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High-field magnetization and magnetoresistance of the *A*-site ordered perovskite oxide $\mathrm{CaCu_3Ti_{4-x}Ru_xO_{12}}$ $(0 \leqslant x \leqslant 4)$

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We have measured high-field magnetization and magnetoresistance of polycrystalline samples of the *A*-site ordered perovskite $\mathrm{CaCu_3Ti_{4-x}Ru_xO_{12}}$ $(0 \leqslant x \leqslant 4)$ utilizing a nondestructive pulsed magnet. We find that the magnetization for $x = 0.5$, 1.0, and 1.5 is nonlinear, and tends to saturate in high fields. This is highly nontrivial because the magnetization for $x = 0$ and 4 is linear in external field up to the highest one. We have analyzed this field dependence based on the thermodynamics of magnetic materials, and propose that the external fields delocalize the holes on the $\mathrm{Cu^{2+}}$ ions in order to maximize the entropy. This scenario is qualitatively consistent with a large magnetoresistance of -70% observed at 4.2 K at 52 T for $x = 1.5$.

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I. INTRODUCTION

Filling-control metal-insulator transition on transition-metal oxides and their derivatives, such as high-T_c superconducting cuprates and colossal magnetoresisitive manganites, has attracted much attention in recent years because of their unique physical properties arising from interacting degrees of freedom between spin, orbital, charge, and lattice.[1] The layered perovskite oxide $\mathrm{La_{2-x}Sr_xCuO_4}$ is a typical example, where $\mathrm{Sr^{2+}}$ substitution for $\mathrm{La^{3+}}$ works as an acceptor to supply a hole.[2] The system evolves from an antiferromagnetic insulator to a paramagnetic metal with increasing x, where the high-temperature superconductivity emerges between the antiferromagnetic and paramagnetic phases. From a microscopic viewpoint, the electronic configuration of a $\mathrm{Cu^{2+}}$ ion $[(3d)^9]$ is regarded as one $3d$ hole per $\mathrm{Cu^{2+}}$. This $3d$ hole is localized on the $\mathrm{Cu^{2+}}$ ion at $x = 0$, and gradually acquires itinerancy with additional hole doping, which is understood in terms of a Kondo coupling with the itinerant hole on the $\mathrm{O^{2-}}$ ion known as the Zhang-Rice singlet.[3] In this sense, a hole on a $\mathrm{Cu^{2+}}$ ion in various copper oxides is on the verge of the localization; it acts as a local moment in some materials, while it acts as an itinerant carrier in others.

Recently, a similar localization-itinerancy crossover of the $\mathrm{Cu^{2+}}$ hole has been reported in the complex copper oxide $\mathrm{CaCu_3Ti_{4-x}Ru_xO_{12}}$.[4–6] This material crystallizes in the $AA'_3B_4\mathrm{O}_{12}$ type ordered perovskite structure with $Im\bar{3}$ symmetry, in which the $\mathrm{Ca^{2+}}$ and $\mathrm{Cu^{2+}}$ ions occupy the A and A' sites to form a doubly periodic unit cell from the primitive perovskite cell (see the inset of Fig. 1). In this system, the ground state runs from an antiferromagnetic insulator at $x = 0$ to a paramagnetic metal at $x = 4$ through a spin-glass-like insulator at $x = 0.5$–1.5. This clearly indicates that the $\mathrm{Cu^{2+}}$ hole systematically changes from a local moment in $x = 0$ to an itinerant carrier in $x = 4$. One significant difference from $\mathrm{La_{2-x}Sr_xCuO_4}$ is that the formal valence of the Cu ion is always 2+ in $\mathrm{CaCu_3Ti_{4-x}Ru_xO_{12}}$. Since the substitution of $\mathrm{Ru^{4+}}$ $[(4d)^4]$ for $\mathrm{Ti^{4+}}$ $[(3d)^0]$ is isovalent substitution, the valence of the Cu ion is not perturbed by the Ru content x. In this sense, the crossover from localization to itinerancy can be more clearly investigated in the present system.

