Direct Observation of Coexistence of Ferromagnetism and Superconductivity in RuSr$_2$(Gd$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$

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Abstract

Recent reports of the detecting of ferromagnetism and superconductivity in ruthenium-cuprates have aroused great interest. Unfortunately, whether the two antagonistic phenomena coexist in the same space in the compounds remains unresolved. By employing the magneto-optical-imaging technique, ferromagnetism and superconductivity were indeed directly observed to coexist in the same space in RuSr$_2$(Gd$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$ within the experimental resolution of $\sim 10 \, \mu$m. The observation sets a length scale limit for models proposed to account for the competition between ferromagnetism and superconductivity, especially $d$-wave superconductivity, in this interesting class of compounds.

74.72.Jt, 74.25.Ha, 85.70.Sq
I. INTRODUCTION

The antagonistic nature between ferromagnetism and superconductivity has long been recognized. By replacing the CuO-chain layers in the charge reservoir blocks of the cuprate high temperature superconductor with RuO$_2$ layers, the ruthenium-cuprate compounds have been formed. On cooling, they have recently been reported to undergo a magnetic transition at a temperature $T_m$ followed by a superconducting transition at a lower temperature $T_s$. For instance, the transition temperatures $(T_m, T_s)$ are (90-180 K, 30-40 K) and (130-133 K, 30-45 K) for Ru-1222 [RuSr$_2$(Gd$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$], RuSr$_2$(Eu$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$], and Ru-1212 [RuSr$_2$GdCu$_2$O$_8$, RuSr$_2$EuCu$_2$O$_8$], respectively. The appearance of a spontaneous magnetic moment in these compounds below $T_m$ at a very low field suggests that the transition at $T_m$ must have a significant ferromagnetic component, in spite of the recent detection of an antiferromagnetic order associated with the Ru-sublattice of Ru-1212 by a neutron diffraction experiment in a field below 1 T. Ferromagnetism and superconductivity have thus been proposed to coexist in Ru-1222 and -1212, an extremely unusual occurrence. Although magnetic studies have unambiguously shown a weak ferromagnetic order below $T_m$, the superconducting transition below $T_s$ has only been demonstrated by resistivity measurements in ruthenium-cuprate polycrystalline samples and without a bulk Meissner effect, the usual signature of a superconducting transition. Therefore, questions remain as to whether the two phenomena coexist in the same location in the samples below $T_s$ and, if so, what the structures of these states are, especially below $T_s$. This is particularly true in view of the absence of a bulk Meissner effect below $T_m$ and the questioning of the very existence of superconductivity in Ru-1212. To address the first question, we have carried out space-resolved magneto-optical imaging of polycrystalline samples of Ru-1222 [RuSr$_2$(Gd$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$] between 5 and 300 K in their superconducting, weak ferromagnetic, and paramagnetic states. The results clearly demonstrate that ferromagnetism and superconductivity do coexist in the same location in the samples examined within our experimental resolution of $\sim 10 \mu$m. The observation sets a new length scale limit for models proposed to account for the competition between ferromagnetism and superconductivity, especially $d$-wave superconductivity, in this interesting class of compounds, namely, superconducting ferromagnets, in which $T_m > T_s$, in contrast to the ferromagnetic superconductors, where $T_s > T_m$, previously investigated.

II. EXPERIMENTAL

The Ru-1222 studied were prepared by the standard solid-state reaction of thoroughly mixed powders of RuO$_2$ (99.95%), SrCO$_3$ (99.99%), Gd$_2$O$_3$ (99.99%), CeO$_2$ (99.99%), and CuO (99.9%), with the cation ratios of Ru:Sr:(Gd$_{0.7}$Ce$_{0.3}$):Cu = 1:2:2:2. Details of sample preparation and its relation to the superconducting and magnetic properties of the samples will be published elsewhere. The structure was determined by powder X-ray diffraction (XRD) using the Rigaku DMAX-IIIB diffractometer; the composition by the energy dispersive analysis of X-ray (EDAX); the resistivity ($\rho$) by the standard four-lead technique, employing the Linear Research Model LR-700 Bridge; the magnetization ($M$) by the Quantum Design SQUID magnetometer; and the magneto-optical imaging (MOI) by a system similar to the one described previously. Our MOI system, which uses indicator films of Bi-substituted yttrium-iron-garnet (Bi:YIG) with in-plane magnetization, consists of an
Olympus polarizing microscope, an Olympus Magnafire Imaging System, and an Oxford Microstat. For comparison with MOI pictures, the surface morphology of the sample was observed at room temperature with a scanning electron microscope (SEM).

