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# Comment on magnetism and superconductivity in rutheno cuprates: $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10}$

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**Abstract.** Both $RuSr_2GdCu_2O_{8-\delta}$ (Ru-1212) and $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) exhibits magnetism and superconductivity, as seen by magnetization vs. temperature behavior measured in 5 Oe field. Zero-field-cooled (ZFC) and field-cooled (FC) magnetization data show branching at around 140 K and 100 K with a cusp at 135 K and 80 K and a diamagnetic transition around 20 K and 30 K in the ZFC part, for Ru-1212 and Ru-1222, respectively. The isothermal magnetization possesses a non-linear contribution due to a ferromagnetic component at low temperatures below 50 K for both samples. The resistance vs. temperature behavior of the samples in applied fields of 0, 3 and 7 T confirmed superconductivity, with a different type of broadening of the superconductivity transition under magnetic fields for Ru-1212 from that known for conventional high-$T_c$ superconductors. The magnetoresistance (MR) is negative above the Ru magnetic ordering temperature at 135 K. Below the Ru magnetic ordering temperature, MR displays a positive peak at low fields and becomes negative at higher fields for Ru-1212. For Ru-1222, MR remains negative both above and below the ordering temperature. A maximum of 2% is observed for the negative MR value at the Ru magnetic ordering temperature. An electron diffraction pattern obtained for the Ru-1212 sample shows two types of superstructure: one has a weak spot at the centre of the *a–b* rectangle, and the other only along the *b* direction. Interestingly, Ru-1222 shows only clean *a–b* and *a–c* planes, without any superstructures.

**Keywords.** Magnetic superconductor; rutheno cuprates; structural analysis; microstructure.

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## 1. Introduction

Coexistence of superconductivity and magnetism is reported for $RuSr_2$(Gd,Sm, Eu)$_{1.6}Ce_{0.4}Cu_2O_{10-\delta}$ (Ru-$1^{(Sr)}2^{(Gd,Sm,Eu,Ce)}22$ or Ru-1222) [1,2] and Ru-$1^{(Sr)}$ $2^{(Gd)}12$ (Ru-1212) [3–6]. Complete physical characterization of these compounds has also been reported [1–10]. We present here the microstructure of both Ru-1212 and Ru-1222. There is a possibility of Ru and Cu cation ordering in charge reservoir of Ru-1212. Besides basic superconducting properties, we also analyze the magneto-transport properties of the two compounds.

## 2. Experimental

Samples of composition $RuSr_2GdCu_2O_{8-\delta}$ and $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ were synthesized through a solid-state reaction route from $RuO_2$, $SrO_2$, $Gd_2O_3$, $CeO_2$ and CuO. Calcinations were carried out on the mixed powders at 1000, 1020, 1040 and 1060°C for 24 h with intermediate grindings. The pressed bar-shaped pellets were annealed in a flow of oxygen at 1075°C for 40 h and subsequently cooled slowly over a span of another 20 h down to room temperature. X-ray diffraction (XRD) patterns were obtained at room temperature (MAC Science: MXP18VAHF[22]; Cu$K_\alpha$ radiation). Thermogravimetric (TG) analysis (MAC Science: TG-DTA 2000 S) was carried out in an Ar atmosphere to check the oxygen-stoichiometry stability. Magnetization measurements were performed on a SQUID magnetometer (Quantum Design: MPMS-5S). Resistivity measurements under applied magnetic fields of 0 to 7 T were made in the temperature range of 5–300 K using a four-point-probe technique. Electron diffraction experiments were carried out using a transmission electron microscope (TEM; Hitachi: H-9000NAR) operated at an accelerating voltage of 300 kV.

