Anisotropic magnetic and superconducting properties of aligned weak-ferromagnetic superconductor RuSr$_2$GdCu$_2$O$_8$

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Abstract. The RuSr$_2$GdCu$_2$O$_8$ Ru-1212 cuprate is a weak-ferromagnetic superconductor with a magnetic ordering of Ru moments at $T_N$(Ru) = 131 K, a superconducting transition in the CuO$_2$ layers at $T_c$ = 56 K, and a low temperature Gd antiferromagnetic ordering at $T_N$(Gd) = 2.5 K. The c-axis aligned powder can be achieved at room temperature using the field-rotation method where the tetragonal c-axis is perpendicular to the aligned magnetic field $B_a$ and along the rotation axis. The anisotropic temperature dependence of magnetic susceptibility for the aligned powder down to 2 K indicates weak anisotropy with $\chi_c > \chi_{ab}$ at room temperature due to strong anisotropic Gd contribution and $\chi_c < \chi_{ab}$ below 185 K where strong Ru anisotropic short-range exchange interaction overtakes the Gd contribution. Anisotropic diamagnetic superconducting intragrain shielding signal of aligned microcrystalline powder-in-epoxy below vortex lattice melting temperature at 39 K in 1-G field is much weaker than the intergrain polycrystalline bulk sample signal due to the small grain size ($d \sim 1$-$10$ $\mu$m), long penetration depth ($\lambda_{ab} \sim 0.6$ $\mu$m, $\lambda_c \sim 2$ $\mu$m) and the two-dimensional (2D) character of CuO$_2$ layers.

1. Introduction
Magnetic superconductivity was reported in the strongly-correlated RuSr$_2$RCu$_2$O$_8$ Ru-1212 cuprate system ($R = \text{Sm, Eu, Gd, Y}$) with the tetragonal space group P4/mmbm [1-5]. The Ru magnetic moments order weak-ferromagnetically (WFM) with ordering temperature $T_N$(Ru) $\sim$ 130 K. High-$T_c$ superconductivity occurs in the quasi-2D CuO$_2$ bi-layers from doped holes with maximum superconducting transition onset $T_c \sim$ 60 K for $R = \text{Gd}$ and coexists with the WFM order. A structural transition from 2D-like P4/mmbm to 3D-like P4/mmm was observed near $R = \text{Sm}$, along with a metal-insulator transition. No superconductivity can be detected for the Mott insulators $R = \text{Pr and Nd}$.

Since oxygen content is close to eight for the oxygen annealed samples, the variation of $T_c$ indicates a self-doping of electrons from CuO$_2$ layers to RuO$_6$ layers, creating holes in CuO$_2$ layers and conduction electrons in RuO$_6$ layers. The Ru L$_3$-edge X-ray absorption near-edge spectrum (XANES) of RuSr$_2$GdCu$_2$O$_8$ indicates that Ru valence is close to Ru$^{5+}$ ($4d$-$t^3_{2g}$, $S = 3/2$) but with a small amount ($\sim 20$ %) of Ru$^{4+}$ ($4d$-$t^4_{2g}$, $S = 1$ in low spin state) or doped electrons [6]. The strong antiferromagnetic superexchange interaction between Ru$^{5+}$ moments is responsible for the basic G-type antiferromagnetic order observed in the neutron diffraction...
study [7]. The weak ferromagnetic component observed from magnetic susceptibility and NMR is probably due to weak-ferromagnetic double-exchange interaction through doped conduction electrons in the metallic RuO$_6$ layers.

![Figure 1](image1.png) **Figure 1.** Powder X-ray diffraction patterns for RuSr$_2$GdCu$_2$O$_8$. (a) random powder, (b) $ab$-plane aligned along $B_a$, and (c) $c$-axis aligned along the rotation axis.

![Figure 2](image2.png) **Figure 2.** The field dependence of paramagnetic moment of RuSr$_2$GdCu$_2$O$_8$ aligned powder up to 7 T at 300 K. Linear paramagnetic magnetic moment.

Since the magnetic and superconducting properties are anisotropic in general, the study of anisotropic physical properties is crucial for this quasi-2D system. In this report, we align the microcrystalline RuSr$_2$GdCu$_2$O$_8$ powder ($\sim$1-10 $\mu$m) in magnetic field to investigate the anisotropic properties.

2. Results and Discussion

The stoichiometric RuSr$_2$GdCu$_2$O$_8$ bulk sample was synthesized by the standard solid-state reactions. High-purity RuO$_2$ (99.99 %), SrCO$_3$ (99.9 %), Gd$_2$O$_3$ (99.99 %) and CuO (99.99 %) preheated powders with the nominal composition ratio of Ru: Sr: Gd: Cu = 1:2:1:2 were well mixed and calcined at 960°C in air for 16 hours. The calcined powders were then pressed into pellets and sintered in flowing O$_2$ gas at 1015°C for 10 hours to form Sr$_2$GdRuO$_6$ and Cu$_2$O precursors. The sintered pellets were then heated at 1060-1065°C in flowing O$_2$ gas for 7 days to form the Ru-1212 phase and slowly furnace cooled to room temperature with a rate of 15°C per hour.

For field alignment at room temperature, RuSr$_2$GdCu$_2$O$_8$ powders with an average microcrystalline grain size of 1-10 $\mu$m were mixed with epoxy (4-hour curing time) in a quartz tube ($\phi = 8$ mm) with the powder:epoxy ratio of 1:5. The quartz tube was placed in a 0.9 T electromagnet and rotated at the speed of 10 rpm with the rotation axis perpendicular to the aligned magnetic field $B_a$. The tetragonal $ab$-plane of the aligned powder is aligned along $B_a$. Since $c$-axis can be in any direction within the plane perpendicular to $B_a$, the rotation perpendicular to $B_a$ forces the microcrystalline $c$-axis to have no choice but to be aligned along the rotation axis.

