A novel heavy-fermion state in CaCu$_3$Ru$_4$O$_{12}$

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We have measured susceptibility, specific heat, resistivity, and thermopower of CaCu$_3$Ti$_{4-x}$Ru$_x$O$_{12}$ and CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$, and have found that CaCu$_3$Ru$_4$O$_{12}$ can be regarded as a heavy-fermion oxide in d-electron systems. The Kondo temperature is near 200 K, and the susceptibility (1.4×10$^{-5}$ emu/Cu mol) and the electron specific heat coefficient (28 mJ/Cu molK$^2$) are moderately enhanced. The resistivity is proportional to $T^2$ at low temperatures, and satisfies the Kadowaki-Woods relation. The heavy-fermion state comes from the interaction between the localized moment of Cu 3d and the conduction electron of Ru 4d. An insulator-metal transition occurs between $x = 1.5$ and $4$ in CaCu$_3$Ti$_{4-x}$Ru$_x$O$_{12}$, which can be regarded as a transition from magnetic insulator to heavy-fermion metal.

KEYWORDS: heavy fermion, transition-metal oxide, ordered perovskite

1. Introduction

A large family of AC$_3$B$_4$O$_{12}$ [A=Na+, Cd$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Y$^{3+}$, Th$^{4+}$ or U$^{4+}$ (R: lanthanide), B=Mn$^{3+}$, Fe$^{3+}$, Al$^{3+}$, Cr$^{3+}$, Ti$^{4+}$, Mn$^{4+}$, Ge$^{4+}$, Ru$^{3+}$, Ir$^{4+}$, Nb$^{5+}$, Th$^{5+}$ or Sb$^{5+}$, C=Cu$^{2+}$ or Mn$^{3+}$] have an ordered perovskite-type structure in which a Jahn-Teller ion such as Cu$^{2+}$ or Mn$^{3+}$ is located in the A site of the perovskite ABO$_3$. They have wide variety of cation compositions, and various substitutions are possible for the A, B and C sites. Although they were synthesized in 1970’s, they had not been studied so much until Subramanian et al. discovered an enormous large dielectric constant of CaCu$_3$Ti$_4$O$_{12}$ in 2000. Many researchers have investigated an origin of the large dielectric constant, which is still controversial at present. Giant magnetoresistance and phase separation in CaMn$_{3-x}$Cu$_{1-y}$Mn$_y$O$_{12}$ are a second example. We think that these interesting physical properties are related to the peculiar crystal structure, and have studied the transport properties of the AC$_3$B$_4$O$_{12}$ compounds.

A heavy-fermion system is a strongly correlated electron system where localized f-electrons interact with conduction electrons through the Kondo effect. In this system, a high and narrow peak appears in the quasiparticle density of states $D$ near the Fermi energy $E_F$. The large $D(E_F)$ is reflected in a large susceptibility and electron specific-heat coefficient. LiV$_2$O$_4$ has been regarded as a typical example of the heavy fermion system in d-electron systems. In LiV$_2$O$_4$, however, V 3d electrons act as conduction electrons and local moments simultaneously. Thus we cannot distinguish the local moment site from the conduction electron site. In this meaning, LiV$_2$O$_4$ is not equivalent to the f-electron heavy-fermion system.

CaCu$_3$Ru$_4$O$_{12}$ is one of the AC$_3$B$_4$O$_{12}$-type oxides, and exhibits a good metallic conduction down to 4 K. It shows higher conductivity than CaRuO$_3$ with less tilted RuO$_6$ octahedra, which would be difficult to understand if only the Ru-O network would be conductive. Subramanian and Sleight proposed “valence degeneracy” for the electronic states of CaCu$_3$Ru$_4$O$_{12}$, where Cu$^{2+}$ would contribute to the electric conduction. Their explanation was, however, phenomenological, and the microscopic mechanism was not clearly understood. In this paper, we will propose that CaCu$_3$Ru$_4$O$_{12}$ is a novel d-electron heavy-fermion system, which is truly equivalent to the f-electron heavy-fermion system in the sense that the local moment (Cu 3d) and the conduction electron (Ru 4d) are clearly distinguished. This is evidenced by the substitution of Mn for Cu in CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$, where the anomalous impurity effects are observed. We have further found that an insulator-metal transition occurs in CaCu$_3$Ti$_{4-x}$Ru$_x$O$_{12}$, which can be regarded as a transition from magnetic insulator to heavy-fermion metal.

