = Na$, Ca, La) are all around $1 \times 10^{-5}$ ($\mu\Omega$ cm K$^{-2}$)/(mJ/Ru mol K$^2$), consistent with such universality. In order to remove the ambiguity in the choice of the unit of $\gamma$, Hussey recently proposed the modified definition $ak_{WH} \equiv A/\gamma^2$. Here a molar quantity $\gamma$ is rescaled to the volumetric quantity $\gamma_v \equiv \gamma Z/(N_a a^3)$, where $Z$ is the number of formula units per unit cell, $N_a$ is Avogadro’s number, and $a$ is a lattice parameter. The modified ratio for all ACu$_3$Ru$_4$O$_{12}$ is evaluated as $ak_{WH} \approx 0.01–0.02$b_0$, where $b_0 \equiv 1 \mu\Omega$ cm K$^{-2}$ cm$^3$ mol$^{-1}$. We note that the rescaled values for all the present compounds happen to be very similar to that of a three-dimensional, $d$-electron heavy-fermion-like oxide LiV$_2$O$_4$ ($ak_{WH} \approx 0.02$b_0$)$.

Following Hussey’s work, Jacko et al. proposed an extended definition of the Kadowaki-Woods ratio applicable to a wide variety of heavy fermions, transition metals, transition-metal oxides, and organic charge transfer salts. They introduced the dimensionless ratio $ak_{WJ} \equiv 4\pi\hbar^2k_B^2f_2(n)/(A/\gamma^2)$, where the function $f_2(n)$ is expressed in terms of the electron density $n$ and spatial dimensionality $d$ of the system. They further proposed the universality $ak_{WJ} \approx 81$. If we assume that CaCu$_3$Ru$_4$O$_{12}$ contains 16 conduction electrons per formula unit of Ru $4d^8$, the electron density is estimated to be $n = 16Z/a^3$, and we obtain $ak_{WJ} \approx 880$ using $f_2(n) = \sqrt{3n^2/\pi^4h^6}$ for a spherical Fermi surface. This evaluation is based on a crude single-band picture. Considering the change in the number of conduction electrons, the values of $ak_{WJ}$ for the other ACu$_3$Ru$_4$O$_{12}$ also lies within a factor of 2 (See Table I). Although these values are an order of magnitude larger than the universal value proposed by Jacko et al., they are within the range of the values for other highly-correlated electron systems.
As shown in Table I, \( \gamma, \chi^{10K} \), and \( A \) exhibit almost systematic increases with varying the \( A \)-site ions from \( \text{Na}^+ \) to \( \text{La}^{3+} \). These parameters are closely related to the density of states \( D(\varepsilon_F) \): \( \gamma \) and \( \chi^{10K} \) are expected to be proportional to \( D(\varepsilon_F) \) and \( A \) is expected to be proportional to \( D^2(\varepsilon_F) \) for Fermi liquids.

Now we attempt to explain these systematic increases first from the standpoint of the rigid band model with the total density of states spectra obtained by the band calculation of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) using exchange correlation potential (shown in Fig. 3 in Ref. 25). A rigid band model relies on the approximation that the change in the valence of an ion induced by some site substitution results only in a shift of \( \varepsilon_F \) without changing the band structure. For \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \), when we substitute \( \text{Na}^+ (\text{La}^{3+}) \) for \( \text{Ca}^{2+} \), that is, when the number of the conduction electrons decreases (increases), \( \varepsilon_F \) would shift to lower (higher) energy in the calculated spectra. Assuming the rigid band model, \( D(\varepsilon_F) \) would decrease (increase) since the calculated spectra has a positive slope around the Fermi energy \( \varepsilon_F \); \( \gamma, \chi^{10K} \), and \( A \) would all decrease (increase). From a crude estimation using the calculated spectra, \( D(\varepsilon_F) \) deviate \( \pm 25\% \) by substituting \( \text{Na}^+ \) or \( \text{La}^{3+} \) (13.4, 17.4, and 22.0 electrons/eV for \( A = \text{Na}, \text{Ca}, \) and \( \text{La} \), respectively). These \( A \)-site substitution results with the rigid band model are reasonably consistent with our observation and support that \( \gamma \) of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) should be mainly enhanced by the band itself. The present analysis implies that the changes in the lattice parameter plays a secondary role in the mass enhancement, consistent with the interpretation by Ramirez et al.\(^{20}\).

To date it has been proposed that the Kondo effect between the localized \( \text{Cu} \) 3d and the itinerant \( \text{Ru} \) 4d electrons may be the origin of the heavy effective mass since the behavior of the maximum around 200 K of the \( \chi-T \) curve of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) is similar to that of the \( f \)-electron heavy fermion compound \( \text{CeSn}_3 \).\(^{34} \) We should stress here that indeed we observe the peak in \( \chi(T) \) ascribable to the Kondo effect only for \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) (See Fig. 4(a)). However, if the Kondo effect is the dominant origin for the mass enhancement of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \), a largest value of \( \gamma \) is expected for \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \). In reality, \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) is not the only one which has a large \( \gamma \) value. The other members, in which the formal valence of \( \text{Cu} \) ions is shifted from (localized) \( 2^+ \), also have large \( \gamma \) values. It is clear that the Kondo effect cannot be the dominant origin of the mass enhancement of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \).

5. Conclusion

We investigated basic physical properties of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} (A = \text{Na}, \text{Na}_{0.5}\text{Ca}_{0.5}, \text{Ca}, \text{Ca}_{0.5}\text{La}_{0.5}, \text{La}) \) to low temperatures. Not only the electronic specific heat coefficients of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \), in which the formal valence of \( \text{Cu} \) ions is \( 2^+ \) leading to localized \( \text{Cu} \) 3d electrons, but also that of the other members of \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \) are relatively large. This fact is inconsistent with the scenario that the Kondo effect plays a dominant role for the mass enhancement of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \).

Nevertheless, since we observed the maximum in \( \chi(T) \) only in \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) around 200 K, which is similar to the maximum for \( f \)-electron heavy fermion compounds \( \text{CeSn}_3 \), the correlation between the localized \( \text{Cu} \) 3d and the itinerant \( \text{Ru} \) 4d electrons (Kondo effect) may in part contribute to the mass enhancement of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) to minor extent. The Kondo effect derived from the localized \( \text{Cu}^{2+} \) electrons cannot be totally neglected for \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \).

The Wilson ratio and Kadowaki-Woods ratio of the present compounds exhibit values similar to those of other heavy-fermion compounds, suggesting the mass enhancement of \( \text{CaCu}_3\text{Ru}_4\text{O}_{12} \) originating mainly from the correlation among the \( \text{Ru} \) 4d electrons. The electronic specific heat coefficient \( \gamma \), the susceptibility value \( \chi^{10K} \), and the \( \rho\cdot T^2 \) coefficient \( A \) exhibit almost systematic increases with varying the valence of \( A \)-site ions from 1+ to 3+. A simple rigid band model can account for our experimental results, supporting that the heavy mass arising from the \( \text{Ru} \) bands and the shape of the bands are important.

More systematic investigation is under progress to characterize the precise variations of \( \gamma \) for other combinations of the \( A \)-site. At the same time it is desirable to determine the valence states of \( \text{Cu} \) and \( \text{Ru} \) ions in \( \text{ACu}_3\text{Ru}_4\text{O}_{12} \) to clarify the roles of the localized and itinerant \( \text{Cu} \) electrons.

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