Absence of a Bulk Meissner State in \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \)

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(July 5, 2021)

Abstract

We have systematically investigated the magnetic, electrical, and structural properties of \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \), in which a long-range ferromagnetic order and superconductivity have been previously reported to coexist. Based on the reversible magnetization results, we conclude that the bulk Meissner state does not exist in this compound and that the condensation energy associated with superconductivity is negligible. The absence of a bulk Meissner state and the superconductivity detected are thus attributed to the possible appearance of a sponge-like crypto-superconducting fine structure in \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \) samples that are found to be chemically homogeneous to 1–2 \( \mu \text{m} \) and electrically uniform to \( \sim 10 \mu \text{m} \) across the sample.

PACS No. 74.25.Ha, 74.72.Jt, 74.25.-q
The general antagonistic nature between superconductivity and magnetism has been long recognized. Over the last two decades, extensive studies [1] have been carried out on a class of compounds known as ferromagnetic superconductors, in which the superconducting transition temperature ($T_s$) is higher than the magnetic transition temperature ($T_m$). While antiferromagnetism coexists with superconductivity, ferromagnetism does not, except in cases where the ferromagnetic order modifies its structure to a spiral or domain-like form to fit the superconducting state [2,3]. Until very recently, the coexistence of ferromagnetism and superconductivity has been observed to occur only below $T_m$ or only over a very narrow temperature region below $T_m$. However, a new class of compounds, called superconducting ferromagnets [4], with a higher $T_m$ than $T_s$ was recently reported to show the coexistence of superconductivity and a uniform ferromagnetic order below $T_s$. They are layered ruthenate-cuprates RuSr$_2$GdCu$_2$O$_8$ (Ru-1212) [5] and RuSr$_2$(RE$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$ (Ru-1222) with RE = Gd or Eu [6]. Their transition temperatures ($T_m$, $T_s$) are (133 K, 14–47 K) for Ru-1212, (180 K, 42 K) for Ru-1222 with RE = Gd, and (122 K, 32 K) for Ru-1222 with RE = Eu. Therefore, the observation is indeed very unusual and extremely interesting. It is particularly so in view of the important role of magnetism in cuprate high temperature superconductivity proposed by many theoretical models [7] and the similar coordination of RuO$_2$ and CuO$_2$ layers in Ru-1212 and Ru-1222, respectively.

Both Ru-1212 and -1222 have a structure [5,6] similar to that of the cuprate high temperature superconductor GdSr$_2$Cu$_3$O$_7$ = CuSr$_2$GdCu$_2$O$_7$ (Gd-123 or Cu-1212) and are derived from Cu-1212 by replacing the CuO-chain layer with the RuO$_2$ layer. For Ru-1222, the oxygen-absent Gd-layer between the two CuO$_2$ layers in Cu-1212 is further replaced by the double fluorite (M$_{0.7}$Ce$_{0.3}$)$_2$O$_2$ block. The charge reservoir block (SrO)(RuO$_2$)(SrO) in these compounds has the same atomic arrangement as the perovskite SrRuO$_3$ [8], which is an itinerant ferromagnet with a $T_m$ of $\sim 160$ K. The detection of a ferromagnetic state in Ru-1212 and -1222 attributed to the Ru-sublattice is therefore rather natural. What is most unexpected and exciting is the detection [5,6] of superconductivity in this ferromagnetically ordered state below $T_s < T_m$ with the superconductivity assigned to the CuO$_2$ layers, similar to the cuprate high temperature superconductors. It was proposed [4] that the RuO$_2$-layer sublattice and the CuO$_2$-layer sublattice are only weakly coupled and the exchange effect due to the Ru-moment in the CuO$_2$ layer is small to allow the two ordered states to coexist. A possible p-pairing of the superconducting electrons was also mentioned, in which spins of the two electrons of the Cooper pair are parallel and the magnetic field effect on its superconductivity is less detrimental, similar to that in the superconducting ruthenate layered compound Sr$_2$RuO$_4$ [9], which has a $T_s \sim 1$ K.

