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Possible ordering of Ru and Cu in the charge-reservoir of magneto-superconductor $RuSr_2GdCu_2O_8$ (Ru-1212): Magnetic, transport, and TEM microstructural studies

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Magnetization vs temperature behavior of $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) measured in an field of 5 Oe, shows a clear branching of zero-field-cooled (ZFC) and field-cooled (FC) curves around 140 K, a cusp at 135 K, and a diamagnetic transition around 20 K (in the ZFC branch). The cusp at 135 K is due to the antiferromagnetic ordering of the Ru moments. The magnetization-field isotherms, below 50 K, show a nonlinear contribution from a ferromagnetic component. The resistance vs temperature behavior of the compound, in applied fields of 0, 3, and 7 T, confirms that the sample is superconducting at around 20 K. The superconducting transition exhibits field broadening of a type different than that known for conventional high T_c superconductors. The magnetoresistance (MR) is negative above the Ru magnetic ordering temperature of 135 K, while below this temperature, MR displays a positive peak in low fields and becomes negative in higher fields. A maximum of 2% is observed for the negative MR value at the Ru magnetic ordering temperature. An electron diffraction pattern obtained for this Ru-1212 sample shows two types of superstructure; one with a weak spot at the center of the $a-b$ rectangle and the other only along the b direction. It is possible that either Ru/Cu or Ru^{4+}/Ru^{5+} ordering of $2b$ periodicity takes place along the b direction. [DOI: 10.1063/1.1456444]

I. INTRODUCTION

Recent observations of coexistence of superconductivity in $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) at low temperatures (~30 K) with bulk magnetic ordering at 133 K has attracted considerable attention.[1–11] A similar situation has been observed earlier for $RuSr_2(Gd,Sm,Eu)_{1.6}Ce_{0.4}Cu_2O_{10-\delta}$ (Ru-1222).[12,13] The Ru-1212 is structurally related to $CuBa_2YCu_2O_{7-\delta}$ (Cu-1212) with Cu in the charge reservoir in the latter replaced by Ru so that the Cu–O chain is replaced by a row of Ru–O octahedral. This results in an increase in the nominal overall oxygen content to 8 per formula unit in Ru-1212.[1–7] Although bulk magnetism due to magnetic ordering of the Ru moments in Ru-1212 has been confirmed from μSR studies,[1] the exact type of ordering is still debated.[1–3,8] In particular, the results of neutron scattering[8] and magnetization studies[1–5] do not agree with each other. While the former concludes the magnetic ordering to be of antiferromagnetic nature, the latter indicates the presence of a ferromagnetic component as well. The appearance of bulk superconductivity in Ru-1212 at low temperatures was initially criticized.[9,10] However, a recent report argues that bulk superconductivity exists in this compound within a magnetically ordered state.[14] Appearance of bulk superconductivity in Ru-1212 has also been confirmed from specific heat (C_P) measurements,[7,15] though the existing reports do not agree with each other in terms of C_P measurements under magnetic field. While one work[7] points towards triplet pairing, the other[15] suggests a normal under-doped high-T_c superconductor (HTSC) situation in Ru-1212. Unlike Cu-1212, Ru-1212 is rather stable in terms of removal/insertion of oxygen.[16] Very recently, it was reported that T_c of Ru-1212 could be increased up to 74 K for optimized value of x in $Ru_{1-x}Cu_xSr_2GdCu_2O_{8-\delta}$.[17] A microstructural analysis of Ru-1212 showed a superstructure along the $a-b$ plane due to tilting of the RuO_6 octahedra.[3] This superstructure was further confirmed from neutron diffraction studies.[18]

In the present contribution we present the results of magnetic, transport and TEM studies on $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) system.