The $x = 0$ phase, i.e., $\mathrm{CaCu_3Ti_4O_{12}}$, shows a huge dielectric constant of 10^4 at room temperature[7] and an antiferromagnetic order below 25 K.[8] Although the mechanism of the large dielectric constant is not yet clarified, the majority in the community think that it comes from an extrinsic origin.[9–12] Nevertheless this dielectric property is interesting, because this extrinsic nature can be artificially controlled to improve the dielectric properties.[13] The magnetism of this material is also interesting, and the ground state changes from antiferromagnetism to ferromagnetism by properly choosing the B site ions.[14,15]

The other end member of $x = 4$, i.e., $\mathrm{CaCu_3Ru_4O_{12}}$, is a paramagnetic metal, where the $\mathrm{Cu^{2+}}$ ion loses the local moment.[16] This metallic compound shows substantial electron specific heat and Fermi-liquid-like resistivity at low temperatures,[4,5] which roughly satisfy the Kadowaki-Woods relation. From the above results, Kobayashi *et al.*[4] proposed that $\mathrm{CaCu_3Ru_4O_{12}}$ is a kind of heavy-fermion or valence-fluctuation system, which is examined in photoemission

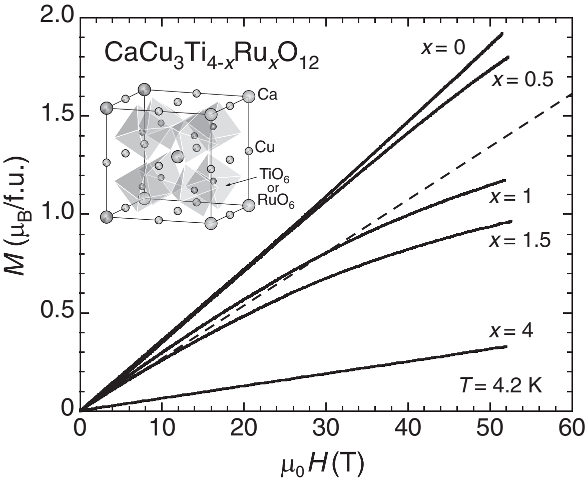

FIG. 1. High-field magnetization of $CaCu_3Ti_{4-x}Ru_xO_{12}$ ($x = 0$, 0.5, 1, 1.5, and 4) at 4.2 K. The broken line is a linear fit to the data of $x = 1.5$ in low magnetic fields. In the inset the crystal structure of $CaCu_3Ti_{4-x}Ru_xO_{12}$ is schematically shown.

experiments.[17,18] This picture has been further examined from first-principle calculation,[19] magnetic resonance,[20,21] and chemical substitution.[22] A possibility of the non-Fermi-liquid behavior is discussed below 1 K, and is compared with other heavy fermion compounds.[23,24] The concept of the delocalization of the Cu^{2+} hole has also been examined in the related compounds, such as $L_{2/3}Cu_3(Ti,Ru)_4O_{12}$,[25] $CaCu_3Co_4O_{12}$,[26] $CaCu_3Ru_{4-x}Mn_xO_{12}$,[27] and $CaCu_3V_4O_{12}$.[28,29]

We emphasize that response to high magnetic fields is particularly important in the present system.[30] In the antiferromagnetic phase of $x = 0$, the exchange energy is evaluated to be 4 meV,[8] which is much smaller than that of $La_{2-x}Sr_xCuO_4$ (100 meV).[2] It should be emphasized that this energy scale is comparable with the Zeeman energy of 40 T for an isolated $S = 1/2$ spin, which is achievable with a nondestructive pulsed magnet. Thus this material offers a good playground to study how the external fields modify the interplay between localization and itinerancy of the Cu^{2+} hole. Here we show the magnetic and transport properties of $CaCu_3Ti_{4-x}Ru_xO_{12}$ in high magnetic fields of up to 52 T. The measured magnetization in the intermediate phase ($0 < x < 4$) is nonlinear, which can be associated with the field-driven delocalization of the Cu^{2+} hole in this system. This concept is at least qualitatively consistent with a large negative magnetoresistance of −70% observed for $x = 1.5$ at 52 T at 4.2 K.

