Anisotropic microcrystalline powder alignment of the weak-ferromagnetic superconductor system \( \text{RuSr}_2\text{RCu}_2\text{O}_8 \) (\( R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Gd}_{0.5}\text{Dy}_{0.5} \))

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Abstract. The powder alignment method is used to investigate the anisotropic physical properties of the weak-ferromagnetic superconductor system \( \text{RuSr}_2\text{RCu}_2\text{O}_8 \) (\( R = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Gd}_{0.5}\text{Dy}_{0.5} \)). Due to weak magnetic anisotropy of this tetragonal system, partially \( c \)-axis aligned microcrystalline powder (diameter \( \sim 1-10 \) \( \mu \)m) in epoxy can be obtained only for \( R = \text{Eu} \) and \( \text{Gd} \) through the field-rotation powder alignment method where \( c \)-axis is perpendicular to the aligned magnetic field \( B_a = 0.9 \) T and parallel to the rotation axis. For smaller rare earth compound \( R = \text{Gd}_{0.5}\text{Dy}_{0.5} \), powder alignment can be achieved using the simple field powder alignment method where \( c \)-axis is partially aligned along the aligned magnetic field. No powder alignment can be achieved for larger rare earths \( R = \text{Pr}, \text{Nd} \) or \( \text{Sm} \) due to the lack of magnetic anisotropy in these compounds. The mechanism of powder alignment at room temperature using the spin-orbital-related anisotropic paramagnetic susceptibility and the low temperature anisotropic physical properties of \( \text{RuSr}_2\text{EuCu}_2\text{O}_8 \) is discussed.

1. Introduction
Magnetic superconductivity was reported in the strongly-correlated \( \text{RuSr}_2\text{RCu}_2\text{O}_8 \) \( \text{Ru-1212} \) cuprate system (\( R = \text{Sm}, \text{Eu}, \text{Gd} \)) with the tetragonal space group \( \text{P}4/\text{mbm} \) [1-4]. The Ru magnetic moments order weak-ferromagnetically (WFM) with ordering temperature \( T_N(\text{Ru}) \sim 130 \) K. High-\( T_c \) superconductivity occurs in the quasi-2D \( \text{CuO}_2 \) 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 \( \text{P}4/\text{mbm} \) to 3D-like \( \text{P}4/\text{mmm} \) 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 \( \text{Nd} \).

The Ru \( \text{L}_3 \)-edge X-ray absorption near-edge spectrum (XANES) of \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \) indicates that Ru valence is close to \( \text{Ru}^{5+} \) (4d\( ^3t_{2g}^0 \), \( S = 3/2 \)) but with a small amount (\( \sim 20 \) %) of \( \text{Ru}^{4+} \) (4d\( ^4t_{2g}^1 \), \( S = 1 \) in low spin state) or doped electrons [5]. The strong antiferromagnetic superexchange interaction between \( \text{Ru}^{5+} \) moments is responsible for the basic G-type antiferromagnetic order observed in the neutron diffraction study [6]. 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 \( \text{RuO}_6 \) layers.
Since the magnetic superexchange and double-exchange interaction is anisotropic in general, the study of anisotropic physical properties is crucial for this quasi-2D system. In this report, we align the microcrystalline powder in magnetic field to investigate these anisotropic properties.

2. Results and Discussion
The stoichiometric RuSr$_2$RCu$_2$O$_8$ (R = Pr, Nd, Sm, Eu, Gd, Gd$_{0.5}$Dy$_{0.5}$) bulk samples were synthesized by the standard solid state reactions. High-purity RuO$_2$ (99.99 %), SrCO$_3$ (99.9 %), CuO (99.99 %), R$_2$O$_3$ (99.99 %) or Pr$_6$O$_{11}$ (99.99 %) preheated powders with the nominal composition ratio of Ru: Sr:R: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 N$_2$ gas at 1015°C for 10 hours to form Sr$_2$RRuO$_6$ 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 powder alignment in magnetic field, samples were ground into powders with an average microcrystalline grain size of 1-10 µm and mixed with epoxy (4-hour curing time) in a quartz tube (φ = 8 mm) with the ratio of powder: epoxy = 1:5. The mixture was placed in a 14 T superconducting magnet at room temperature in flowing N$_2$ gas and slowly hardened overnight as shown in figure 1.