2. Experimentalal

Polycrystalline samples of CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$ ($y = 0$, 0.5, 1 and 1.5), and CaCu$_3$Ru$_4$O$_{12}$ ($y = 0$, 0.1, 0.2 and 0.3) were prepared by a solid-state reaction (Note that the sample of $y = 0$ is identical to that of $y = 4$). Stoichiometric amounts of CaCO$_3$, CuO, Ru$_2$O$_3$, TiO$_2$, and Mn$_3$O$_4$ were mixed, and CuO flux was added to CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$. The mixture was calcined in air at 1000-1050 °C for 20 h for CaCu$_{3-y}$Ru$_x$O$_{12}$, 1050 °C for 48 h for CaCu$_3$Ru$_4$O$_{12}$. The CuO flux in the latter was removed by 1N HCl. The product was finely ground, pressed into a pellet, and sintered in air at 1000-1050 °C for 20 h for CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$.

The X-ray diffraction was measured using a standard diffractometer with Cu $K_\alpha$ radiation as an X-ray source in the $\theta$-$2\theta$ scan mode. The susceptibility was measured from 5 to 300 K by a commercial Superconducting Quantum Interference Device (SQUID, Quantum Design MPMS) in 1 T. The specific heat was measured using a standard relaxation method from 2 to 60 K.
to 300 K in a liquid He cryostat. For CaCu$_3$Ru$_4$O$_{12}$, we extended the measurement down to 0.3 K using a $^3$He cryostat, but did not find any indication of superconductivity. The thermopower was measured using a steady-state technique from 4.2 to 300 K in a liquid He cryostat. A temperature gradient of 0.5 K/mm was generated by a small resistive heater pasted on one edge of a sample, and was monitored by a differential thermocouple made of copper-constantan. The thermopower of the voltage leads was carefully subtracted.

3. Results and Discussion

Figure 1(a) shows the crystal structure of CaCu$_3$Ru$_4$O$_{12}$, which is the AC$_3$B$_4$O$_{12}$ type structure with Cu located at the C site. Since Cu$^{2+}$ is a small ion, the RuO$_6$ octahedra are highly canted to make the lattice parameter smaller than that of CaRuO$_3$ or SrRuO$_3$. Another interesting feature is that the Cu-O distance (1.94 Å) is as short as the Ru-O distance (1.98 Å). Cu is surrounded with four oxygens that are shared with the RuO$_6$ octahedra, and thus we expect a strong hybridization between Cu 3d and O 2p, through which Ru 4d can interact with Cu 3d. As is shown in Fig. 1 (b), the X-ray diffraction pattern of CaCu$_3$Ru$_4$O$_{12}$ is fully indexed as the AC$_3$B$_4$O$_{12}$ structure. Other samples are also fully indexed on the structure reported in the literature except for 5% RuO$_2$ impurity in CaCu$_3$Ti$_{2.5}$Ru$_{1.5}$O$_{12}$.

Figure 2 (a) shows the susceptibility of CaCu$_3$Ti$_{4-x}$Ru$_x$O$_{12}$. We have found that the high-temperature data are well fitted with the expression $\chi(T) = \chi_p + \chi_{loc}(T)$, where $\chi_p$ is the Pauli paramagnetic susceptibility, and $\chi_{loc}$ is the Curie-Weiss-type susceptibility $\chi_{loc}(T) = C/(T + \theta_W)$ (C is the Curie constant, and $\theta_W$ is the Weiss temperature). Figure 2 (b) shows the parameters of $C$, $\chi_p$, and $\theta_W$. $C$ for $x=0$ is $2\times10^{-3}$ emu K/g, which corresponds to 1.3 $\mu_B$/Cu. This indicates that Cu$^{2+}$ for $x = 0$ acts as a local spin moment of $S = 1/2$. With increasing $x$, $C$ rapidly decreases down to $6\times10^{-4}$ emu K/g (0.4 $\mu_B$/Cu) for $x = 1.5$, and instead $\chi_p$ linearly increases. An important feature is that the susceptibility for all the samples seems to merge into a single curve at high temperatures, which suggests that the sum of the contributions of $\chi_{loc}$ and $\chi_p$ is conserved. This strongly suggests that the localized moments on Cu$^{2+}$ becomes itinerant with increasing $x$. $\chi$ of $x = 4$ was fitted only above 200 K, where $C$ is $1.7 \times 10^{-4}$ emu K/g (0.1 $\mu_B$/Cu). It weakly depends on $T$ below 200 K, which will be discussed in the next paragraph. $\theta_W$ and the Neel temperature $T_N$ for $x=0$ are 30 and 27 K, respectively, which is consistent with the previous data. $T_N$ decreases with $x$ and disappears near $x = 2$, which is much faster than the temperatures expected from the dilution effect.