II. EXPERIMENT

Polycrystalline samples of $CaCu_3Ti_{4-x}Ru_xO_{12}$ ($x = 0, 0.5,$ 1, 1.5, and 4) were prepared by a solid-state reaction.[4] High-field magnetization and magnetoresistance measurements in magnetic fields of up to 52 T from 4.2 to 20 K were performed with nondestructive pulsed magnets at KYOKUGEN, Osaka University.[31] The magnetization was measured by an induction method with a standard pickup coil system. Magnetization data were obtained on a powder of the polycrystalline sample. The magnetoresistance was measured using a conventional dc four-probe technique. The magnetic field was applied parallel to the electrical current direction (longitudinal geometry).

III. RESULTS AND DISCUSSION

High-field magnetization at 4.2 K is shown as a function of external field in Fig. 1. The magnetization systematically decreases with increasing Ru content x, which is consistent with the previous reports where the low-temperature susceptibility systematically changes from a Curie-Weiss-like to Pauli-paramagnetic-like susceptibility with increasing x.[4–6] When the Cu^{2+} hole is fully localized, we expect that the saturated magnetization will be about 3 μ_B per formula unit, corresponding to a classical $S = 1/2$ spin per Cu. Indeed, this classical value is experimentally observed; Kim *et al.*[8] measured neutron diffraction of the antiferromagnetic order for $CaCu_3Ti_4O_{12}$, and found that the ordered moment is approximately 0.8 μ_B per Cu. The magnetization at 52 T is 1.9 μ_B per formula unit, which is two-thirds of the fully polarized moment. In this respect, we can understand that the magnetization is linear in external field of up to 52 T. On the other hand, the susceptibility of $CaCu_3Ru_4O_{12}$ ($x = 4$) is almost independent of temperature, which is regarded as the Pauli paramagnetism of itinerant electrons. According to the first principle calculation, the conduction bands consists mainly of Ru 4d, and the density of states at the Fermi level is evaluated to be 6.7 states/eV formula unit.[19] If we estimate the Fermi energy to be a simple ratio of the valence electron number to the density of states, the Fermi energy will be around 2.3 eV for 16 electrons in the valence bands (four 4d electrons per Ru) per formula unit. Thus the magnetization is again expected to be linear in external field unless the Zeeman energy exceeds the Fermi energy.

In contrast to the simple magnetization for $x = 0$ and 4, the magnetization of the intermediate phases ($x = 0.5$, 1.0, and 1.5) is highly nontrivial. As is clearly seen in Fig. 1, their magnetization is substantially nonlinear in external field, and tends to saturate in high fields. The initial slope of the magnetization is roughly equal to a simple arithmetic average of the magnetization of the two end phases, which implies that the magnetization can be understood as a simple mixture between $x = 0$ and 4. However, the magnetization bends toward $x = 4$ in high fields and, in particular, dM/dH for $x = 1.5$ is close to dM/dH for $x = 4$ around 52 T. Considering that the local moment on the Cu^{2+} ion in $x = 0$ is delocalized in $x = 4$, we suggest that the external field drives the delocalization of the hole on the Cu^{2+} ion.

Next we show the temperature dependence of the high-field magnetization for $x = 1.5$ in Fig. 2. With increasing temperature, the magnetization gradually decreases, but the nonlinear behavior remains intact. This indicates that the field-driven delocalization works below 20 K. The inset of Fig. 2 shows the temperature dependence of M/μ_0H calculated from the measured magnetization. A broken curve is the field-cooled susceptibility in a static field of 7 T measured with a commercial SQUID (superconducting quantum interference device) magnetometer. The isothermal M/μ_0H decreases with increasing field. The 7 T data look like a Curie-Weiss-like susceptibility above 10 K, which is consistent with the previous reports.[4–6] With increasing external fields,

