A POSSIBLE CRYPTO-SUPERCONDUCTING STRUCTURE IN A SUPERCONDUCTING FERROMAGNET

C. W. Chu¹,², Y. Y. Xue¹, S. Tsui¹, J. Cmaidalka³, A. K. Heilman¹, B. Lorenz¹ and R. L. Meng¹

¹Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5932
²Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720
³Department of Chemistry and Texas Center for Superconductivity, University of Houston, Houston, TX 77204-5932
(November 2, 2018)

Abstract

We have measured the dc and ac electrical and magnetic properties in various magnetic fields of the recently reported superconducting ferromagnet RuSr₂GdCu₂O₈. Our reversible magnetization measurements demonstrate the absence of a bulk Meissner state in the compound below the superconducting transition temperature. Several scenarios that might account for the absence of a bulk Meissner state, including the possible presence of a sponge-like non-uniform superconducting or a crypto-superconducting structure in the chemically uniform Ru-1212, have been proposed and discussed.

Submitted to Physica C (November 1, 1999); accepted for publication (December 24, 1999)
I. INTRODUCTION

It has long been demonstrated [1] that, while an antiferromagnetic order can coexist with a uniform superconducting order (in a Meissner state), a long-range ferromagnetic order cannot. However, it was later shown [1] that a non-uniform ferromagnetic order could coexist with superconductivity. This non-uniform ferromagnetic order manifests itself in the form of a spiral structure, or a domain-like structure, that reduces the compound’s effectiveness in suppressing superconductivity. At the same time, it was also shown that superconductivity suppresses the ferromagnetic order. Many ternary compounds, comprised of both superconducting and ferromagnetic sublattices, indeed exhibit these fascinating magnetic structures in the superconducting state. For instance, ErRh$_4$B$_4$ [2] superconducts below its superconducting transition temperature ($T_s$) of 8.7 K and orders ferromagnetically below its transition temperature ($T_m$) of 0.8 K, before returning to a normal state below a re-entrant temperature ($T_r$) of 0.7 K. A spiral ferromagnetic structure was found to coexist with the superconducting state in this compound between $T_m$ and $T_r$. On the other hand, a domain-like ferromagnetic structure was observed between $T_m$ and $T_r$ of HoMo$_6$S$_8$ [3] and HoMo$_6$Se$_8$ [4] with ($T_s$, $T_m$, $T_r$) of (1.8 K, 0.7 K, 0.65 K) and (5.5 K, 0.53 K, 0 K), respectively. A spontaneous vortex lattice state was also proposed [5] for the case in which the internal field of the ferromagnet (4$\pi$M) is greater than the lower critical field ($H_{c1}$) but lower than the upper critical field ($H_{c2}$). The compounds previously studied always have a $T_s$ higher than $T_m$ and have been known as ferromagnetic superconductors [5]. In these ferromagnetic superconductors, superconductivity is the dominant state and the ferromagnetic state is modified with a non-uniform structure to fit the superconducting state.

Recently, several ruthenate-cuprates have been reported to undergo a transition at $T_m$ to a ferromagnetic state that coexists with a superconducting state at a lower transition temperature $T_s$. They are RuSr$_2$GdCu$_2$O$_8$ (Ru-1212) [6] and RuSr$_2$(R$_{0.7}$Ce$_{0.3}$)$_2$Cu$_2$O$_{10}$ (Ru-1222) [7], in which R = Gd or Eu, with ($T_m$, $T_s$) of (133 K, 14–47 K) for Ru-1212, (180 K, 42 K) for Ru-1222 when R = Gd, and (122 K, 32 K) for Ru-1222 when R = Eu. They have therefore been called superconducting ferromagnets [8]. The ferromagnetic state below $T_m$ has been firmly established [6,8] to be bulk and uniform to a scale of $\sim$ 20 Å across the samples, as examined by magnetization, muon-relaxation, and Mössbauer measurements. However, the cited evidence for superconductivity [6,8] rests entirely on the zero resistivity ($\rho$) observed and a diamagnetic shift of the dc magnetic susceptibility ($\chi_{dc}$) measured in the zero-field-cooled (ZFC) mode. No diamagnetic shift has been detected in $\chi_{dc}$ of these samples when measured in the field-cooled (FC) mode. It is known that a diamagnetic shift in the ZFC-$\chi_{dc}$, which is a measure of the superconducting shielding effect and consistent with the zero-$\rho$ observed, is not proof for the existence of the Meissner state, a conventional criterion for the existence of bulk superconductivity. To determine the possibility of a nearly perfect pinning in Ru-1212 that reduces the size of the diamagnetic shift in FC-$\chi_{dc}$, we have recently determined [9] the reversible magnetization ($M_r$) of the sample as a function of field ($H$) [10]. The results showed that a Meissner state exists in no more than a few percent of the bulk sample, if it exists at all. Several possibilities have been proposed [9] to account for the absence of a bulk Meissner state in Ru-1212: the possible formation of a spontaneous vortex state in the bulk superconducting ferromagnet Ru-1212; the possible presence of a spatially non-uniform superconducting structure in the chemically uniform
Ru-1212; and the possible appearance of a filamentary superconductivity associated with a crypto-superconducting fine structure in a chemically uniform superconducting ferromagnet or with an impurity phase in this otherwise non-superconducting ferromagnet. In this paper, we further examine these possibilities proposed for the absence of the bulk Meissner effect in superconducting ferromagnets.

