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Transport properties and specific heat of $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ in magnetic fields

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The magnetoresistance (MR) and specific heat in magnetic fields for the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ are presented. Resistive measurements in high magnetic fields show that the field dependence of the transition temperature is significantly different from those observed in other high-T_c cuprates. The sample $RuSr_2GdCu_2O_8$ shows a systematic change in magnetoresistance (MR): The MR is negative at temperatures above the magnetic ordering temperature (T_{Curie}); Below T_{Curie} the MR displays a positive peak at low fields, but becomes negative at high fields. However, the sample $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ shows a negative MR in the whole measuring temperature range. Both of the samples show a maximum negative magnetoresistance at about T_{Curie}. The specific heat anomaly is suppressed by the field, and the peak-temperature slightly moves down with the field.

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INTRODUCTION

Recently, coexistence of superconductivity and ferromagnetism has been reported in the hybrid ruthenate-cuprate compounds $RuSr_2GdCu_2O_8$ (Ru-1212) and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ (Ru-1222).[1–9] A very recent powder neutron scattering study by Lynn et al. has provided convincing evidence that the Ru moments order antiferromangeically at $T_N=136(2)$ K, coincident with the reported onset of ferromagnetism.[10] In contrast to ferromagnetic superconductors, in which the superconducting transition temperature (T_c) is higher than the magnetic transition temperature T_m, the T_m of Ru-1212 and Ru-1222 is higher than T_c, so they have been called superconducting ferromagnets.[4] The superconductivity in superconducting ferromagnets arises in the state with a well developed magnetic order, contrary to previous studies of which ferromagnetism arises in the superconducting state. Both the tetragonal Ru-1212 and Ru-1222 are derived from the $LnBa_2Cu_3O_7$ (LnBCO) structure (Ln: lanthanide), the Ru ions replace the Cu(1), and only one distinct Cu site (corresponding to Cu(2)) exists, with fivefold pyramidal coordination. For Ru-1212, the Cu-O layers are connected by perovskite $SrRuO_3$ layers through the apical oxygen atoms. For Ru-1222, the Ln layer in LnBCO is replaced by inserting a fluorite type $(Ln,Ce)O_2$ layer, thus shifting alternate perovskite blocks by $(a+b)/2$. Ru-1212 and Ru-1222 contain the two CuO_2 planes and one RuO_2 layer in the unit cell.

The remaining unresolved question concerns the homogeneity of the superconducting (SC) phase. Evidence in favor of bulk SC state has been obtained for Ru-1212 from differential heat capacity measurements.[11] However, Chu *et al.* recently cast doubts as to whether Ru-1212 is a bulk superconductor.[12] They find that a bulk Meissner effect does not exist in Ru-1212. Alternatively, they suggest that the absence of a Meissner effect could be attributed to the creation of a spontaneous vortex phase (SVP). Such a SVP can be expected to form in a FM superconductor if the spontaneous magnetization, $4\pi M$, exceeds the lower critical field H_{c1} [such as $4\pi M>H_{c1}$ $(T=0)$].[8,12,13] Otherwise, if $H_{c1}(T=0)>4\pi M$, the Meissner state will be stable at low temperature. More recently, Bernhard *et al.*[14] presented low-field dc magnetization measurements on polycrystalline Ru-1212 samples, which show evidence that a bulk Meissner state develops in the pure compounds at low temperature, with $T^{\mathrm{ms}}\leqslant 30$ K varying from sample to sample. They showed that the SVP, which forms an intermediate temperature $T^{\mathrm{ms}}<T<T_c$, is characterized by unique thermal hysteresis effects. They believed that the absence of a Meissner-phase in Ru-1212 as reported by Chu *et al.*[12] can be explained in term of a moderate reduction of H_{c1} due to impurity scattering or grain size effects.