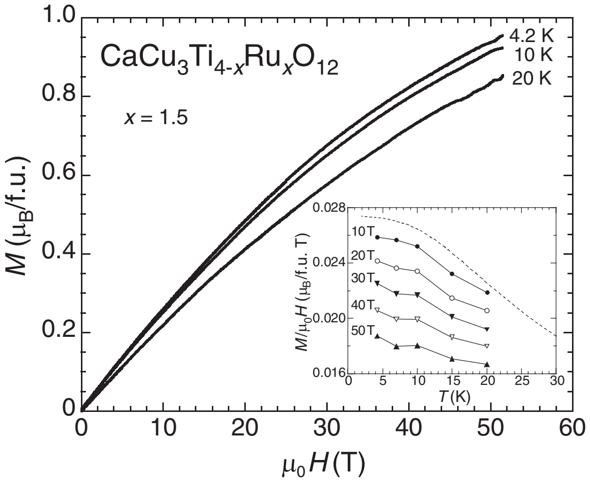

FIG. 2. High-field magnetization for $x = 1.5$ at various temperatures. The inset shows the temperature dependence of $M/\mu_0 H$ calculated from the isothermal magnetization. A broken curve is the field-cooled susceptibility at an external static field $\mu_0 H = 7$ T.

$M/\mu_0 H$ systematically decreases with weaker temperature dependence, and looks more Pauli-paramagnetic-like. This is consistent with our proposed picture that the external field increases a portion of the delocalized hole on the Cu^{2+} ion.

Before going to a phenomenological analysis of the nonlinear magnetization, we should compare the data in Figs. 1 and 2 with the magnetization of spin glasses that show similar nonlinear magnetization.[32] Spin glasses in alloys belong to a frustrated spin system in which the ferromagnetic and antiferromagnetic interactions compete. As such, the magnetic moments slowly polarize with external fields to show a sublinear dependence of the magnetization. The magnetization curves in Figs. 1 and 2 resemble those of spin glasses at first glance, but one significant difference is a typical field scale. Clearly, the spin glasses are easily polarized with a much lower magnetic field because ferromagnetic interaction (though partially) works between spins. On the other hand, the title compound is a solid solution of the antiferromagnet and paramagnet, and no magnetic frustration is suggested. Although the low-field susceptibility for $x = 1.5$ exhibits a spin-glass-like hysteresis between zero-field-cooled and field-cooled processes below $T_{SG} = 8.5$ K,[6] we do not think that this hysteresis is relevant to the nonlinearity of the magnetization because it survives up to 52 T at 20 K, which is far larger than the energy scale of the spin-glass-like order of 8.5 K.

Let us discuss a possible mechanism of the field-induced delocalization from a viewpoint of thermodynamics. We start with Maxwell's relation, where the temperature dependence of the magnetization is equal to the field dependence of the entropy, given as

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T. \tag{1}$$

We can evaluate the quantity of the left-hand side of Eq. (1) from the high-field magnetization curve shown in Fig. 2. From the inset of Fig. 2, we find that the magnetization roughly linearly increases with decreasing temperature from 20 down to 10 K, which justifies the assumption that the slope is equal to $\partial M/\partial T$. Figure 3 shows the temperature slope of the magnetization between 10 and 20 K given by $(M_{20\,\mathrm{K}} - M_{10\,\mathrm{K}})/10$ K, which we identify to $\partial M/\partial T$. $\partial M/\partial T$ exhibits a complicated field dependence; $\partial M/\partial T$ is roughly linear in H below around 20 T, while it is independent of H above around 30 T. This is already visible in the inset of Fig. 2, where the temperature slope at 50 T is smaller than that at 10 T. A crossover field is close to the field above which the magnetization begins to saturate.

