Anomalous physical properties of underdoped weak-ferromagnetic superconductor 

\textbf{RuSr}_2\textbf{EuCu}_2\textbf{O}_8

B. C. Chang, C. Y. Yang, and H. C. Kuo

\textit{Department of Physics, National Tsing Hua University, Hsinchu 300, Taiwan, Republic of China}

J. C. Ho

\textit{Department of Physics, Wichita State University, Wichita, Kansas 67260-0032, U.S.A.}

C. B. Tsai and Y. Y. Chen

\textit{Institute of Physics, Academia Sinica, Taipei 115, Taiwan, Republic of China}

D. C. Ling

\textit{Department of Physics, Tamkang University, Tamsui 251, Taiwan, Republic of China}

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Similar to the optimal-doped, weak-ferromagnetic (WFM induced by canted antiferromagnetism, \(T_{\text{Curie}} = 131\) K) and superconducting (\(T_c = 56\) K) \textit{RuSr}_2\textit{GdCu}_2\textit{O}_8, the underdoped \textit{RuSr}_2\textit{EuCu}_2\textit{O}_8 \((T_{\text{Curie}} = 133\) K, \(T_c = 36\) K) also exhibited a spontaneous vortex state (SVS) between 16 K and 36 K. The low field (\(\pm 20\) G) superconducting hysteresis loop indicates a weak and narrow Meissner state region of average lower critical field \(B_{\text{c1-ave}}^\text{(0)}(T) = B_{\text{c1-ave}}^\text{(0)}(0)(1 - (T/T_{\text{SVS}})^2)\), with \(B_{\text{c1-ave}}^\text{(0)} = 7\) G and \(T_{\text{SVS}} = 16\) K. The vortex melting transition \(T_{\text{melting}} = 21\) K below \(T_c\) obtained from the broad resistivity drop and the onset of diamagnetic signal indicates a vortex liquid region due to the coexistence and interplay between superconductivity and WFM order. No visible jump in specific heat was observed near \(T_c\) for Eu- and Gd-compound. This is not surprising, since the electronic specific heat is easily overshadowed by the large phonon and weak-ferromagnetic contributions. Furthermore, a broad resistivity transition due to low vortex melting temperature would also lead to a correspondingly reduced height of any specific heat jump. Finally, with the baseline from the nonmagnetic Eu-compound, specific heat data analysis confirms the magnetic entropy associated with antiferromagnetic ordering of \(\text{Gd}^{3+} (J = S = 7/2)\) at 2.5 K to be close to \(N_k \ln 8\) as expected.

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\textbf{I. INTRODUCTION}

Anomalous physical properties have been observed recently in the weak-ferromagnetic (WFM induced by canted antiferromagnetism) and high-\(T_c\) superconducting \textit{RuSr}_2\textit{RCu}_2\textit{O}_8 system (Ru-1212 with \(R = \text{Sm, Eu, Gd, and Y}\)) having a tetragonal TlBa_2CaCu_2O_7-type structure. \cite{2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48}

Possible superconductivity was also reported in Ca-substituted WFM compounds \textit{RuCa}_2\textit{RCu}_2\textit{O}_8 (\(R = \text{Pr-Gd}\)). \cite{49,50,51}

The weak-ferromagnetism in these strongly-correlated electron systems originates from the long range order of Ru moments in the RuO_6 octahedra due to a strong Ru-4d_{xy,y,z,xz}-O-2p_{x,y,z} hybridization with a Curie temperature \(T_{\text{Curie}} \sim 131\) K. A G-type antiferromagnetic order probably occurs with Ru\(^{5+}\) moment \(\mu\) canted along the tetragonal basal plane, even through the small net spontaneous magnetic moment \(\mu_s \ll \mu(Ru^{5+})\) is too small to be detected in neutron diffraction. \cite{4,5,9,10,22}

The Ru valence of 4+ and 5+ was determined from x-ray absorption near edge measurements. \cite{23,24}