It is believed that the magnetic order arises from ordering of Ru ions in the RuO_2 layer, the transport occurs in the CuO_2 layers. In this paper, we investigate the interaction between the transport carriers and the ferromagnetic Ru moments by magnetotransport property measurements. The specific heat is also studied in the fields up to 6 T. It was found that the specific heat anomaly is suppressed by the field, and the peak-temperature moves down with the field. This is different from that reported by Tallon *et al.*[11]

EXPERIMENT

Similar to previous reports,[1,5,6,12] $RuSr_2GdCu_2O_8$ was synthesized by solid-state reaction of stoichiometric powders of RuO_2, $SrCO_3$, Gd_2O_3 and CuO. Required amounts of these materials were ground, preheated at 960 °C in air for 10 h, then reground and reacted as pellets at 1010 °C in flowing nitrogen for 24 h to obtain precursor material (Sr_2GdRuO_6 and Cu_2O) and minimize the formation of $SrRuO_3$.[1] These resulting samples are pulverized, pressed into pellets and calcined at 1050 °C in air for 24 h with an intermediate grinding. In each reaction, the sample was cooled to room temperature by furnace. Subsequently, the as-prepared sample $RuSr_2GdCu_2O_8$ was annealed in flowing oxygen at 1050 °C for 72 h. To synthesize $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$, stoichiometric powders of RuO_2, $SrCO_3$, Gd_2O_3, CeO_2, and CuO were preheated in air and calcined in flowing nitrogen similar to the synthesis of $RuSr_2GdCu_2O_8$, then the samples were reground, pressed into pellets and calcined in flowing oxygen. Finally, the samples were annealed in an oxygen pressure of 50 bars. With the exception that preheating in air was at 960 °C for 10 h, all reactions were performed at 1050 °C for 24 h. Powder x-ray diffraction (XRD) measurements were carried out in Rigaku D/max-γA x-ray diffractometer with graphite monochromatized Cu K_α radiation ($\lambda = 1.5406$ Å). Resistivity measurements were performed by the standard four-probe method down to 4.2 K. The specific heat was measured between 4.2 K to 300 K in an adiabatic, continuous-heating type calorimeter using platinum thermometry in magnetic fields up to 14 T. Absolute accuracy is 0.8% from 15 K to 300 K and the precision is about 0.05%. The heating rate was 15 mK/sec over the whole temperature range. Magnetoresistance was measured with the magnetic field up to 14 T using an Oxford Instruments superconducting magnet.

RESULTS AND DISCUSSION

Powder x-ray diffraction (XRD) measurements indicate that all the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ are single phase (>95%) materials and have the tetragonal structure with lattice parameter of $a = 3.838$ Å and $c = 11.559$ Å, and $a = 3.844(1)$ Å and $c = 28.615(7)$ Å, respectively. In the x-ray diffraction patterns for the samples Ru-1212 and 1222, only one very weak peak at 2θ of about 30.75° cannot be indexed, and which was identified to be from the double perovskite Sr_2GdRuO_6. Our attempts to completely get rid of the impurity phase were unsuccessful.

Figure 1 shows the resistivity transitions for both Ru-1212 and Ru-1222 samples measured in magnetic fields up to 12 T. The two samples show nearly the same behavior. We observe a broad resistive transition with a sharp onset temperature at ~50 K, which decreases with increasing magnetic field for the samples Ru-1212 and Ru-1222. The zero-resistance temperature shows a similar decrease to that of the onset transition. It decreases rapidly at low fields, while slowly at high fields. This behavior is similar to that observed by Chu *et al.*[12] in the Ru-1212 system. It is worthy to point out that little difference in the superconducting transition is observed between 8 and 12 T for the sample Ru-1212. The zero-resistance temperature stays almost unchanged for fields higher than 8 T for both of the samples Ru-1212 and Ru-1222. These results indicate that the field dependence of the zero resistance temperature for Ru-1212 and Ru-1222 is quite different from those observed in other high-T_c cuprates which are governed by the giant flux motion at low temperature. The observed behavior is also not consistent with the picture of strong flux pining in a conventional three-dimensional system. This result suggests that the vortex dynamics of hybrid ruthenate-cuprate compounds may be intrinsically different from that of the other high temperature superconducting cuprates.