## 3. Results and discussion

### 3.1 *Structure*

X-ray diffraction pattern of both Ru-1212 and Ru-1222 samples showed them to be essentially of single phase (plots not shown). The former crystallizes in the space group P4/mmm with lattice parameters, $a=b=3.8337(6)$ Å and $c=11.4926(9)$ Å and the latter in the space group I4/mmm with $a=b=3.8337(6)$ Å and $c=27.4926(9)$ Å. Small amount of $SrRuO_3$ is also seen. Both the phases are structurally related to the $CuA_2QCu_2O_{7-\delta}$ (Cu-$1^{(A)}2^{(Q)}12$ or Cu-1212, e.g. $CuBa_2YCu_2O_{7-\delta}$) phase with Cu in the charge reservoir replaced by Ru such that the Cu–O chain is replaced by a $RuO_2$ sheet. In the Ru-1222 structure, furthermore, a three-layer fluorite-type block instead of a single oxygen-free R (= rare earth element) layer is inserted between the two $CuO_2$ planes of the Cu-1212 structure [11].

### 3.2 *Superconductivity and magnetism*

Figure 1 shows the magnetic susceptibility ($\chi$) vs. temperature ($T$) behavior in the temperature range of 5 K–160 K for the Ru-1212 sample with an applied field of 5 Oe, in both ZFC (zero-field-cooled) and FC (field-cooled) conditions. The ZFC and FC curves start branching at around 140 K with a cusp at 135 K and a diamagnetic transition around 20 K in the ZFC part. The down-turn cusp at 135 K is indicative of antiferromagnetic nature of Ru-spins ordering. Co-existence of superconductivity and magnetism in Ru-1212 was shown recently from NMR experiments [12]. $\chi$ vs. $T$ behavior for the Ru-1222 sample measured under conditions identical to those for the Ru-1212 sample is shown in the inset of figure 1. The ZFC and FC curves start branching at around 140 K with a sharp upward turn at 100 K. The ZFC branch shows further a cusp at 85 K and a diamagnetic transition around 30 K. This is in agreement with earlier reports [1,2].

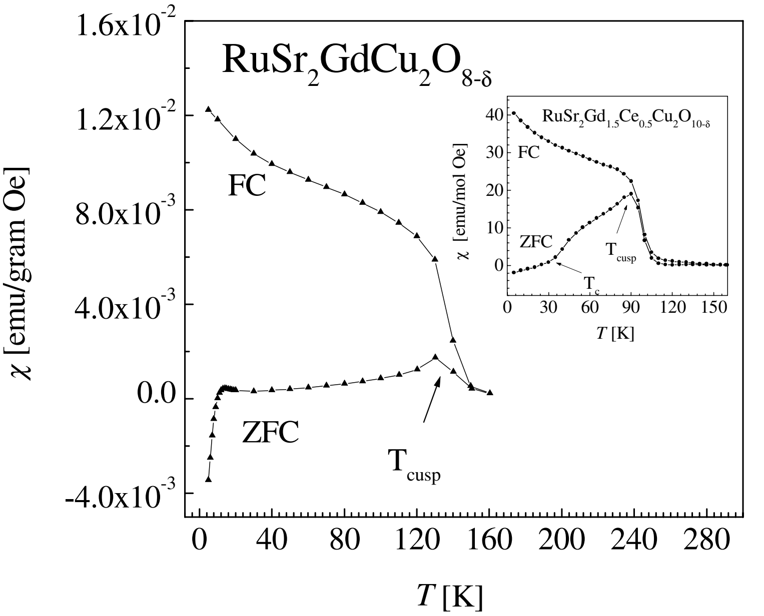



**Figure 1.** $\chi$–$T$ plot for the Ru-1212 sample with both FC and ZFC situations in an applied field of 5 Oe. Inset shows the same for the Ru-1222 sample.