With its quasi-two-dimensional CuO_2 bi-layers separated by a rare earth layer in the Ru-1212 structure, \textit{RuSr}_2\textit{GdCu}_2\textit{O}_8 has the highest resistivity-onset temperature \(T_c \sim 60\) K among different Ru-1212 compounds. \cite{1,2,4,5,31} A broad resistivity transition width \(\Delta T_c = T_c(\text{onset}) - T_c(\text{zero}) = T_c - T_{\text{melting}} \sim 15-20\) K is most likely a consequence of coexistence and interplay between superconductivity and WFM order. The magnetic signal is observed only near \(T_{\text{melting}}\) instead of \(T_c\), and a reasonable large Meissner signal can be detected only in zero-field-cooled (ZFC) mode. \cite{27} Lower \(T_c > 40\) K and 12 K were observed for Eu-compound and Sm-compound, respectively. \cite{47} No superconductivity can be detected in RuSr_2RCu_2O_8 (\(R = \text{Pr, Nd}\)). \cite{31} While a superconducting \textit{RuSr}_2\textit{YCu}_2\textit{O}_8 phase is stable only under the high pressure. \cite{21,26}

Interest of the current work stimulates from a recent report of spontaneous vortex state (SVS) between 30 K and 56 K in \textit{RuSr}_2\textit{GdCu}_2\textit{O}_8. \cite{25} However, the compound undergoes a low temperature antiferromagnetic ordering arising from \(\text{Gd}^{3+}\) at 2.5 K. To avoid this complication, isostructural \textit{RuSr}_2\textit{EuCu}_2\textit{O}_8 with nonmagnetic \(\text{Eu}^{2+}\) ions was chosen as a prototype material in this study to evaluate the anomalous magnetic, transport, calorimetric properties and \(d\)-wave nature near and below \(T_c = 36\) K. The calorimetric data were further used as a basis in elucidating the magnetic entropy associated with the \(\text{Gd}^{3+}\) ordering.
II. EXPERIMENTAL

Stoichiometric RuSr$_2$RCu$_2$O$_8$ samples were synthesized by solid-state reactions. High-purity RuO$_2$ (99.99 %), SrCO$_3$ (99.9 %), R$_2$O$_3$ (99.99 %) (R = Pr, Nd, Sm, Eu, and Gd), and CuO (99.9 %), in the nominal composition ratios of Ru:Sr:RCu = 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 RuSr$_2$RO$_6$ and Cu$_2$O precursors. This step is crucial in order to avoid the formation of impurity phases. The N$_2$-sintered pellets were heated at 1060°C in flowing O$_2$ gas for 10 hours to form the Ru-1212 phase, then oxygen-annealed at a slightly higher 1065°C for 7 days and slowly furnace-cooled to room temperature with a rate of 15°C per hour.

Powder x-ray diffraction data were collected with a Rigaku Rotaflex 18-kW rotating-anode diffractometer using Cu-K$_\alpha$ radiation. Four-probe electrical resistivity measurements were performed with a Linear Research LR-700 ac (16Hz) resistance bridge from 2 K to 300 K. Magnetic susceptibility and magnetic hysteresis measurements were performed with a Quantum Design µ-metal shielded SQUID superconducting quantum interference device (SQUID) magnetometer. Calorimetric measurements were made from 1 K to 70 K by using a thermal relaxation microcalorimeter. A mg-size sample was attached with a minute amount of grease to a sapphire holder to ensure good thermal coupling. The sample holder had a Cernox temperature sensor and a Ni-Cr alloy film heater. The holder was linked thermally to a copper block by four Au-Cu alloy wires. The temperature of the block could be raised in steps but held constant when a heat pulse was applied. Following each heat pulse, the sample temperature relaxation rate was monitored to yield a time constant $\tau$. The total heat capacity was calculated from the expression $C = \kappa \tau$, where $\kappa$ is the thermal conductance of Au-Cu wires. The heat capacity of the holder was measured separately for addenda correction. The molar specific heat of the sample was then obtained from $C = (c + m_{addenda})/(m/M)$ with m and M being the sample’s mass and molar mass, respectively.

III. RESULTS AND DISCUSSION

Figure 1 summarizes structural and superconducting properties, as a function of R$^{3+}$ ionic radius r (coordination number CN = 8), of various RuSr$_2$RCu$_2$O$_{8-\delta}$ system (R = Pr-Y). $T_c$ decreases from a maximum value of 60 K for optimal-doped Gd (r = 0.105 nm) to 36 K for underdoped Eu (r = 0.107 nm), and < 10 K for Sm (r = 0.108 nm). Larger rare earth ions of Nd (0.112 nm) and Pr (0.113 nm) lead to a metal-insulator transition. Powder x-ray Rietveld refinement study indicates that the insulating phase is stabilized in the undistorted tetragonal phase (space group P4/mmm) with a larger lattice parameter $a \sim 0.390$-0.392 nm, which gives a reasonable Ru$^{5+}$-O bond length of $d \sim 0.197$ nm if the oxygen content is slightly deficient ($\delta > 0$). On the other hand, the metallic phase with smaller rare earth ions can be stabilized in the full-oxygenated ($\delta \sim 0$), distorted tetragonal phase (space group P4/mmb) with smaller $a/\sqrt{2} \sim 0.383$-0.385 nm but still a reasonable Ru-O bond length through RuO$_6$ octahedron rotation.