As mentioned earlier, the microscopic mechanism of the delocalization of the Cu$^{2+}$ moment seen in Fig. 2 was not yet understood. We propose that the localized Cu$^{2+}$ moment starts to be itinerant through the Kondo coupling with Ru 4d, and finally forms a heavy-fermion state. Here we will show convincing evidence for the heavy-fermion state of CaCu$_3$Ru$_4$O$_{12}$. First, CaCu$_3$Ru$_4$O$_{12}$ shows a typical susceptibility of heavy-fermion metals. As is shown in Fig. 3 (a), $\chi$ of

![Fig. 1. (a) Crystal structure and (b) X-ray diffraction pattern of CaCu$_3$Ru$_4$O$_{12}$.](image-url)
CaCu$_3$Ru$_4$O$_{12}$ quite resembles that of CeSn$_3$, a typical heavy-fermion metal. A value of $1.4 \times 10^{-3}$emu/Cu mol is two orders of magnitude larger than the value of free electrons, and a peak at 200 K is an indication of the Kondo resonance. These results strongly indicate that the Ru 4d electron interacts with the localized Cu moment to make a heavy-fermion state below 200 K. The second piece of the evidence is a large electron specific heat. Figure 3(b) shows the specific heat of CaCu$_3$Ru$_4$O$_{12}$. The electron specific heat coefficient ($\gamma$) is observed to be 28 mJ/Cu molK$^2$ that is about 20-30 times larger than the value of free electrons. The Willson ratio $R_W = \pi^2 k_B^2 \chi_p / 3 \mu_B^2 \gamma$ is 3.8, which is in an excellent agreement with other heavy-fermion compounds. Thirdly, the resistivity exhibits typical features of heavy fermion metals. As shown in Fig. 3(b), the resistivity ($\rho$) of CaCu$_3$Ru$_4$O$_{12}$ is plotted as a function of $T^2$, which clearly shows the relation of $\rho = AT^2 + \rho_0$ as is expected in the Fermi liquid. The coefficient $A$ is evaluated to be $6 \times 10^{-8}$ Ωcm/K$^2$, which satisfies the Kadokawa-Woods relation: $A/\gamma^2$ is nearly the same value as that for heavy-fermion metals.

We would like to mention some novelties of the heavy-fermion state in CaCu$_3$Ru$_4$O$_{12}$. First of all, this is the first compound in which Cu$^{2+}$ (3$d^9$) behaves like Ce$^{3+}$ (4$f^1$) to make conduction electrons heavy. This comes from the peculiar structure that RuO$_2$ octahedra and the Cu-O placket are connected in a edge-shared manner. Second, this can be regarded as a conductive perovskite in which the A site is responsible for electric conduction. This is so rare that BiNiO$_3$ would be the only one example ever reported, which is insulating at low temperatures. Thirdly, the conduction electrons are Ru 4d, which can be also magnetic. As is well known, the perovskite oxide SrRuO$_3$ is a ferromagnetic metal. It is thus surprising that the ground state of CaCu$_3$Ru$_4$O$_{12}$ is “nonmagnetic”, though almost all cations are magnetic.