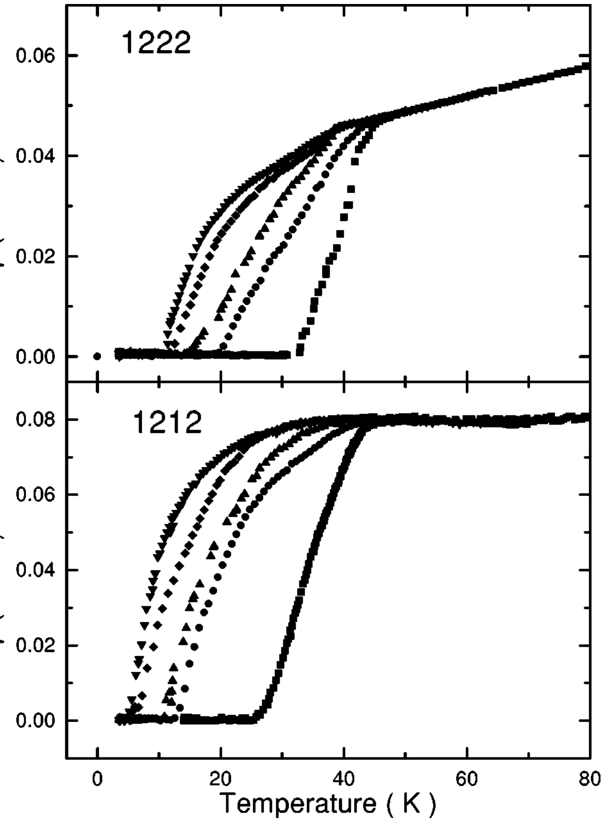

FIG. 1. The temperature dependence of resistivity in magnetic fields of up to 12 T for the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$; squares: 0 T; circles: 2 T; up triangles: 4 T; diamonds: 8 T; down triangles: 12 T.

Figure 2 shows the magnetoresistance data for temperatures above and below T_{Curie}, which is 132 K and 175 K for the samples Ru-1212 and Ru-1222, respectively. The sample Ru-1212 shows a negative magnetoresistance for temperatures higher than T_{Curie}. The magnetoresistance decreases as H^2 for temperatures well above T_{Curie}. It is believed that this field dependence arises from the freezing out of spin-disorder scattering as the Ru moments become aligned with the magnetic field.[9] The magnetoresistance shows an H-linear dependence over the range of H investigated close to T_{Curie}. For $T < T_{Curie}$, the magnetoresistance behavior is quite different from that for $T > T_{Curie}$. Below T_{Curie} a positive magnetoresistance peak is observed at low fields. The amplitude of the peak increases with decreasing temperature. This behavior is consistent with that reported by McCrone *et al.* in Ru-1212[9] The Ru-1222 magnetoresistance is negative for temperatures ranging from 300 K to the superconducting onset temperature, the peak appearing in Ru-1212 at low fields and below T_{Curie} is not observed. However, it is found that the field dependence of the MR for $T > T_{Curie}$ is the same as that observed in Ru-1212, that is: the MR is proportional to H^2. The MR shows an H-linear behavior near the magnetic ordering temperature. In summay, the MR behavior for the sample Ru-1222 is consistent with that for the sample Ru-1212 except a positive peak is observed at low fields in Ru-1212. The difference in MR between Ru-1212 and Ru-1222 could be due to the weak-ferromagnetic behavior of Ru-1222, in