II. EXPERIMENT

The Ru-1212 sample was synthesized through a solid-state reaction route from stoichiometric amounts of RuO_2, SrO_2, Gd_2O_3, and CuO. Calcinations were carried out on mixed powders at 1000 °C, 1020 °C, and 1040 °C each for 24 h with intermediate grindings. The bar-shaped pellets were annealed in flowing oxygen at 1060 °C for 40 h and subsequently cooled slowly over a span of 20 h to room temperature. X-ray diffraction (XRD) patterns were obtained for the sample at room temperature. Magnetization measurements were carried out on a superconducting quantum interference device (SQUID) magnetometer (Quantum Design: MPMS-5S). Resistivity measurements under magnetic fields of 0–7

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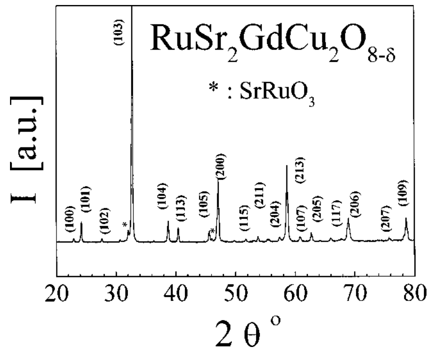

FIG. 1. X-ray diffraction pattern obtained for the Ru-1212 sample.

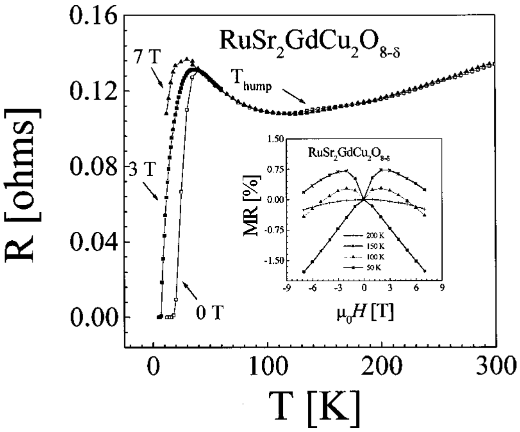

FIG. 2. $R-T$ plots in 0, 3 and 7 T applied fields for the Ru-1212 sample. Inset shows the MR at various temperatures and applied fields for the same sample.

T were performed in the temperature range of 5–300 K using a four point method (Quantum Design: PPMS). Electron diffraction patterns were obtained using a transmission electron microscope (TEM; Hitachi H-9000) operated at an accelerating voltage of 300 kV.

III. RESULTS AND DISCUSSION

The present $RuSr_2GdCu_2O_{8-\delta}$ sample possesses a tetragonal Ru-1212 structure with space group, $P4/mmm$, and lattice parameters, $a=b=3.8337(6)$ Å and $c=11.4926(9)$ Å. The x-ray pattern of the sample is shown in Fig. 1. Small amount of $SrRuO_3$ is seen as an impurity phase, as marked on the pattern.

