
15 May 2002

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V. P. Awana et al., "Possible Ordering of Ru and Cu in the Charge-Reservoir of Magneto-Superconductor $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212): Magnetic, Transport, and TEM Microstructural Studies," *Journal of Applied Physics*, vol. 91, no. 10, pp. 8501-8503, American Institute of Physics (AIP), May 2002.

The definitive version is available at <https://doi.org/10.1063/1.1456444>

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Possible ordering of Ru and Cu in the charge-reservoir of magneto-superconductor $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212): Magnetic, transport, and TEM microstructural studies

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Magnetization vs temperature behavior of $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ (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 $\text{Ru}^{4+}/\text{Ru}^{5+}$ ordering of $2b$ periodicity takes place along the b direction. © 2002 American Institute of Physics. [DOI: 10.1063/1.1456444]

I. INTRODUCTION

Recent observations of coexistence of superconductivity in $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ (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 $\text{RuSr}_2(\text{Gd,Sm,Eu})_{1.6}\text{Ce}_{0.4}\text{Cu}_2\text{O}_{10-\delta}$ (Ru-1222).^{12,13} The Ru-1212 is structurally related to $\text{CuBa}_2\text{YCu}_2\text{O}_{7-\delta}$ (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 scattering⁸ and magnetization studies¹⁻⁵ 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 re-

ports do not agree with each other in terms of C_p measurements under magnetic field. While one work⁷ points towards triplet pairing, the other¹⁵ 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 $\text{Ru}_{1-x}\text{Cu}_x\text{Sr}_2\text{GdCu}_2\text{O}_{8-\delta}$.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 $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ (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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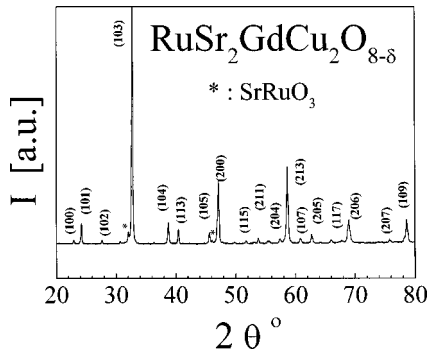


FIG. 1. X-ray diffraction pattern obtained for the Ru-1212 sample.

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 $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ 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 $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ block, might be stacked between superconducting $\text{Ru}_{1-x}\text{Cu}_x\text{Sr}_2\text{GdCu}_2\text{O}_{8-\delta}$, blocks resulting in a sort of SIS

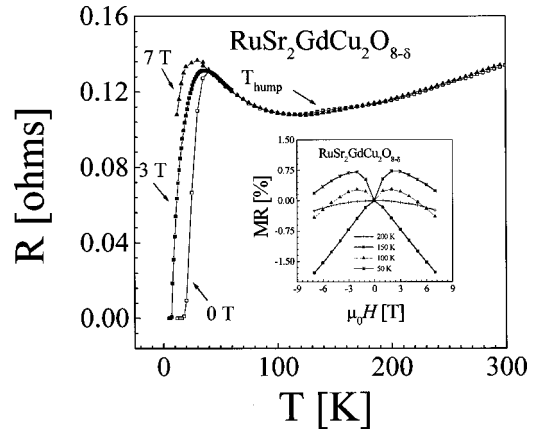


FIG. 2. $R-T$ plots in 0, 3 and 7 T applied fields for the Ru-1212 sample. Inset shows the MR at various temperatures and applied fields for the same sample.

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

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

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

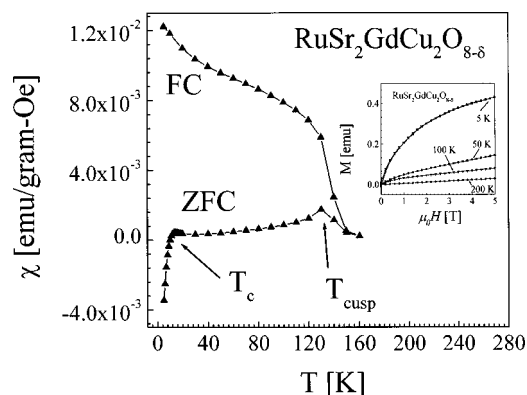


FIG. 3. M - T plot for the Ru-1212 sample with both FC and ZFC situations in an applied field of 5 Oe. Inset shows the isothermal magnetization vs applied field plots at various temperatures.

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 $\text{Ru}_{1-x}\text{Cu}_x\text{Sr}_2\text{GdCu}_2\text{O}_{8-\delta}$, may be present within the $\text{RuSr}_2\text{GdCu}_2\text{O}_{8-\delta}$ 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 ($\text{Ru}^{5+}/\text{Ru}^{4+}$) 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

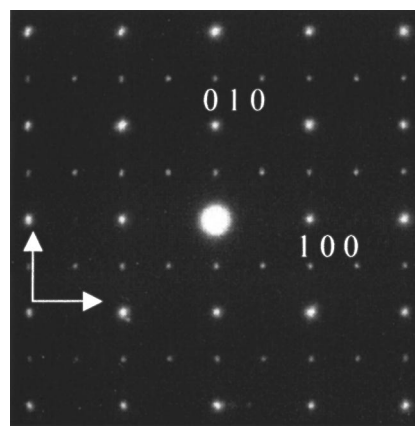


FIG. 4. Electron diffraction pattern for the Ru-1212 sample with incident beam $\parallel c$ axis.

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 $\text{Ru}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{GdCu}_2\text{O}_8$ lying in minority with stoichiometric compound $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. 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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