III. RESULTS AND DISCUSSION

The powder XRD pattern in Fig. 1 shows that the Ru-1222 sample is rather pure but has slight traces of possible impurities of SrRuO₃ and Gd₂Ru₂O₇. The Ru-1222 phase exhibits a tetragonal structure with lattice parameters: \( a = 3.841(2) \) and \( c = 28.62(1) \), in good agreement with previous reports. The EDAX data show a uniform composition across the samples to a spatial resolution of 1–2 \( \mu \text{m} \). Figure 2 shows the temperature dependence of \( \rho \) of Ru-1222 at ambient as well as at 5 T. The sample shows a metallic behavior above \( T_s \), a sudden \( \rho \)-drop with an onset temperature \( \sim 38 \text{ K} \), and zero-\( \rho \) temperature \( \sim 28 \text{ K} \), which is broadened and shifted toward a lower temperature by a magnetic field, characteristic of a superconducting transition. The low-field magnetic susceptibility (\( \chi \)) at 1.2 Oe in both the zero-field-cooled (ZFC) and field-cooled (FC) modes is given as a function of temperature in Fig. 3. A large diamagnetic shift is observed in the ZFC-\( \chi \) below \( T_s \sim 30 \text{ K} \), representing a large superconducting shielding in the sample and consistent with the \( \rho \)-results. The behavior of ZFC-\( \chi \) at temperatures above \( T_s \) shows a magnetic transition near \( T_m \sim 90 \text{ K} \), although the shape of ZFC-\( \chi \) above \( T_s \) depends on the detailed nature of the magnetic state and the field-history of the measurement. The FC-\( \chi \) at low field displays a large upturn at \( T_m \sim 90 \text{ K} \), proceeded by a small rise at \( \sim 130 \text{ K} \), similar to that previously observed. The low-field FC-\( \chi \) rise at \( T_m \sim 90 \text{ K} \) shows that a spontaneous magnetic moment appears below \( T_m \), indicative of a weak ferromagnetic transition, in agreement with the previous report. A small increase at \( \sim 130 \text{ K} \) is also evident and may be associated with the magnetic impurity phase of SrRuO₃, Gd₂Ru₂O₇, or other reasons to be described later. In contrast to an earlier observation, FC-\( \chi \) displays a slight drop in our Ru-1222 samples near \( T_s \sim 30 \text{ K} \), similar to a superconducting Meissner transition of a small volume fraction, prior to its resumption of a small increase below \( \sim 22 \text{ K} \). However, the magnitude of such a diamagnetic shift in the FC-\( \chi \) was found to depend on the sample and is rapidly suppressed by an external field. It becomes zero in fields above \( \sim 5 \text{ Oe} \) for the sample shown in Fig. 3, reminiscent of a transition associated with the phase-lock of an aggregation of small Josephson-coupled superconducting grains or domains. Recently, a similar diamagnetic shift in the FC-\( \chi \) was also detected in Ru-1212, but was attributed to a possible spontaneous-vortex-state to Meissner-state transition on cooling.

We have also examined the superconducting remnant state of the sample, which was achieved by cooling the sample to its superconducting state to 5 K in the absence of a magnetic field, followed by increasing the field to 560 Oe (for reasons that will be evident later) to reach its critical state, and finally reducing the field back to zero. A magnetic field is thus trapped by the sample in its remnant state due to the persistent supercurrent at 5 K. As the sample is warmed up, the trapped field is expected to decrease to zero at \( T_s \) in accordance with the decrease of critical current in the sample with increasing temperature. This was indeed observed as shown in the inset to Fig. 3, except that the residual field vanishes not at \( T_s \), but only above \( T_m \). This is attributed to the fact that the magnetization shown in the inset to Fig. 3 consists of two contributions: the persistent supercurrent that
vanishes at $T_s$ and the ferromagnetic moment that vanishes only at $T_m$. However, the former decreases with increasing temperature to $T_s$ at a much greater rate than the latter.