Indeed, the powder x-ray diffraction pattern for the oxygen-annealed RuSr$_2$EuCu$_2$O$_{8-\delta}$ sample indicates a single phase with tetragonal lattice parameters of $a = 0.5435(5)$ nm and $c = 1.1552(9)$ nm. A Raman scattering peak of 265 cm$^{-1}$ indicates that the A$_{1g}$ mode symmetry belong to a P4/mmb instead of P4/mmm group. Accordingly, with RuO$_6$ octahedra rotation angle $\theta \sim 14^\circ$ around the c-axis and oxygen parameter $\delta \sim 0$, Rietveld refinement analysis with a small residual error factor $R = 5.31\%$ yields a reasonable Ru-O bond length $d = (a/2\sqrt{2})(1 - \sin^2\theta)^{-1/2} = 0.198$ nm. It is close to the minimum calculated bond length $d$(Ru$^{5+}$-O) of 0.197 nm.

Figure 2 shows the temperature dependence of field-cooled (FC) and zero-field-cooled (ZFC) magnetization susceptibility $4\pi \chi V$ at 1-G for bulk and powder RuSr$_2$EuCu$_2$O$_8$ samples. Weak-ferromagnetic ordering occurs at $T_{Curie} = 133$ K. Similar to RuSr$_2$GdCu$_2$O$_8$, this Eu-compound has its electrical resistivity data, which are also included in Fig. 2, exhibiting a non-Fermi-liquid-like behavior above $T_{Curie}$. The linearly temperature-dependant values of 10.0 mΩ cm at 300 K and 5.5 mΩ cm at 160 K give an extrapolated value of 2.6 mΩ cm at 0 K, yielding a ratio $\rho(300\, K)/\rho(0\, K)$ of 3.9. Below $T_{Curie}$, a $T^2$ behavior prevails. The onset of deviation at 36 K from such a temperature dependence is taken as the superconducting transition temperature $T_c$. The melting temperature of superconducting vortex

![Graph showing superconducting transition $T_c$ and tetragonal lattice parameters $a$, $c$ with rare earth ionic radius $R^{3+}$ (coordination number CN = 8) for RuSr$_2$RCu$_2$O$_{8-\delta}$ system (R = Pr-Y).](image)
liquid is assigned to $T_{\text{melting}} = 21$ K, where resistivity reaches zero. The broad transition width of 15 K is the common feature for all reported Ru-1212 compounds. It indicates that the superconducting Josephson coupling along the tetragonal $c$-axis between Cu-O bi-layers may be partially blocked by the magnetic dipole field $B_{\text{dipole}}$ of ordered Ru moments in the Ru-O layers.

The Meissner shielding at 2 K is complete ($4\pi\chi_V = 4\pi M/B_0 \sim 1.3$) for ZFC bulk sample, but much reduced (-0.1) in the powder sample. However, in 1-G FC mode, no such an effect can be detected below $T_{\text{melting}}$ due to strong flux pinning.