II. EXPERIMENTAL

Ru-1212 samples investigated here were either the same ones previously studied or freshly prepared by thoroughly reacting a mixture of RuO$_2$, SrCO$_3$, Gd$_2$O$_3$, and CuO, with a cation composition of Ru:Sr:Gd:Cu = 1:2:1:2, following steps previously reported, including the prolonged annealing at 1060 °C. The structure was determined by powder X-ray diffraction (XRD), using the Rigaku DMAX-IIIB diffractometer; the resistivity by the standard four-lead technique, employing the Linear Research Model LR-700 Bridge; and both the $dc$ and $ac$ magnetizations by the Quantum Design SQUID magnetometer. Powder samples were prepared by pulverizing the pellets after prolonged annealing and selecting particles of different sizes by using sieves of different meshes.

III. RESULTS AND DISCUSSION

The samples investigated are pure Ru-1212 within the XRD resolution of a few percent. They display a tetragonal structure with a space group $P4/mmm$. The lattice parameters are $a = 3.8375(8)$ Å and $c = 11.560(2)$ Å in good agreement with values reported previously. The scanning electron microscope results show grains of 1–5 µm in size and the scanning microprobe data show a uniform composition across the sample to a scale of 1–2 µm.

The temperature dependence of $\chi_{dc}$ is shown in Fig. 1 and was measured at 5 Oe during both the ZFC and FC modes. A strong diamagnetic shift at $\sim 25$ K is detected in the ZFC-$\chi_{dc}$, but not in the FC-$\chi_{dc}$, similar to previous studies. It should be noted that such a diamagnetic shift in ZFC-$\chi_{dc}$ was sometimes absent from some samples that have the same XRD pattern. The temperature dependence of $\rho$ is exhibited in Fig. 2. A drastic $\rho$-drop starting at $\sim 45$ K and reaching zero at $\sim 30$ K ($\equiv T_s$) is observed. In the presence of a magnetic field, $T_s$ is suppressed to $\sim 8$ K at 7 T, characteristic of a superconducting transition below $T_s$.

To determine if the absence of a diamagnetic shift in the FC-$\chi$ in the Ru-1212 sample is associated with a possible strong pinning, we determined $M_r$ as a function of $H$ from negative to positive $H$ in very fine $H$-steps, especially in the low-$H$ region. Since the surface pinning in cuprate superconductors is small, $M_r$ can be taken as $(1/2)(M_+ + M_-)$, where $M_+$ and $M_-$ are magnetizations measured during the increasing and the decreasing of the field, respectively. The results of $M_r(H)$ and $dM_r(H)/dH$ are summarized in Fig. 3. $M_r$ does not exhibit any clear deviation from the almost linear $M_r-H$ relation; nor does $dM_r(H)/dH$ display the large initial increase expected of a Meissner state as $H$ passes over $H_{c1}$, even for $H$ as small as $\pm 0.25$ Oe. The results demonstrate unambiguously the absence of a bulk Meissner state in the Ru-1212 samples investigated down to 0 Oe. The slight initial increase
in $dM_r/dH$ with $H$ enables us to estimate that no more than a few percent of the bulk sample is in the true Meissner state, if the state exists at all.

In a superconducting ferromagnet with a $T_m > T_s$, a spontaneous magnetization $M$ occurs below $T_m$. If the internal field associated with the moments $4\pi M$ is greater than $H_{c1}$, but smaller than $H_{c2}$, a spontaneous vortex lattice has been proposed to form below $T_s$, similar to that predicted \[1\] for a ferromagnetic superconductor where $T_s > T_m$. Since $4\pi M$ and $H_{c1}$ are temperature-dependent, there may exist two scenarios for the superconducting ferromagnet. When its $4\pi M$ is always greater than $H_{c1}$ below $T_m$, the compound will undergo a paramagnetic-to-ferromagnetic transition at $T_m$ and then enter the spontaneous vortex state at and below $T_s$, as shown in Fig. 4a. This was proposed to be a possible case for Ru-1212 \[3\]. When the growth of $H_{c1}$ outpaces that of $4\pi M$ below a certain temperature $T_{so}$, as shown in Fig. 4b, the compound first undergoes a paramagnetic-to-ferromagnetic transition at $T_m$ upon cooling and then enters the spontaneous vortex state at $T_s$, before it recovers the Meissner state at $T_{so}$. Such a case has been suggested to take place in Ru-1222 \[8\], although the Meissner state below $T_{so}$ was not evident in their FC-$\chi_{dc}$. Another possible scenario is a triplet superconducting pairing, in which $T_m$ may coincide with $T_s$ \[11\]. In this scenario, the compound will directly enter the spontaneous state at $T_s$ from its paramagnetic state when $4\pi M > H_{c1}$ (Fig. 4c) or recover its Meissner state if $4\pi M$ becomes smaller than $H_{c1}$ below $T_{so}$ (Fig. 4d). We conjecture that the superconducting Sr$_2$RuO$_4$ may fall into this third category.