Figure 2 shows the resistance vs temperature $(R-T)$ plot for the Ru-1212 sample in magnetic fields of 0 T, 3 T, and 7 T. In the absence of a magnetic field, the $R-T$ behavior is metallic down to 150 K and semiconducting between 150 K and 25 K, with a superconducting transition onset (T_c^{onset}) at 25 K and $R=0$ below 20 K. This behavior is typical of an underdoped HTSC copper oxide system. Also observed is an upward hump (T_{hump}) in the $R-T$ curves at around 140 K, which indicates the possibility of antiferromagnetic ordering of the Ru moments. The $R-T$ behavior in an applied field of 7 T is nearly the same as that in zero applied field at temperatures above T_c^{onset}, except that T_{hump} is completely smeared out due to a possible change in the magnetic structure. Also in 7 T applied field, the values of T_c^{onset} decreases down to around 10 K and $R=0$ is not observed down to 5 K. In an intermediate field of 3 T, both T_c^{onset} and $T_c^{R=0}$ are lowered (from 25 K) to 20 K and (from 20 K) to 10 K, respectively. For conventional HTSC, T_c^{onset} remains nearly the same in applied fields, while $T_c^{R=0}$ decreases. This leads to an increased transition width $(T_c^{\text{onset}}-T_c^{R=0})$ as the magnetic field is applied. Thus the type of magnetic field broadening of the transition in Ru-1212 is different than that for conventional HTSC. In earlier reports on Ru-1212, the T_c^{onset} was also found to decrease as in the present case.[4,9,10,15] The broadening of the transition width in a magnetic field is presumably due to the formation of superconducting-normal-superconducting/superconducting-insulator-superconducting (SNS/SIS), junctions/clusters in the sample, as reported earlier.[19] A nonsuperconducting $RuSr_2GdCu_2O_{8-\delta}$ block, might be stacked between superconducting $Ru_{1-x}Cu_xSr_2GdCu_2O_{8-\delta}$, blocks resulting in a sort of SIS or SNS junction inside the material. The inset in Fig. 2 shows the magnetoresistance (MR) behavior of the present Ru-1212 sample as a function of field and temperature. The MR value is negative in fields up to 7 T at temperatures of 150 and 200 K, which are above the magnetic ordering temperature of Ru moments. The maximum negative MR of around 2% is observed at 150 K, which is close to the magnetic ordering temperature of Ru moments (~140 K). At 100 K and 50 K, which are below the Ru magnetic ordering temperature, the MR value displays a positive peak at a low field and becomes negative at higher fields. This observation is in general agreement with previous reports.[5,15]

Figure 3 shows the magnetic moment vs temperature behavior in the temperature range of 5–160 K in an applied field of 5 Oe, in both zero-field-cooled (ZFC) and field-cooled (FC) situations. As temperature decreases, one observes a branching in ZFC and FC curves around 140 K, a cusp at 135 K and a diamagnetic transition in the ZFC part around 20 K. The downturn at 135 K is indicative of the antiferromagnetic nature of the Ru moments. The FC part is seen increasing and later saturating due to the contribution from paramagnetic Gd moments. The inset in Fig. 3 shows the isothermal magnetization (M) vs applied field (H) behavior for the Ru-1212 sample at various temperatures. The isothermal magnetization as a function of magnetic field may be viewed as

$$M(H)=\chi H+\sigma_s(H), \qquad (1)$$

where χH is the linear contribution from "antiferromagnetic" Ru moments and paramagnetic Gd moments and $\sigma_s(H)$ represents the weak ferromagnetism due to "canted" Ru moments. The weak ferromagnetic contribution starts to appear only below 100 K and at high fields above ~3 T. Above 100 K, the magnetization vs field plot remains purely linear. The appearance of a ferromagnetic component at low temperatures within antiferromagnetically ordered Ru spins may happen due to slight canting of moments. Some neutron diffraction data clearly indicate such a possibility.[8]

The MR peak, at around 3 T, below the Ru magnetic ordering temperature, may have a common origin with the nonlinearity in the isothermal magnetization. Ru-1212 has

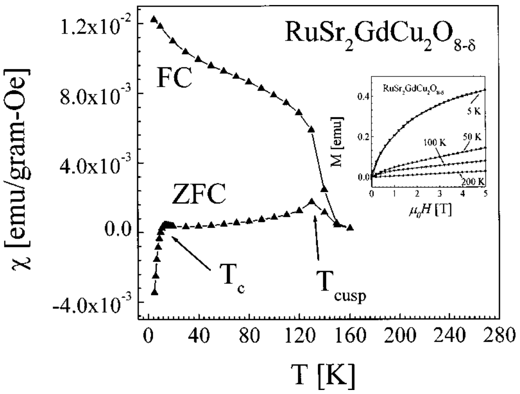

FIG. 3. $M-T$ plot for the Ru-1212 sample with both FC and ZFC situations in an applied field of 5 Oe. Inset shows the isothermal magnetization vs applied field plots at various temperatures.