The ferromagnetic state in Ru-1212 and -1222 has been firmly established to be bulk and uniform to a scale of $\sim 20$ Å across the samples examined [5,6,10]. However, the evidence for superconductivity reported to date [5,6,11] in these compounds has been entirely based on the diamagnetic shift in the magnetic susceptibility ($\chi$) measured in the zero-field-cooled (ZFC) mode and the zero resistivity ($\rho$) in samples when cooled to below $T_s$. However, no diamagnetic $\chi$-shift in the field-cooled (FC) mode, the conventional signature of a bulk superconducting state, has been reported. This raises two interesting questions: Is the bulk Meissner state indeed absent in these compounds with bulk superconductivity, and if it is, why? We have therefore examined the superconducting state of Ru-1212 samples prepared under different conditions. We found that there exist no bulk Meissner state and only a
negligible superconducting condensation energy in the chemically and electrically uniform Ru-1212 samples studied below $T_s$ that show magnetic, electrical, and structural properties similar to those previously observed [5,7,12]. The absence of a bulk Meissner state and the superconductivity detected are therefore attributed to the possible formation of a sponge-like crypto-superconducting fine structure in Ru-1212.

The samples investigated were prepared by thoroughly reacting a mixed powder of RuO$_2$ (99.95%), SrCO$_3$ (99.99%), Gd$_2$O$_3$ (99.99%) and CuO (99.9%), with a cation composition of Ru:Sr:Gd:Cu = 1:2:1:2, in steps similar to those previously reported [5,6,11,13]. The mixed powder was first heated to 900–960 °C in air or in flowing oxygen for 10–16 hr to decompose the SrCO$_3$. The heated oxide was then pulverized, pelletized, and calcined in air, flowing nitrogen, or flowing argon at 1010–1020 °C for 10–16 hr. The process was repeated for some samples. The pellets were then powdered, pelletized, and heated in flowing oxygen at 1050–1060 °C for 10–16 hr. Some of the pellets were subsequently annealed in flowing oxygen for 6–7 days at 1055–1070 °C. The structure was determined by powder X-ray diffraction (XRD), using the Rigaku DMAX-IIIB diffractometer; the $\rho$ by the standard four-lead technique, employing the Linear Research Model LR700 Bridge; and the $\chi$ by the Quantum Design SQUID Magnetometer.

The powder XRD patterns of all of our nominal Ru-1212 samples show Ru-1212 as the major phase, with zero to various amounts of Sr$_2$GdRuO$_6$ and SrRuO$_3$ as minor magnetic impurities, depending on the sample preparation conditions. The prolonged annealing at 1055–1070 °C does not seem to influence the XRD pattern but does increase the sample density. In the present study, we report only the results of samples that have undergone prolonged annealing and are pure within our XRD resolution of $\sim 3\%$. The XRD pattern is in excellent agreement with the Rietveld refinement profile for a tetragonal Ru-1212 with space group $P4_2/mmm$ as shown in Fig. 1. The lattice parameters so-determined are $a = 3.8375(8)$ Å and $c = 11.560(2)$ Å, in good agreement with values reported previously [12]. Scanning electron microscope data show uniform composition across the sample except voids and also grains of dimensions $\sim 1–5$ µm.

The $\chi$ measured at 5 Oe during both the FC and ZFC modes is displayed in the inset of Fig. 1 as a function of temperature. A strong diamagnetic shift starting at $\sim 25$ K ($T_s$) is clearly evidenced in the ZFC-$\chi$ but not in the FC-$\chi$, although a ferromagnetic transition appears at $\sim 130$ K in both $\chi$’s, similar to the previous report [3]. The diamagnetic shift detected corresponds to a shielding volume fraction of $> 100\%$ before the demagnetization correction. A drastic drop of $\rho$, measured by a current density of $\sim 0.5$ A/cm$^2$, starting at $\sim 45$ K and reaching zero at $\sim 30$ K ($T_s$) is observed, similar to that previously reported [3,14]. $H$ broadens slightly the transition and shifts the zero-$\rho$ temperature from $\sim 30$ to $\sim 8$ K at 7 T, characteristic of a superconducting transition below its $T_s$.