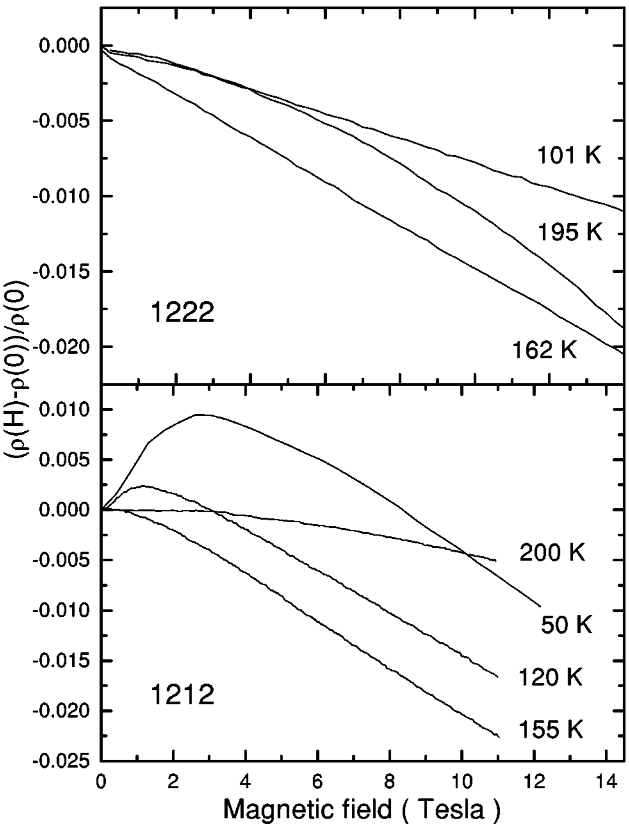

FIG. 2. The magnetic field dependence of magnetoresistance for the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$ at various temperatures.

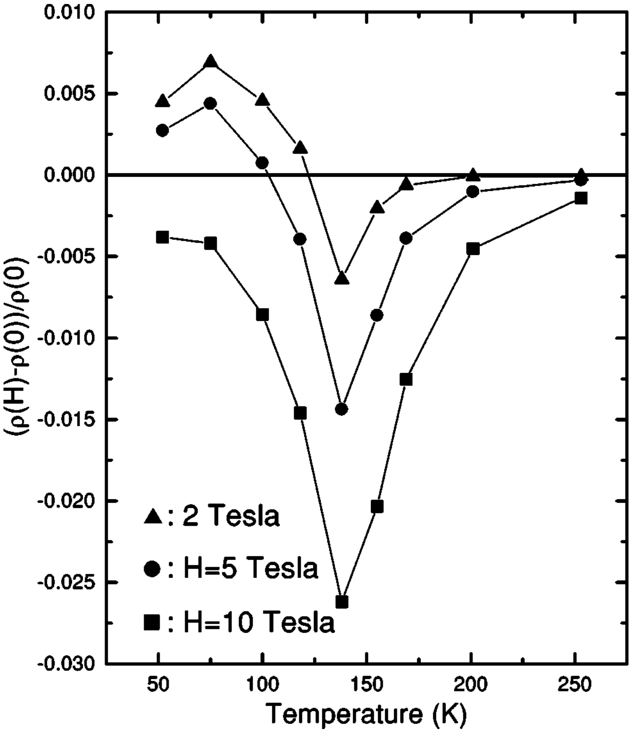

FIG. 3. The temperature dependence of magnetoresistance for the sample $RuSr_2GdCu_2O_8$ at various magnetic fields.

which magnetic ordering at $T_N(\mathrm{Ru}) = 175$ K is observed at low field and the $T_N(\mathrm{Ru})$ is rapidly shifted to low temperature with increasing the applied field.[3]