### 3.3 *Magneto-transport*

Figure 2 shows the resistance ($R$) vs. $T$ plot for the Ru-1212 sample in 0, 3 and 7 T applied fields. The $R$–$T$ behavior without any applied magnetic field is metallic down to 150 K and semiconducting between 150 K and 25 K, with a superconducting transition onset ($T_c^{\text{onset}}$) at 25 K and $R = 0$ at 20 K. This behavior is typical of underdoped HTSC compounds. Also observed is an upward hump ($T_{\text{hump}}$) in $R$–$T$ at around 140 K, which indicates the possibility of antiferromagnetic ordering of Ru spins. The $R$–$T$ behavior under an applied field of 7 T is nearly the same above $T_c^{\text{onset}}$, except that $T_{\text{hump}}$ is completely smeared out due to possible change in the magnetic structure. Also, in 7 T applied field, the $T_c^{\text{onset}}$ decreases to around 10 K and $R = 0$ is not observed down to 5 K. In an intermediate field of 3 T, both $T_c^{\text{onset}}$ and $T_c^{R=0}$ decreased to 20 and 10 K, respectively. For conventional HTSC, $T_c^{\text{onset}}$ remains nearly the same under all the applied fields, with decreasing $T_c^{R=0}$ and an increased transition width ($T_c^{\text{onset}} - T_c^{R=0}$). Therefore, a different type of broadening of the transition under a magnetic field is obtained for Ru-1212 from that reported for conventional HTSC. In earlier reports on Ru-1212, a decrease in the $T_c^{\text{onset}}$ under a magnetic field similar to that observed in the present case was reported [3–5,10]. Inset of figure 3 shows the magnetoresistance (MR) behavior of the Ru-1212 sample at various fields and temperatures. MR is negative in applied fields up to 7 T above the magnetic ordering temperature, i.e. at 150 K and 200 K. Maximum negative MR of up to 2% is observed at 150 K, which is close to the magnetic ordering temperature of around 140 K. At temperatures below the

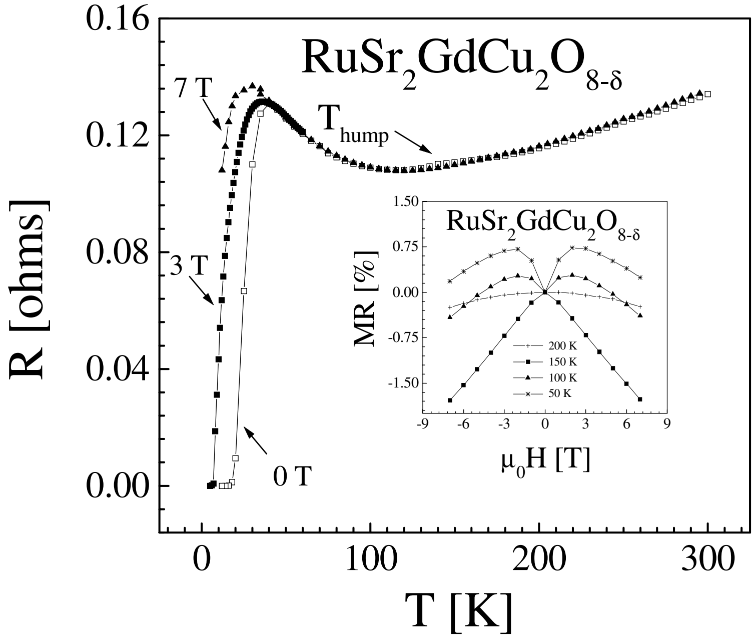


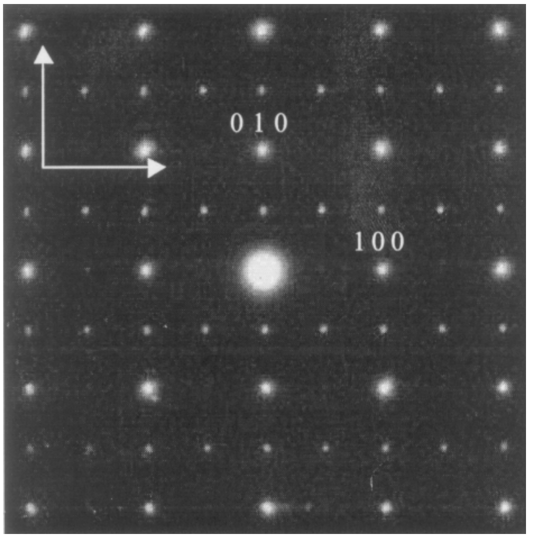

**Figure 2.** *R–T* plots in 0, 3 and 7 T applied fields for the Ru-1212 sample. Inset shows the MR at various temperatures and applied fields for the same.

ordering temperature (100 K and 50 K), MR displays a positive peak at low fields and becomes negative at higher fields. This behavior is in general agreement with previous reports [4,13].