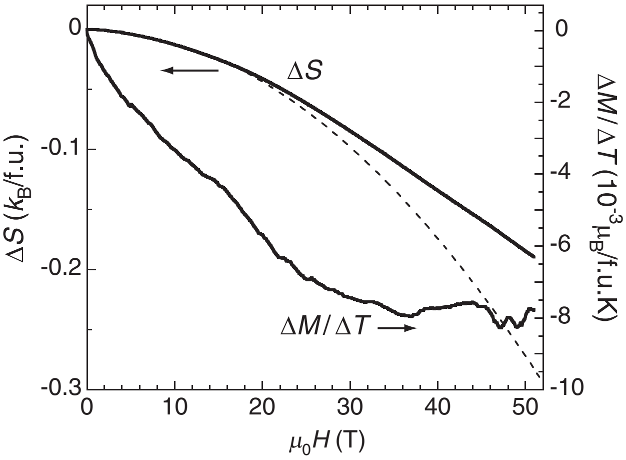

FIG. 3. Entropy decrease $[\Delta S = \int_0^H (\partial M/\partial T) dH]$ plotted as a function of external field. The temperature dependence of the magnetization $\Delta M/\Delta T = (M_{20\,\mathrm{K}} - M_{10\,\mathrm{K}})/10$ K is also plotted as a function of external field, which is identified to $\partial M/\partial T$. The dotted curve represents the extrapolation of ΔS from low fields (see text).

Using Eq. (1), we obtain the entropy change ΔS by integrating $\partial M/\partial T$ as

$$\Delta S(H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'. \tag{2}$$

The value of ΔS is plotted as a function of field in Fig. 3, which is always negative at all the fields measured. This is reasonable, because an external field suppresses the thermal fluctuation of spins. In a conventional magnet, ΔS decreases in proportion to H^2, as shown by the dotted curve in Fig. 3, because M is linear in H. In the present system, however, the entropy decrease is milder than that expected from the dotted curve, which implies that additional entropy is induced by magnetic fields.

This additional entropy can be explained in terms of the field-induced delocalization. When the one hole is completely localized on the Cu^{2+} ion, the maximum entropy is $k_B \ln 2$ from the spin degrees of freedom. If it is delocalized, it can move along the Cu-O-Ru network. Since the resistivity is high and the Cu-O-Ru network is highly disordered, the charge transport will be dominated by a variable-range-hopping process, where the mobile hole acquires the entropy from the hopping site configuration. A well-known case is the Heikes formula,[33] which gives the entropy per carrier as

$$k_B \ln \frac{2(1-p)}{p}, \tag{3}$$

where p is the ratio of the carrier number to the site number available for hopping. The term $\ln[(1-p)/p]$ corresponds to the configuration entropy which is added to the spin entropy of $k_B \ln 2$. This additional entropy can be associated with the zero-field entropy at high temperature observed in this compound. Tsukada *et al.*[6] found that the electronic entropy for $x = 0.5$ and 1.5 exceeds $3k_B \ln 2$ (the maximum spin entropy of Cu^{2+}) above 60 K. In particular, the $x = 0.5$ sample shows a significantly large entropy, which is unlikely to come from the doped Ru $4d$ electrons alone. Such behavior cannot be understood without the charge degrees of freedom of the Cu^{2+} holes.

Based on the entropy argument above, we will propose an origin of the field-induced delocalization. Usually, magnetic fields favor a phase having a larger magnetization because the system gains the internal energy $-MdH$ with field. In the present case, the antiferromagnetic phase has a larger magnetization, and the magnetic field is expected to stabilize this phase. Thus one can expect field-induced *localization*, which is incompatible with the observation in Fig. 1. We suggest that the field-induced delocalization is basically entropy-driven. When the entropy gain $-SdT$ overcomes the internal energy loss $-MdH$, the system favors a more entropic phase. Of course, this discussion is purely phenomenological; the microscopic origin should be clarified by microscopic measurements such as magnetic resonance and photoemission spectroscopy.

Next let us examine the field-driven delocalization of the Cu^{2+} hole in the charge sector. Figure 4 shows the high-field magnetoresistance ($\Delta\rho/\rho_0$) as a function of external field at 4.2, 7, and 10 K for $x = 1.5$. A large negative magnetoresistance of 70% is observed at 4.2 K. We measured the magnetoresistance of the same sample in static magnetic fields of up to 14 T, and found that the magnetoresistance is isotropic between the longitudinal and the transverse configurations (not shown). This suggests that the large magnetoresistance does not arise from the orbital contribution due to the Lorentz force, but from the spin contribution.