In a Type II superconductor, a strong flux pinning potential reduces the size of the diamagnetic signal of the FC-$\chi$, which, in the extreme case, can lead to the apparent absence of a bulk Meissner effect. We have therefore examined the reversible or equilibrium magnetization $M_r$ [15], which excludes the flux pinning effect, as a function of $H$ at temperatures below $T_s$. $M_r(H)$ is determined as the average between the magnetizations measured at $H$ during field increase ($M_+$) and during field decrease ($M_-$), i.e. $M_r \equiv [M_+(H)] + [M_-(H)]/2$, ignoring the surface pinning, which is expected to be negligible for cuprate superconductors. For a Type-II superconductor, $dM_r/dH$ is expected to exhibit a large increase from
−1/4π to a positive value as \( H \) passes over the lower critical field \( (H_{c1}) \), then to decrease with further \( H \)-increase, and finally to diminish for \( H \geq \) the upper critical field \( (H_{c2}) \). For a superconductor with a long-range ferromagnetic order, such as the case of Ru-1212, the situation may be complicated by the possible asymmetrical ferromagnetic hysteresis. Steps have been developed to minimize such an effect \[16\]. The ferromagnetism will result in an additional positive contribution to \( dM_r/dH \), which decreases with increasing field. Both \( M_r \) and \( dM_r/dH \) of Ru-1212 are determined in different field ranges: ±5000 Oe in steps of 100 Oe, ±300 Oe in steps of 10 Oe, ±100 Oe in steps of 1 Oe, and ±30 Oe in steps of 0.25 Oe. The results for ±300 Oe are shown in Fig. 2. \( M_r \) does not show any deviation from the almost linear magnetic \( H \)-dependence nor does \( dM_r/dH \) display the large increase expected of a Meissner state as \( H \) passes over \( H_{c1} \), even for \( H \) as small as ±0.25 Oe. The results unambiguously show the absence of a bulk Meissner state in our Ru-1212 samples to \( H = 0 \). However, the initial slight increase of \( dM_r/dH \) with \( H \) allows us to estimate that no more than a few percent of a bulk Meissner state exists in the samples investigated.

A spontaneous vortex lattice (SVL) has been proposed to form in a ferromagnetic superconductor \[15\] or in a superconducting ferromagnet \[14\], provided that the internal magnetic field \((4\pi M_m)\) associated with the magnetic moment \((M_m)\) is greater than \(H_{c1}\) but smaller than \(H_{c2}\). The formation of the SVL can substantially reduce the size of the Meissner signal, similar to that observed in Ru-1212. However, the condensation energy per volume \((F_s)\) associated with the superconductivity in Ru-1212 may be estimated as

\[
F_s = (1/4\pi) \int_0^{H_{c2}} M_s dH,
\]

which can still be large, since \(H_{c2} > 7\) T \(\gg\) \(4\pi M_m \sim 200-700\) Oe, where \(M_s\) is the reversible moment associated with superconductivity. In Ru-1212, \(M_r = M_s + M_m\). To determine \(M_s\), we have measured \(M_r\)’s of the superconducting Ru-1212 and the non-superconducting Ru-1212Zn \([\text{RuSr}2\text{GdCu1.94Zn0.06O8}]\) at 5 K (\(<T_s\) of Ru-1212) and 50 K (\(>T_s\)) up to 600 Oe. Both Ru-1212 and Ru-1212Zn exhibit a similar \(T_m\) of 130 ± 2 K. \(M_s\) is then obtained as \([M_r_{Ru-1212} (5\) K) − \(M_r_{Ru-1212Zn} (5\) K)] − \([M_r_{Ru-1212} (50\) K) − \(M_r_{Ru-1212Zn} (50\) K)] and is shown in Fig. 3. The second term in the parentheses is used to eliminate the change in magnetic properties induced by the Zn-substitution. The \(M_r (= M_s)\) of a \(\text{YBa}_2\text{Cu}_3\text{O}_{6.6}\) (YBCO) sample with a bulk Meissner state and a \(T_s = 40\) K, was also measured at 5 K and is displayed with previous high field data \[17\] in the same figure for comparison. It is evidenced that \(F_s\) of Ru-1212 at 5 K is very small and lies within the resolution of the measurements of \(\sim\) a few % of that of YBCO at the same temperature. This is also in agreement with the absence of a bulk Meissner state detected by us. It was shown \[17\] previously that the condensation energy so determined is in agreement with that measured calorimetrically. Therefore, a specific heat anomaly \((\Delta C_p)\) associated with \(F_s\) at \(T_s\) of only a few % that for a bulk superconductor with a similar \(T_s\) is expected. This is in contrast to the \(\Delta C_p\) at \(T_s\) recently reported to be of the same size as that for Bi-1212 \[18\]. Adding to the puzzle is the enhancement of the peak-temperature of \(\Delta C_p\) by field detected \[19\], reminiscent of an antiferromagnetic origin of the \(\Delta C_p\). It is known that the antiferromagnet \(\text{Sr}_2\text{GdRuO}_6\) appears often in Ru-1212 and has a Ne\(\ddot{e}\)l temperature \(\sim 30\)'s K. A possible small inclusion \(< 1\)% of such an antiferromagnet in the Ru-1212 sample can account for the observation. Repeating the \(C_p\)-measurement on Ru-1212 samples with < 1% \(\text{Sr}_2\text{GdRuO}_6\) is warranted,
although the measurement is far from being trivial, as already demonstrated [18], because of the strong magnetic contribution from the sample.