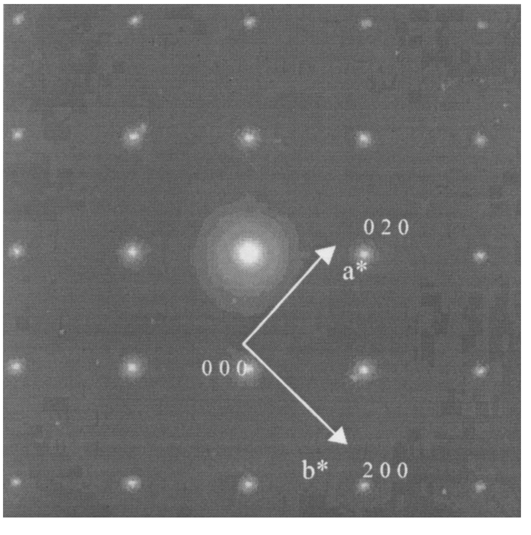
Resistance vs. temperature behavior ($R$ vs. $T$) in 0 and 7 T fields (plots not shown) for Ru-1222 in zero field is metallic down to 270 K and semiconducting below 270 K until superconductivity starts with $T_c^{\mathrm{onset}}$ at 30 K and $T_c^{R=0}$ at 23 K. MR data of the present Ru-1222 sample at various temperatures and fields reveal a small negative MR effect in the whole temperature range [14]. Below 100 K, the magnitude of MR is nearly the same in all applied fields. The nature of the MR effect is of the tunneling-magneto-resistance (TMR) type as judged from the curve shape. At 150 K, the MR curve shape is different from and the MR value is less than those for $T < 100$ K. It is also noted that the MR behavior of the Ru-1222 sample is different from that of Ru-1212, which is presented in the previous paragraph.

### 3.4 *Microstructure*

Figure 3a depicts the electron diffraction pattern of the *a–b* plane for the Ru-1212 sample. Two superstructures are seen: one weak spot at the centre of the *a–b* rectangle, due to tilting of the $RuO_6$ octahedra and the other along the *b* direction. Earlier microstructural analysis of Ru-1212 showed only one superstructure along the *a–b* plane presumably due to the tilting of the $RuO_6$ octahedra [8]. There is a possibility that either Ru/Cu or vacancy




(a)




(b)

**Figure 3.** Electron diffraction pattern for (**a**) the Ru-1212 and (**b**) Ru-1222 crystals with electron beam along the *c*-axis.

ordering of 2*b* periodicity is taking place along the *b* direction. We suggest that superconducting clusters of composition $Ru_{1-x}Cu_xSr_2GdCu_2O_{8-\delta}$ may be present within the $RuSr_2GdCu_2O_{8-\delta}$ phase giving rise to SNS/SIS junctions in the resulting material. This explains the different type of broadening of resistive transition under a magnetic field for many Ru-1212 samples [3–5,10] along with the present one. We would like to mention that possible presence of SNS/SIS junctions in various Ru-1212 samples could be strictly sample dependent. We argue that all reported Ru-1212 samples exhibiting coexistence of superconductivity and magnetism, may not be homogeneous in composition, but 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/occupancies in superconductive oxide materials. Also we would like to mention that we get the '*b*-direction clean *a–b* plane' with only $RuO_6$ tilting superstructure in the same sample. Electron diffraction pattern from the *a–c* plane of the Ru-1212 sample is seen clean without any superstructures. The compound has clear compositional variation (phase separation) in terms of the presence of $Ru_{1-x}Cu_xSr_2GdCu_2O_8$ (*b*-direction weak spot) and $RuSr_2GdCu_2O_8$ (*b*-direction clean). Interestingly, the former compositions are superconducting but not magnetic. This means the former is responsible for superconductivity and the latter for magnetism. Our TEM results clearly refute the co-existence of magnetism and superconductivity in stoichiometric $RuSr_2GdCu_2O_8$. Superconductivity and magnetism are spatially separated and exist in different compositions; namely $Ru_{1-x}Cu_xSr_2GdCu_2O_8$ and $RuSr_2GdCu_2O_8$.