Since the magnetoresistance is a second-order effect between conduction electrons and external fields, various intermediate processes are possible, which makes it difficult to clarify their origin experimentally. Therefore, let us suffice it to say that the magnetoresistance observed here is difficult to be associated with any origins known thus far. Main causes of negative magnetoresistance are (i) ferromagnetic interaction/fluctuation,[32,34,35] (ii) double exchange interaction,[36,37] (iii) the Kondo coupling,[38] and (iv) localization with strong spin-orbit or impurity spin scattering.[39–41] Clearly we can exclude the possibilities of (i) and (ii), because there is no trace of ferromagnetic interaction in the present system. As for (iii), we expect $\ln H$ dependence for the magnetoresistance together with $\ln T$ dependence for the zero-field resistance, which is not observed experimentally. The possibility of (iv) is also excluded by comparing the magnetoconductivity $\Delta\sigma$ shown in the inset of Fig. 4 with theoretical calculation. According to the weak localization theory, $\Delta\sigma$ should be proportional to $\sqrt{H}$ and the magnitude increases with decreasing temperature,[41] which is highly incompatible with the measured data.

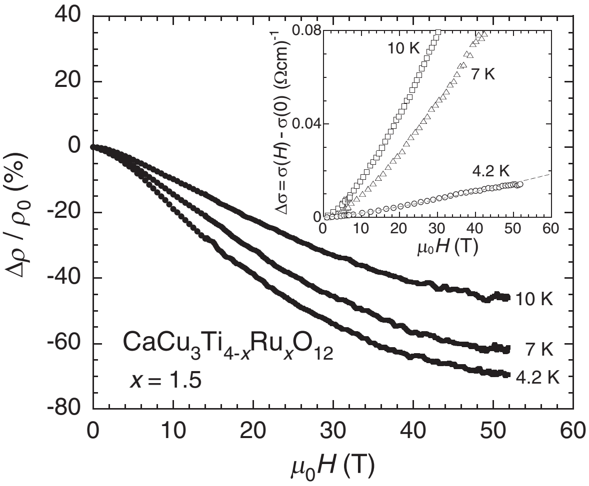

FIG. 4. High-field magnetoresistance of $CaCu_3Ti_{4-x}Ru_xO_{12}$ ($x = 1.5$) at 4.2, 7, and 10 K. The inset shows the field dependence of $\Delta\sigma = \sigma(H) - \sigma(0)$.

Finally, we will make a brief comment on the relationship of the negative magnetoresistance to the field-driven delocalization picture. When the magnetic fields delocalize the Cu^{2+} holes, they can increase the carrier concentration Δn and concomitantly increase the conductivity as $\Delta\sigma \sim \Delta n$. This is rarely seen in the magnetoresistance of other disordered materials, and the magnetic fields usually modify the mobility as $\Delta\sigma \sim \Delta\mu$. Accordingly, the observed magnetoconductivity includes the two contributions as $n\Delta\mu + \mu\Delta n$, which cannot be separated at this stage. Thus the origin of the magnetoconductivity should be further investigated by measuring other transport parameters such as the Hall and Seebeck coefficients in high fields.

IV. SUMMARY

In summary, we have investigated the high-field magnetization and magnetoresistance of the A-site ordered perovskite oxide $CaCu_3Ti_{4-x}Ru_xO_{12}$ ($0 \leqslant x \leqslant 4$). The magnetization for the end phases ($x = 0$ and 4) is linear in external field, whereas that for $0.5 \leqslant x \leqslant 1.5$ tends to saturate in high fields. For $x = 1.5$, a large negative magnetoresistance of -70% is observed. We have qualitatively explained the nonlinear magnetization and the negative magnetoresistance, and have proposed a possible mechanism of the field-induced delocalization, where the holes on the Cu^{2+} ions are delocalized in order to maximize the entropy related to the hopping site configuration. The present study has revealed that the hole on the Cu^{2+} ion in $CaCu_3Ti_{4-x}Ru_xO_{12}$ is on the verge of localization, which is partially delocalized by external fields. Since the argument given here is based on the thermodynamics, this is independent of the details of the system. To clarify a microscopic origin for the field-driven delocalization, a precise structure analysis and microscopic measurements like magnetic resonance in high magnetic fields are indispensable.

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