The MOI technique\cite{[citation]} is employed to “see” directly the magnetism generated by the Ru-1222 sample. The imaging is based on the large Faraday effect in the garnet film, which is mounted in direct contact with the sample. The optical arrangement is such that the incoming plane-polarized light is rotated proportionally to the local magnetic field on the sample surface, and by crossing the analyzer an image is formed where the brightness directly corresponds to the local value of the magnetic field. The spatial resolution of the present system is better than 10 $\mu$m.

The Ru-1222 samples for MOI were dry-polished with 0.3 $\mu$m sandpaper. To monitor the evolution of the magnetic moment we cooled the sample in external fields ($H$) of $\sim 0.5$, 14, and 83 Oe and determined the MOI images of the Ru-1222 in its paramagnetic, ferromagnetic, and superconducting states. The typical results at 83 Oe, clearer than but similar to those at lower fields, are shown in Figs. 4a-c with the relative brightness proportional to the magnetic field generated by the sample. In the pictures, one should ignore the sharp-edged contrasts, which are domain boundaries intrinsic of the Bi:YIG indicator film. At 95 K $> T_m \sim 90$ K, where $M$ is very small, the magnetic induction of the sample $B = (H + 4\pi M) \equiv H$, and the sample is thus indistinguishable from its background (Fig. 4a). At 62 K $< T_m$, $M$ has a large positive value and $B$ becomes much greater than $H$. The sample becomes brighter than the background (Fig. 4b). At 5 K, no decrease of sample brightness was detected and, instead, the sample became even brighter (Fig. 4c). This is in agreement with the FC-$\chi$ data (Fig. 3), where the magnetic moment at 5 K is greater than that at 62 K and the small drop in moment at $\sim 22$ K vanishes at the measuring field of 14 Oe. It should be noted that even at the weak earth field of $\sim 0.5$ Oe, a bright sample image was still detected, indicative of the existence of magnetic flux in the sample in its superconducting state. This is consistent with the previous suggestion\cite{[citation]} of the absence in Ru-1212 of a bulk Meissner state. In Figs. 4b-c, bright, granular magnetic structures are clearly observed below $T_m$. This is attributable to the granular structure of the polycrystalline sample as revealed by our SEM data. There is little difference in the images below $T_m$, suggesting that these structures are mainly due to the magnetic contribution in the sample. There should be a superconducting contribution to the magnetic behavior of the sample during field cooling to below $T_s$. However, the increasing brightness of these granular structures with lowering temperatures below $T_s$, which indicates a strong magnetic field due to ferromagnetism, prevents us from separating the superconducting from the magnetic contribution in the sample.

To identify the superconducting behavior of the Ru-1222 sample, we recorded MOI images of the same sample in its superconducting remnant state, as described earlier, at different temperatures. As pointed out earlier, in the remnant state, the field trapped in the sample is associated with the persistent supercurrent and is thus expected to generate a bright structure corresponding to the superconducting parts of the sample. The superconducting remnant state at 5 K was initially obtained by the application and the subsequent removal of a field of 576 Oe that is strong enough to generate a magnetic granular structure resolvable by our MOI system near $T_s$. The MOI results of the Ru-1222 sample are shown in Figs. 5a-c, with the relative brightness proportional to the strength of the field trapped. Indeed, a bright granular structure was observed at 5 K $< T_s$ (Fig. 5a). When the sample
is warmed up, the trapped field decreases rapidly and continuously due to the decreasing persistent supercurrent, as evidenced by the rapidly diminishing brightness of the granular structure (Fig. 5b). At temperatures above \( T_s \), the granular structure disappears completely (Fig. 5c), showing directly that it is caused by superconductivity. This cannot be associated with a remnant magnetism of the sample because the brightness decreases too rapidly. This is in agreement with our magnetization results of the sample, in its superconducting remnant state achieved in a similar field, that is shown in the inset to Fig. 5.