Figure 4(a) shows $\rho$ of CaCu$_3$Ti$_{1-x}$Ru$_x$O$_{12}$, which changes from $10^3$ ($x=0$) to $10^{-4}$ Ωcm ($x=4$) at 300 K. The temperature dependence also changes from insulating to metallic, and an insulator-metal transition occurs between $x=1.5$ and $x=4$. Figure 4(b) shows the thermopower ($S$) of CaCu$_3$Ti$_{1-x}$Ru$_x$O$_{12}$. Most unexpectedly, $S$ suddenly decreases from 100 μV/K for $x=0.5$ to a few μV/K for $x=1.0$, whereas $\rho$ for $x=1.0$ is still high. Since the small thermopower is a hallmark of a metal, this indicates that the delocalization of the 3d holes on Cu$^{2+}$, i.e., the Kondo coupling with the Ru 4d electron, already occurs at $x=1$. We infer from the Curie constant in Fig. 2(b) that a half of the 3d holes on Cu$^{2+}$, i.e., $x=4$. Figure 4(b) shows the thermopower ($S$) of CaCu$_3$Ti$_{1-x}$Ru$_x$O$_{12}$. Most unexpectedly, $S$ suddenly decreases from 100 μV/K for $x=0.5$ to a few μV/K for $x=1.0$, whereas $\rho$ for $x=1.0$ is still high. Since the small thermopower is a hallmark of a metal, this indicates that the delocalization of the 3d holes on Cu$^{2+}$, i.e., the Kondo coupling with the Ru 4d electron, already occurs at $x=1$. We infer from the Curie constant in Fig. 2(b) that a half of the 3d holes on Cu$^{2+}$, i.e., $x=4$. Although the Kondo coupling between Ru 4d and Cu 3d exists, the conduction path is seriously segmentized at $x=1$. This is the reason of the high resistivity for $x=1$. In contrast, the thermopower is a direct probe for the entropy per conductive carriers, it is less affected by the insulating region in the sample. In fact, $E_F=1.4$ eV estimated for 50% of Cu$^{2+}$ gives the diffusive term of the thermopower $k_B T / e E_F = 1$ μV/K at 300 K, which is consistent with the observed data. We further note that the thermopower of CaCu$_3$Ru$_4$O$_{12}$ is similar to that of CeSn$_3$, which is consistent with the data in Fig. 2.

Figure 5(a) shows $\rho$ of CaCu$_3$Ru$_4$O$_{12}$. $\rho$ systematically increases with $y$, which further supports that the Cu site contributes to the conduction. $\rho$ for the Mn-doped samples is understood in terms of the sum of $\rho$ for $y=0$ and the impurity-scattering term induced by Mn. The impurity scattering is usually independent of...
temperature, and the resistivity of an impurity-doped sample is shifted upward in parallel to the resistivity of a pure sample. However, this is not the case. The residual resistivity at 4 K is roughly proportional to the Mn content, as is seen in the impurity scattering of a conventional metal. On the other hand, the resistivity is nearly independent of y at room temperature. This can be also understood from the heavy-fermion scenario. At room temperature (above the Kondo temperature), Mn$^{3+}$ and Cu$^{2+}$ seem similar magnetic scatterers to the conduction electrons. In contrast, the Cu 3d moments coherently move with the conduction electrons below the Kondo temperature, where only the Mn$^{3+}$ remains as a scatterer.

Figure 5(b) shows $\chi$ of CaCu$_{3-y}$Mn$_y$Ru$_4$O$_{12}$, which obeys the Curie law for y > 0. The Curie constant for y > 0 corresponds to 2 $\mu_B$/Mn, which is a half of the value expected from Mn$^{3+}$ ($S = 2$). We do not understand the reason of the unusual small moment of Mn$^{3+}$. One possibility is that Mn$^{3+}$ is antiferromagnetically coupled with the neighboring Cu$^{2+}$. As shown in the inset, $\chi$ exhibits a kink near 200 K which means that the Kondo coupling remains against the Mn doping. This is consistent with the metallic nature of the Mn-doped samples.

4. Summary

The susceptibility, electron specific heat, resistivity and thermopower of CaCu$_3$Ru$_4$O$_{12}$ are consistently and quantitatively understood as those of a heavy-fermion metal with the Kondo temperature of 200 K. This comes from the interaction between Cu 3d and Ru 4d electrons. The former corresponds to the localized f electron, and the latter corresponds to the conduction electron. In this sense, CaCu$_3$Ru$_4$O$_{12}$ is a complete analogue to the f-electron heavy fermion metal. We have further found that a insulator-metal transition in CaCu$_3$Ti$_{3-y}$Ru$_y$O$_{12}$, which can be regarded as a transition from magnetic insulator to heavy fermion state, through which the hole on Cu$^{2+}$ starts to be itinerant by the help of the Kondo coupling with Ru 4d.

Before completion of the present manuscript, we found the preprint of Ramirez et al. on the preprint archives (cond-mat/0403742). They discussed the itinerancy of the Cu$^{2+}$ moment in LaCu$_3$Ti$_{4-x}$Ru$_x$O$_{12}$. However, they did not show susceptibility data of CaCu$_3$Ru$_4$O$_{12}$, and did not mention the heavy-fermion state either.

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