The powder X-ray diffraction patterns for RuSr$_2$GdCu$_2$O$_8$ random powder, partially $ab$-plane aligned along $B_a$, and partially $c$-axis aligned along the rotation axis are shown collectively in figure 1. For $ab$-plane aligned along $B_a$, enhanced ($hk0$) diffraction lines are observed. For $c$-axis aligned along the rotation axis, enhanced (00$l$) diffraction lines are observed.

Magnetic moment and susceptibility data were collected with a Quantum Design 1-T $\mu$-metal shielded MPMS2 or a 7-T MPMS superconducting quantum interference device (SQUID)
magnetometer from 2 K to room temperature. Figure 2 shows the field dependence of paramagnetic moment of RuSr$_2$GdCu$_2$O$_8$ aligned powder up to 7 T at 300 K. Since $ab$-plane is aligned along the aligned field at room temperature, magnetic anisotropy of $\chi_{ab} > \chi_{c}$ at 300 K is expected. However, 300 K data show weak magnetic anisotropy with linear paramagnetic magnetic moment $m_{ab} \sim 0.95 m_c$ or susceptibility $\chi = m / B_a$ with $\chi_{ab} < \chi_{c}$.

The temperature dependence of logarithmic molar magnetic susceptibility of RuSr$_2$GdCu$_2$O$_8$ aligned powder in 1-T applied magnetic field is shown in figure 3. A crossover of $\chi_{ab} < \chi_{c}$ at 300 K and $\chi_{ab} > \chi_{c}$ at lower temperature was observed around 185 K, with a weak-ferromagnetic ordering temperature $T_N (\text{Ru}) = 131$ K.

The magnetic anisotropy of $\chi_{ab} < \chi_{c}$ observed at 300 K is mainly due to the contribution of magnetic Gd$^{3+}$ ions ($J = 7/2$). The anisotropy of $\chi_{ab}(\text{Gd}) < \chi_{c}(\text{Gd})$ is from the tetragonal GdO$_8$ cage with anisotropic $g$-factor $g_{ab} < g_c$, but with little $4f$ wavefunction overlap with the neighbor oxygen 2$p$ orbital.

Although there are three types of magnetic moments in this magnetic superconductor: Ru$^{5+}$ ($S = 3/2$) with doped electrons or Ru$^{4+}$ ($S = 1$), Cu$^{2+}$ ($S = 1/2$) with doped holes, and Gd$^{3+}$ moment ($J = 7/2$), not all moments have the same contribution in powder alignment. In the aligned magnetic field, anisotropic orbital wavefunction is tied to the spin direction, and a strong spin-orbital related short-range anisotropic exchange interaction at 300 K should dominate the magnetic alignment. In the present case, it is believed that Ru moment with the strong short-range anisotropic double-exchange/superexchange interaction along the $ab$-plane due to the Jahn-Teller distortion of RuO$_6$ octahedron with $\chi_{ab}(\text{Ru}) > \chi_{c}(\text{Ru})$ is the dominant factor for $ab$-plane alignment along B$_a$ at 300 K. The shorter Ru-O(1) bond length in the tetragonal $ab$-basal plane provides strong $4d_{xy}(\text{Ru})$-$2p_{yz/yz}(\text{O}(1))$-$4d_{xy}(\text{Ru})$ wavefunction overlap. This exchange interaction increases with decreasing temperature, and eventually total $\chi_{ab} > \chi_{c}$ was observed below 185 K as expected. The weak-ferromagnetic state below 131 K is due to the long range order of this anisotropic double-exchange/superexchange interaction.

The reciprocal molar magnetic susceptibility $1/\chi_{ab}$ and $1/\chi_{c}$ of RuSr$_2$GdCu$_2$O$_8$ aligned powder are shown in figure 4. A Curie-Weiss behavior $\chi = C/(T - \theta_p)$ was observed in the high temperature paramagnetic region above 200 K with a Curie-Weiss intercept $\theta_p = 60$ K and the effective magnetic moment $\mu^c_{eff} = 7.44 \mu_B$ per formula unit along the $c$-axis, and $\mu^ab_{eff} = 7.26 \mu_B$ per formula unit along the $ab$-plane. Diamagnetic superconducting transition $T_c(\text{dia})$ at 39 K and Gd ordering temperature $T_N(\text{Gd}) = 2.5$ K are not clearly shown in this plot.
Low temperature, low field (1-G field-cooled (FC) and zero-field-cooled (ZFC)) anisotropic magnetic and superconducting properties of RuSr$_2$GdCu$_2$O$_8$ aligned powder are shown in figure 5. All data show a clear $T_N$(Ru) at 131 K with $\chi_{ab}$ > $\chi_c$ in the weak-ferromagnetic state. In the superconducting state, diamagnetic vortex melting temperature $T_c$(dia) = 39 K and spontaneous vortex state temperature $T_{SVS}$ = 30 K are clearly observed. The antiferromagnetic $T_N$(Gd) order is observed at 2.5 K.

The electrical resistivity data in figure 6 indicates a high superconducting onset temperature of 56 K, with a much lower $T_c$(zero) = $T_c$(dia) at the vortex melting temperature of 39 K. Anisotropic diamagnetic superconducting intragrain shielding signal of aligned powder in epoxy is much weaker than the intergrain bulk sample signal due to the small powder size ($d$ ~ 1-10 $\mu$m), long penetration depth ($\lambda_{ab}$ ~ 0.6 $\mu$m, $\lambda_c$ ~ 2 $\mu$m) and the two-dimensional (2D) character of CuO$_2$ layers. Slightly larger diamagnetic signal for random powder is probably due to partially intergrain shielding through partial grain contact.

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