Finally, to determine whether the superconductivity and ferromagnetism originate from the same place in the sample, we decided to compare the granular structures caused by the ferromagnetism and superconductivity, respectively, at a higher magnification with more enhanced brightness and contrast. Figure 6a shows the superconducting granular structure of the Ru-1222 sample obtained in its remnant state at 5 K. Figure 6b displays the ferromagnetic granular structure of the same area on the sample in its ferromagnetic state at 62 K. Both pictures are obtained from the same rectangular areas marked in Figs. 5a and 4b, respectively. It is clear that the two structures are essentially identical within the resolution of our MOI system, i.e. they almost fall on top of each other. The difference in the brightness of the two structures is due to the different magnetic field strengths generated by the two states. Therefore, the observation directly demonstrates that superconductivity and ferromagnetism do occur in the same location in the Ru-1212 sample within a resolution of \( \sim 10 \) \( \mu \text{m} \).

Many studies have been carried out on the nature of this superconducting state in the (weak) ferromagnetic background. Depending on the relative strengths of the superconducting and ferromagnetic interactions, various transition sequences have been proposed between the paramagnetic, (weak) ferromagnetic, spontaneous vortex, and Meissner phases in the superconducting ferromagnets. The failure to detect a bulk superconducting state nor a superconducting condensation energy led to the suggestion of a possible novel crypto-superconducting state in the superconducting ferromagnet, Ru-1212. Such a state can have a fine granular microstructure beset by the ferromagnetic walls between the antiferromagnetic “domains,” or a non-uniform filamentary structure existing in the less magnetic walls between the ferromagnetic domains. This appears to be consistent with a recent model calculation. However, based on the recent observation of a diamagnetic shift in the FC-\( \chi \), a paramagnetic \( \rightarrow \) (weak) ferromagnetic \( \rightarrow \) spontaneous-vortex \( \rightarrow \) Meissner phase transition sequence in Ru-1212 upon cooling has also been proposed. Unfortunately, the magnitude of the diamagnetic shift in Ru-1212 near 30 K decreases rapidly with an applied magnetic field and drops to zero at \( \sim 12 \) Oe, similar to that observed here in Ru-1222, reminiscent of a phase-lock transition of an aggregate of superconducting fine grains. In view of the ubiquitous electronic phase separation in the underdoped superconducting cuprates and the colossal magnetoresistant manganites, we also envision a possible similar phase separation in these underdoped Ru-1212 and -1222 samples near or below their magnetic transition, leaving an electronically non-uniform magnetic system. Such a system can have nanoscale interdispersions of different ferromagnetic strengths with superconductivity residing in the less magnetic (or even antiferromagnetic) dispersions. While the present investigation cannot distinguish one scenario from the other mentioned above, it sets a limit on the length scale of the superconducting grains or domains that is much less than 10 \( \mu \text{m} \). It should be noted that the superconducting grains or domains to which we refer here are consid-
ered to be part of and thus smaller than the crystalline grains revealed by the SEM and/or MOI data. Further refinement in the length scale depends critically on the availability of single-crystalline and/or epitaxial thin-film samples of Ru-1222 and -1212. By fine-tuning the magnetic and superconducting interactions, superconducting ferromagnets will provide a unique opportunity for the study of the interplay between magnetism and superconductivity, and particularly between ferromagnetism and $d$-wave superconductivity in cuprates.

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FIGURES

FIG. 1. The XRD pattern of Ru-1222 sample: * - impurities.

FIG. 2. $\rho(T)$ of Ru-1222: (a) 0 T and (b) 5 T.

FIG. 3. ZFC - $\chi(T)$ (a) and FC - $\chi(T)$ (b) at 1.2 Oe: Inset - The decay of the superconducting remnant moment achieved at 5 K after the application and subsequent removal of 560 Oe. The minimum $M$ that will give discernable magnetic bulk (· · ·) or granular structure (— - — -) by the MOI technique is also given.

FIG. 4. MOIs of Ru-1222 field cooled in 83 Oe at (a) 95 K, (b) 62 K, and (c) 5 K.

FIG. 5. MOIs of Ru-1222 in its remnant state achieved at a maximum field of 576 Oe was applied on warming in zero field at (a) 5 K, (b) 20 K, and (c) 40 K.

FIG. 6. Comparison between the superconducting granular structure (a) at 5 K with the magnetic granular structure (b) at 62 K in Ru-1222. They are the same areas as those marked by the rectangles in Figs. 5a and 4b, respectively.
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