Figure 3 shows the temperature dependence of the MR for applied fields of 2, 5, and 10 T for the Ru-1212 sample. It is found that a maximum negative MR occurs at T_{Curie}, and the absolute value of the MR decreases monotonically away from T_{Curie}. At high fields the MR is always negative over the whole temperature range. At low fields the MR is positive below T_{Curie}, and negative above T_{Curie}. For the Ru-1222 sample, a negative maximum MR is also observed at T_{Curie}. These results suggest the MR behavior observed in Ru-1212 and Ru-1222 is dominated by the interaction between the carriers and Ru moments. McCrone *et al.* made a good fit to the data for the temperatures well above T_{Curie}, giving the exchange interaction between the spins and conduction carriers of 27–47 meV.[9] There are two possible scenarios for the exchange interaction between conduction carriers and the spins. One is that the transport occurs in the CuO_2 planes, the RuO_2 layer is a local-moment ordering. The other is that significant current flows in the RuO_2 planes, and the MR is determined by the interaction between Ru spins and RuO_2 carriers, which can be large without affecting the superconductivity. However, the behavior of resistivity and thermoelectric power observed in Ru-1212 and Ru-1222 samples is similar to that for other cuprate superconductors. So it is difficult to understand the resistivity and thermoelectric power data within this scenario. However, it can not be understood why such a large exchange interaction between the carriers in CuO_2 layers and the spins in RuO_2 layers does not affect superconductivity. In addition, how to understand the different vortex dynamics of the hybrid ruthenate-cuprate compounds from other cuprate superconductors is another open question.

Figure 4 shows the specific heat C/T and $\Delta C/T$ as a function of temperature in magnetic fields from 0 to 6 T for the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$. The $\Delta C/T$ is obtained by subtracting C_{fit}/T from the C/T. The C_{fit} was obtained by fitting the raw data without specific anomaly. It is very clear that there exists a specific heat jump at the temperatures of about 34 K and 38 K for the samples $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O_y$, respectively. The temperature corresponding to the specific heat anomaly is the same as the superconducting transition temperature. The magnitude of the $\Delta C/T$ is about 0.08 $\mathrm{mJ/gK^2}$ without magnetic field for the two samples, being comparable to other cuprates. The existence of a sizable specific heat confirms the presence of bulk superconductivity. A remarkable feature of the $\Delta C/T$ versus T curves for the Ru-1212 and Ru-1222 samples is that the specific jump onset temperature is independent of the applied magnetic field, which is seen in Figs. 4(a) and 4(b) for both of the samples. This is consistent with that observed in $YBa_2Cu_3O_{7-\delta}$.[15] Junod *et al.* explained that this phenomenon results from a compensation of two effect: the decrease of the mean-field critical temperature and the simultaneous increase of the transition width. A reduction in the amplitude of the specific heat jump and a very slight shift down to the low temperatures for the peak (T_c) are observed in both of Ru-1212 and Ru-1222. This is also