As described earlier, the samples investigated are structurally pure to the XRD resolution of \( \sim 3\% \) and chemically uniform to the microprobe resolution of 1–2 \( \mu \text{m} \) across the sample. Recently, both the \( ac \) and \( dc \) magnetizations of Ru-1212 samples, all powdered sequentially from the same bulk piece of ours to particles of sizes varying from 10 to 800 \( \mu \text{m} \) with grain sizes of 1–5 \( \mu \text{m} \), were measured in fields ranging from \( 10^{-4} \) to \( 10^2 \text{ Oe} \) [19]. It was found that the hysteric part of the \( dc \chi \) and the imaginary part of the \( ac \chi \) scale linearly with the size of the particles (\( d \)) but the real part of the \( ac \chi \) decreases with \( d \) systematically and drastically. The former, which is a measure of critical current density and of the electrical connectivity throughout the particles, suggests that the Ru-1212 sample examined is electrically uniform to \( \sim 10 \mu \text{m} \) and the latter, which is a measure of screening, implies a penetration depth as large as 30–50 \( \mu \text{m} \), suggesting a very small effective carrier density, which is consistent with the negligible condensation energy observed by us.

To account for the absence of a bulk Meissner state, the appearance of negligible condensation energy, and the presence of a large effective penetration depth in a structurally pure (\( \sim 3\% \)), chemically uniform (to \( \sim 1–2 \mu \text{m} \)), and electrically homogeneous (to 10 \( \mu \text{m} \)) Ru-1212, we propose that there may exist a sponge-like superconducting network distributed uniformly across the Ru-1212 sample. In other words, the superconducting order may have modified itself with a fine structure (crypto-superconductivity) in order to fit the ferromagnetic state in the superconducting ferromagnet Ru-1212, in a way very similar to the proposed crypto-ferromagnetism in a ferromagnetic superconductor. One possible scenario is for crypto-superconductivity to exist in the ferromagnet-domain boundaries where the magnetic field can be smaller than \( H_{c2} \) and the magnetic scattering is suppressed. The possible formation of these fine ferromagnet-domains in the chemically uniform itinerant ferromagnet Ru-1212, driven by the electromagnetic interaction, appears to be not unreasonable in view of what has been observed recently in the closely related highly correlated colossal magnetoresistance manganites [20].

In conclusion, we have studied the structural, electrical, and magnetic properties of Ru-1212 samples prepared under different conditions previously reported. The reversible magnetization data clearly show the absence of a bulk Meissner state in Ru-1212 samples that are structurally pure, chemically homogeneous, and electrically uniform. By examining the difference between the reversible magnetization of the superconducting Ru-1212 and the non-superconducting Ru-1212Zn, we conclude that the condensation energy associated with the superconducting state is very small, not more than a few \% of a bulk cuprate superconductor with a similar \( T_s \). To account for the observations, we propose the possible formation of crypto-superconductivity in the superconducting ferromagnet, similar to the formation of crypto-ferromagnetism in a ferromagnetic superconductor previously suggested.

Work done in Houston is supported in part by NSF Grant No. DMR-9804325, the T. L. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center for Superconductivity at the University of Houston; and at Lawrence Berkeley Laboratory by the Director, Office of Energy Research, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
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FIGURES

FIG. 1. XRD pattern of Ru-1212: dots — data and solid line — Rietveld refinement profile. The inset shows both the FC-\(\chi\) (\(\nabla\)) and the ZFC-\(\chi\) (\(\bigcirc\)) measured at 5 Oe.

FIG. 2. \(M_r\) and \(dM_r/dH\) vs. \(H\) of Ru-1212 at 2 K.

FIG. 3. \(M_s\) vs. \(H\) for Ru-1212 (●) and for YBCO (□, △) at 5 K. Refer to the text for the determination of \(M_s\). The inset shows \(M_r\) vs. \(H\) for superconducting Ru-1212 (●) and non-superconducting Ru-1212Zn (□) at 5 K.
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