The powder X-ray diffraction pattern of three typical aligned powder-in-epoxy samples RuSr$_2$RCu$_2$O$_8$ (R = Sm, Eu, Gd$_{0.5}$Dy$_{0.5}$) are shown collectively in figure 2. For R = Sm (as well as for R = Pr and Nd), no magnetic alignment can be achieved. The lack of magnetic anisotropy may closely relate to the variation of tetragonal lattice parameters where $c/3 \sim a/\sqrt{2}$ for R = Sm with $a = 0.5448$ nm and $c = 1.1560$ nm (space group P4/mmbm) as shown in figure 3. For R = Eu (as well as for R = Gd), partially $ab$-plane aligned along aligned magnetic field $B_{0}$ is observed through the appearance of enhanced (hk0) diffraction lines. A small amount of SrRuO$_3$ impurity is present. The $ab$-plane alignment may be due to the fact that $c/3 > a/\sqrt{2}$ for R = Eu ($a = 0.5435$ nm, $c = 1.1572$ nm). For metastable compound R = Gd$_{0.5}$Dy$_{0.5}$ near the phase boundary with some unreacted precursor Sr$_2$RRuO$_6$, partially c-axis alignment along $B_{0}$ is detected with enhanced (00l) lines due to $c/3 < a/\sqrt{2}$ in this compound ($a = 0.5426$ nm, $c = 1.1508$ nm).

The phase diagram in figure 3 indicates a structural transition from tetragonal 3D-like P4/mmm ($c/3 \sim a$) to 2D-like P4/mmbm ($c/3 \neq a/\sqrt{2}$) near R = Sm, along with an insulator to
Figure 3. The variation of superconducting transition $T_c$ and tetragonal lattice parameters $a$, $c$ with rare earth ionic radius $R^{3+}$ for RuSr$_2$RCu$_2$O$_8$ system ($R =$ Pr-Dy).

Figure 4. Block diagram for the field-rotation powder alignment method with $c$-axis perpendicular to aligned magnetic field and along the rotation axis.

Figure 5. Powder X-ray diffraction patterns for RuSr$_2$EuCu$_2$O$_8$. (a) random powder, (b) $ab$-plane aligned along $B_a$, (c) $c$-axis aligned along rotation axis.

Figure 6. The temperature-dependence of logarithmic molar magnetic susceptibility $\chi_{ab}$ and $\chi_c$ of aligned RuSr$_2$EuCu$_2$O$_8$ powder in 1 T applied magnetic field.

metal transition. Superconductivity appears only in the quasi-2D metallic region with resistivity onset transition temperature $T_c \sim 0$ for $R =$ Sm, $T_c = 36$ K for $R =$ Eu, $T_c = 56$ K for Gd, and $T_c = 55$ K for metastable $R =$ Gd$_{0.5}$Dy$_{0.5}$.

For $R =$ Eu with $ab$-plane aligned along $B_a$, $c$-axis can be in any direction within the plane perpendicular to $B_a$. To obtain the $c$-axis aligned powder, a field-rotation alignment method is used as shown in figure 4. Since $ab$-plane is fixed along $B_a$, the rotation (10 rpm) 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 of RuSr$_2$EuCu$_2$O$_8$ random powder ($hkl$), partially $ab$-plane aligned along $B_a$ ($hk0$), and partially $c$-axis aligned along the rotation axis (00$l$) are shown collectively in figure 5.

The temperature dependence of logarithmic molar magnetic susceptibility of aligned RuSr$_2$EuCu$_2$O$_8$ powder along $c$-axis and $ab$-plane in 1-T applied magnetic field are shown in figure 6. Weak paramagnetic anisotropy of $\chi_{ab} = 0.95 \chi_c$ was observed at 300 K, and a crossover
to $\chi_{ab} > \chi_c$ was detected below 190 K with a weak-ferromagnetic ordering temperature $T_N(Ru) = 133$ K. Superconducting diamagnetic signal $T_c(dia)$ at 21 K (resistivity zero point) is very weak in large 1-T field [7].

The $\chi_{ab} < \chi_c$ observed at 300 K is mainly due to the contribution from excited rare earth magnetic Eu$^{3+}$ ion ($J = 1$). The $\chi_{ab}(Eu) < \chi_c(Eu)$ is due to the anisotropic Eu $g$-factor $g_{ab} < g_c$ in the tetragonal EuO$_8$ cage. Since there is little 4$f$ wavefunction overlap with the neighbor oxygen 2$p$ orbital, the exited Eu$^{3+}$ moments has little contribution in powder alignment.

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 excited Eu$^{3+}$ moment at room temperature ($J = 1$), 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 $\chi_{ab}(Ru) > \chi_c(Ru)$ 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 4$d_{xy}$(Ru)-2$p_{x/y}$(O(1))$-4d_{xy}$(Ru) wavefunction overlap. This exchange interaction increases with decreasing temperature, and eventually total $\chi_{ab} > \chi_c$ was observed below 190 K as expected. The weak-ferromagnetic state below 133 K is due to the long range order of this anisotropic double-exchange/superexchange interaction.

3. Conclusion

Anisotropic powder alignment is achieved for RuSr$_2$RCu$_2$O$_8$ weak-ferromagnetic superconductors (R = Eu, Gd, and Gd$_{0.5}$Dy$_{0.5}$). For R = Eu with $T_N(Ru) = 133$ K, the $c$-axis alignment along the rotation axis with $ab$-plane parallel to the aligned magnetic field is due to the spin-orbital related short-range anisotropic exchange interaction between Ru moments at room temperature.

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4. References

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