Figure 3b shows an electron diffraction pattern from the *a–b* plane of the Ru-1222. Interestingly, the *a–b* plane observed here is clean without any superstructure seen for the *a–b* plane of Ru-1212. It is likely that tilting of the $RuO_6$ octahedra is not present in Ru-1222. Electron diffraction pattern from the *a–c* plane of the Ru-1222 sample is seen clean without any superstructures.

## 4. Conclusions

We have presented the results of our magnetic, transport and TEM studies on $RuSr_2GdCu_2O_8$ and $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10}$ system. Both compounds show magnetism and superconductivity. We suggest that intermixing of Ru and Cu at the charge-reservoir cation site takes place in $RuSr_2GdCu_2O_8$. TEM studies enabled us to distinguish clearly the Ru and Cu atoms due to large difference in their atomic numbers, which was near impossible to be seen by neutron diffraction. We believe that the Ru and Cu intermixed phase is responsible for superconductivity but not magnetism. We have argued that magnetism and superconductivity are spatially separated in $RuSr_2GdCu_2O_8$.

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## References

[1] I Felner, U Asaf, Y Levi and O Millo, *Phys. Rev.* **B55**, R3374 (1997)
[2] I Felner and U Asaf, *Int. J. Mod. Phys.* **B12**, 3220 (1998)

[3] C Bernhard, J L Tallon, Ch Niedermayer, Th Blasius, A Golnik, E Brücher, R K Kremer, D R Noakes, C E Stronack and E J Asnaldo, *Phys. Rev.* **B59**, 14099 (1999)
[4] J L Tallon, C Bernhard, M E Bowden, T M Soto, B Walker, P W Gilberd, M R Preseland, J P Attfield, A C McLaughlin and A N Fitch, *IEEE J. Appl. Supercond.* **9**, 1696 (1999)
[5] D J Pingle, J L Tallon, B G Walker and H J Tordhal, *Phys. Rev.* **B59**, R11679 (1999)
[6] L Bauernfeind, W Widder and H F Braun, *Physica* **C254**, 151 (1995)
[7] J W Lynn, B Keimer, C Ulrich, C Bernhard and J L Tallon, *Phys. Rev.* **B61**, R14964 (2000)
[8] A C McLaughlin, W Zhou, J P Attfield, A N Fitch and J L Tallon, *Phys. Rev.* **B60**, 7512 (1999)
[9] O Chmaissem, J D Jorgensen, H Shaked, P Dollar and J L Tallon, *Phys. Rev.* **B61**, 6401 (2000)
[10] C W Chu, Y Y Xue, S Tsui, J Cmaidalka, A K Heilman, B Lorenz and R L Meng, *Physica* **C335**, 231 (2000)
[11] N Sakai, T Maeda, H Yamauchi and S Tanaka, *Physica* **C212**, 75 (1993)
[12] Y Tokunaga, H Kotegawa, K Ishida, Y Kitaoka, H Takigawa and J Akimitsu, *Phys. Rev. Lett.* **86**, 5767 (2001)
[13] X H Chen, Z Sun, K Q Wang, S Y Li, Y M Xiong, M Yu and L Z Cao, *Phys. Rev.* **B63**, 64506 (2001)
[14] V P S Awana, S Ichihara, M Karppinen and H Yamauchi, to appear in *Physica C* (2002)