Low-field ($\pm 20$ G) superconducting hysteresis loop at 2 K for bulk sample RuSr$_2$EuCu$_2$O$_8$ and RuSr$_2$GdCu$_2$O$_8$ as reference are shown in Fig. 3. The initial magnetization curve deviates from straight line at 2 G and 3 G for the Eu- and Gd-compounds, respectively. The narrow region of full Meissner effect roughly reflects the temperature-dependent lower critical field in the $ab$-plane $B_{c2}^{\text{ave}}(T)$. The average lower critical field $B_{c1}^{\text{ave}}(T)$ for bulk sample as determined from the peak of initial diamagnetic magnetization curves is 7 G for $R = $ Eu and 13 G for $R = $ Gd. The effect on the exact peak value due to the surface barrier pinning is neglected. For RuSr$_2$EuCu$_2$O$_8$, $B_{c1}^{\text{ave}}$ decreases steadily from 7 G at 2 K to 6 G at 5 K, 4 G at 10 K, and below 1 G at 15 K. A simple empirical parabolic fitting gives $B_{c1}^{\text{ave}}(T) = B_{c1}^{\text{ave}}(0)[1 - (T/T_{SVS})^2]$, with average $B_{c1}^{\text{ave}}(0) \sim 7$ G and spontaneous vortex state temperature $T_{SVS} = 16$ K. The Ginzburg-Landau anisotropy formula $B_{c1}^{\text{ave}} = (2B_{c1}^{\text{ave}} + B_{c2}^{\text{ave}})/3$, then provides an estimated $c$-axis lower critical field $B_{c1}^{\text{ave}}$ $\sim 17$ G and anisotropy parameter $\sim 8.5$.

The lower field superconducting phase diagram for the polycrystalline bulk sample is shown in Fig. 4. The average lower critical field $B_{c2}^{\text{ave}}$ separates the Meissner state and vortex state. The upper critical field $B_{c2}$ and vortex melting field $B_{\text{melting}}$ determined from magnetoresistivity measurements are field-independent below 20 G. The WFM-induced internal dipole field $B_{\text{dipole}}$ of 8.8 G on the CuO$_2$ bi-layers is estimated using extrapolated $B_{c1}^{\text{ave}}$ value at $T = 0$, $(B_{c1}^{\text{ave}}(0) + B_{\text{dipole}})/B_{c1}^{\text{ave}}(0) = T_{c}/T_{SVS}$. It further yields a small net spontaneous magnetic moment $\mu_s$ of 0.1 $\mu_B$ per Ru, based on the relation of $B_{dipole} \sim 2\mu_s/(c/2)^3$, where $c/2 = 0.58$ nm is the distance between midpoint of CuO$_2$ bi-layers and two nearest-neighbor Ru moments. If the WFM structure is indeed a G-type antiferromagnetic order with 1.5 $\mu_B$ for Ru$^{5+}$ in $t_{2g}$ states canted along the tetragonal basal plane, the small $\mu_s$ would give a canting angle of $4^\circ$ from the tetragonal $c$-axis and be difficult to be detected in neutron diffraction with a resolution $\sim 0.1 \mu_B$.

The molar specific heat data up to 70 K in Fig. 5 show a good agreement between Eu- and Gd-compounds,
except that a peak reflects the antiferromagnetic Gd$^{3+}$ ordering near $T_N \sim 2.5$ K. Consistent with previous results for lower-$T_c$ Gd-compounds in zero applied magnetic field.$^{15,28}$ No visible jump in specific heat was observed near $T_c = 36$ K. This is not surprising, since only the electronic component in specific heat would change with superconducting transition, but it is easily overshadowed by the much larger phonon contribution. Specifically, assuming a same magnitude as that observed in La$_{1.85}$Sr$_{0.15}$CuO$_4$ ($\Delta C \sim 0.33$ J/mol K at $T_c = 37$ K) and YBa$_2$Cu$_3$O$_7$ ($\Delta C \sim 4.6$ J/mol K at $T_c = 92$ K) an estimated $\Delta C \sim 1$ J/mol K at $T_c$ here is only about 1% of total specific heat, falling below the experimental precision. In addition, the broad resistivity transition due to vortex melting would further points to a correspondingly reduced height of $\Delta C$.

It would be of interest to obtain information on the Gd$^{3+}$ ordering. To do so, delineation of various contributions to the total specific heat begins with the non-magnetic Eu-compound up to 7 K. In the format of $C/T$ versus $T^2$, the data in Fig. 6 can be well fitted by the sum of four terms with different temperature dependence:

$$C = \beta T^3 + \alpha T^2 + \gamma T + \eta/T^2.$$  

The coefficient of the first term, $\beta = 0.89$ mJ/mol K$^4$, can be used to derive a Debye temperature $\theta_D$ of the lattice,