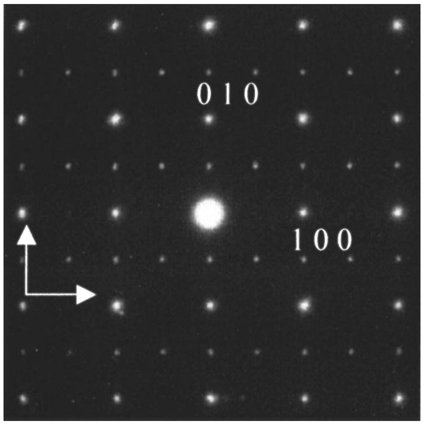

FIG. 4. Electron diffraction pattern for the Ru-1212 sample with incident beam // c axis.

been reported to be predominantly of antiferromagnetic Ru moments nature in low fields but mainly ferromagnetic in high fields.[20] This gets further credence from the fact that in the $R-T$ data (Fig. 2), T_{hump} is completely smeared out at 7 T due to change in the magnetic structure from an antiferromagnetic one to ferromagnetic one. In the higher magnetic fields, the antiferromagnetic ordering of the Ru moments develops a ferromagnetic component due to canting of moments, and changes the MR nature from small positive to small negative.

Figure 4 shows an electron diffraction pattern of the $a-b$ plane of the Ru-1212 sample. Two types of superstructure are seen: one weak spot at the center of the $a-b$ rectangle and the other along the b direction. An earlier microstructural analysis of Ru-1212 showed only one type of superstructure along the $a-b$ plane due to the tilting of the RuO$_6$ octahedra, as confirmed from neutron diffraction studies.[17] In the present case either Ru/Cu or vacancy ordering of $2b$ periodicity may take place along the b direction. It seems that certain superconducting clusters of the composition $\mathrm{Ru}_{1-x}\mathrm{Cu}_x\mathrm{Sr}_2\mathrm{GdCu}_2\mathrm{O}_{8-\delta}$, may be present within the $\mathrm{RuSr}_2\mathrm{GdCu}_2\mathrm{O}_{8-\delta}$ phase, giving rise to SNS/SIS junctions in the resulting material. This may account for the different type of broadening of the resistive transition in magnetic field for many Ru-1212 samples[4,9,10,15] including the present one. We would like to mention that possible presence of SNS/SIS junctions is strictly sample dependent. We argue that all reported Ru-1212 magnetosuperconducting samples may not be homogeneous in composition, and Ru/Cu ordering at the charge-reservoir cation site may be present in some of them. In particular, Ru/Cu ordering becomes more complicated as the two elements cannot be distinguished without ambiguity by neutron diffraction, a technique mainly used for fixing various cation positions in materials. Besides Ru/Cu mixing, another possibility worth considering would be the charge ordering at Ru-site. In particular, the mixed valence of Ru(Ru^{5+}/Ru^{4+}) has recently been demonstrated from x-ray absorption near edge spectroscopy (XANES) studies.[11] Finally we would like to mention that we also obtain regions within the same sample, which possess only the zero-centered spot and not the b-axis superstructure spot. In fact the b-axis super structure regions are much less abundant than the normal zero-centered ones. This shows that ordering is possibly from Ru and Cu instead of universally distributed Ru^{4+} and Ru^{5+} in the compound. There are regions of composition $\mathrm{Ru}_{0.5}\mathrm{Cu}_{0.5}\mathrm{Sr}_2\mathrm{GdCu}_2\mathrm{O}_8$ lying in minority with stoichiometric compound $\mathrm{RuSr}_2\mathrm{GdCu}_2\mathrm{O}_8$. Interestingly the former composition is reported to be superconducting but not magnetic.[17] Our results clearly indicate the possibility of phase separation in Ru-1212 compound and hence refute the coexistence of superconductivity and magnetism in intrinsically pure Ru-1212.

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