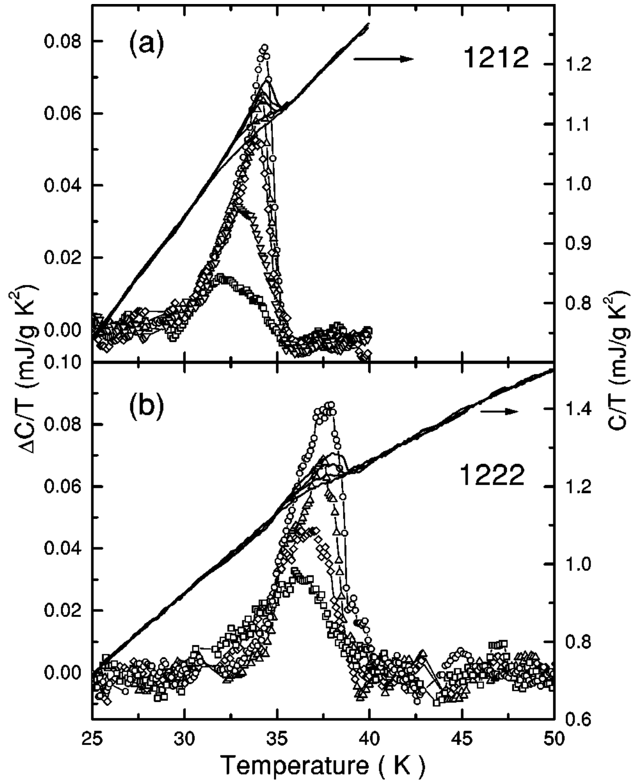

FIG. 4. The specific heat C/T and $\Delta C/T$ in magnetic fields as a function of temperature for the samples $\mathrm{RuSr_2GdCu_2O_8}$ (circles: 0 T; up triangles: 1 T; diamonds: 2 T; down triangles: 4 T; squares: 6 T; solid lines for C/T) and $\mathrm{RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O}_y$ (circles: 0 T; up triangles: 1 T; diamonds: 3 T; squares: 6 T; solid lines for C/T).

similar to that observed in $\mathrm{YBa_2Cu_3O_{7-\delta}}$.[15] In contrast, Tallon *et al.* recently reported differential heat capacity ($\gamma = C/T$) measurements in magnetic fields for the sample Ru-1212. They found that T_c determined by the midpoint (or maximum)slope in $\gamma(T)$ moves up some 4.5 K when the field is increased to 4 or 5 T.[11] This upward shift in T_c with field was ascribed to the triplet pairing, which is enhanced in a magnetic field. Chu *et al.*[12] argued that the possible inclusion of a very small amount of the antiferromagnetic phase $\mathrm{Sr_2GdRuO_6}$ in Ru-1212 and Ru-1222 samples can give rise a ΔC_p of a magnitude similar to that of the underdoped cuprate superconductor, because of the large entropy associated with the transition at about 30 K. To rule out this possiblity, we measured the specific heat of the nonsuperconducting $\mathrm{RuSr_2GdCu_2O_8}$ sample. No specific heat anomaly is observed in the temperature range between 20 K and 50 K. The amount of the impurity phase $\mathrm{Sr_2GdCuO_6}$ in the nonsuperconducting $\mathrm{RuSr_2GdCu_2O_8}$ is the same as the superconducting sample we studied because the nonsuperconducting sample was obtained by annealing the superconducting sample in flowing nitrogen at 500 °C for 48 h. This result further suggests that the specific heat jump arises from the superconducting transition. However, it is difficult to understand the difference between a slight shift down to low temperatures with the magnetic field in T_c determined by specific heat measurements and an apparent decrease of superconducting transition onset with magnetic field in the low field range determined by resistivity measurements.

CONCLUSION

The samples $\mathrm{RuSr_2GdCu_2O_8}$ (Ru-1212) and $\mathrm{RuSr_2Gd_{1.4}Ce_{0.6}Cu_2O}_y$ (Ru-1222) have been studied by resistivity, and specific heat in magnetic fields and magnetoresistance. It is found that zero-resistance temperature rapidly decreases with the magnetic field at low fields as well as the onset transition temperature, while the zero-resistance temperature stays almost unchanged for the fields higher than 8 T for both of the samples Ru-1212 and Ru-1222, suggesting that the vortex dynamics of hybrid ruthenate-cuprate compounds may be intrinsically different from that of the other high temperature superconducting cuprates. A maximum negative MR appears at T_{Curie} for both of the samples, MR shows a H^2 dependence well above T_{Curie}, while a H-linear dependence close to T_{Curie} for the samples Ru-1212 and Ru-1222. The sample Ru-1212 also shows a positive MR below T_{Curie} at low magnetic fields. A reduction of the amplitude of the specific heat jump and a very slight shift down to the low temperatures for the peak (T_c) with increasing applied field are observed in both Ru-1212 and Ru-1222. This is also similar to that observed in $\mathrm{YBa_2Cu_3O_{7-\delta}}$.[15] In contrast, Tallon *et al.* recently report a field-induced increase in T_c by differential heat capacity ($\gamma = C/T$) measurements for the sample Ru-1212.

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