$$\beta = n(12\pi^4/5)N_A k/\theta_D^3,$$

where $N_A$ is Avogadro’s number, $k$ the Boltzmann constant, and the number of atoms per formula unit $n = 14$. The $\theta_D$ value of 312 K thus obtained supports the validity of the $T^3$-dependence approximation in Debye model for the lattice specific heat below 7 K $\sim \theta_D/50$. The quadratic term has two possible sources: the nodal line excitation for $d$-wave pairing symmetry and the spin wave excitation of WFM Ru sublattice. The fact that the observed $\alpha$ value of 4.2 mJ/mol K is much larger than 0.1 mJ/mol K of YBa$_2$Cu$_3$O$_7$ could be an indication of a less important nodal line excitation, but an enhanced spin wave excitation. The linear term is considered normally as an electronic contribution, which is not expected to exist in a superconductor at temperature much lower than $T_c$. While the observed coefficient $\gamma = 7.3$ mJ/mol K$^2$ is comparable to that of some cuprates, its origin remains to be identified. One plausible explanation is based on the complicated magnetic structure and mixed valence. Such a scenario could lead to a spin glass-like lattice, for which an even larger linear term in specific heat has been observed in another Ru compound of Ba$_2$PrRuO$_6$.54

The last term with a $T^{-2}$ dependence is most likely the high-temperature tail of a Schottky anomaly. Its occurrence at the relatively low temperatures suggests nuclear energy splittings being the cause. Such energy splittings occur typically for nuclei having a spin I and magnetic moment $\mu_n$ in a hyperfine magnetic field $H_{hf}$. For the calorimetric measurements under consideration, they are most likely associated with the Ru nuclei, since the 4$d$ magnetic moments of ordered Ru ions are spatially fixed, polarizing the $s$-electrons and producing a net spin at the nuclei, yielding a hyperfine field. There are two Ru isotopes with non-zero $\mu_n$: $^{89}$Ru (fractional natural abundance $A = 0.1276$, $I = 5/2$, and $\mu_n = 0.6413$) and $^{101}$Ru ($A = 0.1706$, $I = 5/2$, and $\mu_n = -0.7188$). However, nuclear energy splittings can also be caused by the interaction between the quadrupole moment of a nucleus and the electric field gradient produced by neighboring atoms. The electric field gradient could be quite high in the layered compound. Meanwhile, Cu and Eu or $^{155}$Gd ($A = 14.7\%$) and $^{157}$Gd ($A = 15.7\%$) nuclei all have non-zero quadrupole moment. Without the full knowledge of magnetic hyperfine field and electric field gradient, it is not feasible at present to delineate the experimentally obtained $\eta$ of 6.63 mJ K/mol into the two different con-
The results are shown in Fig. 7. Using the format of heat associated with antiferromagnetic Gd$^{3+}$ ordering in RuSr$_2$GdCu$_2$O$_8$, one can then obtain the magnetic contribution to specific heat associated with antiferromagnetic Gd$^{3+}$ ordering as

$$C_m = C_{Gd} - C_{Eu}.$$

The areal integral in Fig. 7, including that associated with the broad shoulder should yield the magnetic entropy,

$$S_m = \int \left(\frac{C_m}{T}\right) dT.$$

As shown in the inset, $S_m$ reaches a saturation value of 17.6 J/mol K around 10 K. Considering the built-in approximation in Eq. (4), it agrees exceptionally well with the theoretical value of $N_A k \ln(2J+1) = N_A k \ln 8 = 17.2$ J/mol K for the complete ordering of Gd$^{3+}$.

IV. CONCLUSION

The lower critical field with $B_{c2}(0) = 7$ G and $T_{SVS} = 16$ K indicates the existence of a spontaneous vortex state (SVS) between 16 K and $T_c$ of 36 K. This SVS state is closely related to the weak-ferromagnetic order with a net spontaneous magnetic moment of $\sim 0.1 \mu_B$/Ru, which generates a weak magnetic dipole field around 8.8 G in the CuO$_2$ bi-layers. The vortex melting transition temperature at 21 K obtained from resistivity measurements and the onset of diamagnetic signal indicates a broad vortex liquid region due to the coexistence and interplay between superconductivity and WFM order. No visible specific heat jump was observed near $T_c$ for Eu- and Gd-compound, since the electronic specific heat is easily overshadowed by the large phonon contributions and the expected jump would spread over a wide range of temperature due to vortex melting. Finally, the magnetic entropy associated with Gd$^{3+}$ antiferromagnetic ordering at 2.5 K is confirmed to be close to $N_A k \ln 8$ for $J = S = 7/2$.

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* Electronic address: hcku@phys.nthu.edu.tw

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