In the above discussions, a bulk superconducting state is assumed to exist in the superconducting ferromagnet below $T_s$. Its existence is usually best demonstrated by the detection of a specific heat anomaly ($\Delta C_p$) at $T_s$. A $\Delta C_p$ was indeed reported \[12\] in Ru-1212 near $T_s$, with a magnitude close to that of an underdoped superconducting cuprate. Unfortunately, it was also reported that while the magnitude of $\Delta C_p$ is suppressed by an externally applied $H$, as expected of a bulk superconducting transition, the peak temperature of $\Delta C_p$ increases with $H$, in strong contrast to the $T_s$-suppression by $H$ observed. This suggests that the detected $\Delta C_p$ may be of a magnetic origin. It is known \[3\] that Sr$_2$GdRuO$_6$, which forms easily in the Ru-1212 matrix, is an antiferromagnet with a Neé temperature close to $T_s$ at $\sim 30$ K and a transition drastically suppressed by $H$ \[9\]. The presence of a few tenths of a percent of Sr$_2$GdRuO$_6$ as an impurity in Ru-1212 can easily account for the $\Delta C_p$-anomaly detected near $T_s$ \[12\].

In view of the possible absence of $\Delta C_p$, and thus of bulk superconductivity in Ru-1212, we decided to investigate both the chemical and the electrical uniformity of the Ru-1212 samples. As mentioned earlier, the XRD pattern of our samples shows only the Ru-1212 phase within our experimental resolution of a few percent. The microprobe scan indicates that the sample is chemically uniform to a scale of $\sim 1–2 \mu m$ in agreement with previous report \[3\]. To determine the electrical uniformity of the sample in terms of its superconducting property, we examined the superconducting shielding effect of Ru-1212 powder samples of different particle sizes by measuring the ac magnetization ($M_{ac}$) as a function of the ac field ($H_{ac}$) in fine steps to $\sim 10^{-4}$ Oe in zero dc field. Details of the experiment will be published elsewhere \[13\]. Typical results of the ac susceptibility $\chi_{ac} \equiv M_{ac}/H_{ac}$ for samples of particle sizes down to $20 \mu m$, all pulverized sequentially from the same bulk sample of $\sim 6$ mm, at 2 K are displayed in Fig. 5. For the $6$ mm bulk sample, $-4\pi\chi_{ac}$ varies negligibly with $H_{ac} < 0.1$ Oe, but decreases rapidly with $H_{ac} > 1$ Oe. The $ac$
superconducting shielding effect as measured by $-4\pi\chi_{ac}$ before the demagnetization factor correction is $\sim 200\%$. As the particle size decreases, $-4\pi\chi_{ac}$ decreases, but remains almost $H_{ac}$-independent until $H_{ac} > 1$ Oe. To assure that the $-4\pi\chi_{ac}$-drop is not caused by the degradation of the samples due to pulverization, we compared the $M_r$'s for both the bulk and the powdered sample of a particle-size of 50 $\mu$m as shown in the inset in Fig. 1. The same $M_r$ was detected for the two samples, suggesting that the powdered samples retain their integrity.

For a uniform bulk superconductor, $\chi_{ac}$ is expected to be independent of the particle-size, provided that the penetration depth $\lambda \ll d$, where $d$ is the size of the particle. However, the field $H'_{ac}$, beyond which $-4\pi\chi_{ac}$ starts to decrease, is determined by $J_c d$, where $J_c$ is the critical current density of the compound, and is expected to decrease with $d$, according to the Bean model. This is borne out by our results for a similar experiment on the uniform bulk and powdered superconducting YBa$_2$Cu$_3$O$_7$ [13]. Therefore, our observation in Ru-1212 is in variance with what is expected of a uniform bulk superconductor in two respects: the $\chi_{ac}$-decrease with $d$ and the almost $d$-independent $H'_{ac} \sim 0.5$ Oe. The $H'_{ac}$ predicted by the Bean model is also shown in Fig. 5 for comparison. These variances can be explained by assuming that Ru-1212 is a bulk superconductor and has a penetration depth $\lambda \sim 50$ $\mu$m. However, the estimated $\lambda \sim 50$ $\mu$m seems to be too large for a cuprate superconductor which has a reported $\lambda$ value usually about 20–100 times smaller. To explain the large $\lambda$, we assume that there may exist a sponge-like superconducting network uniformly distributed across the Ru-1212 sample to a scale of $< 20$ $\mu$m. In other words, the superconducting order may have modified itself with such a non-uniform fine structure (crypto-superconductivity) in order to fit into the ferromagnetic state in the superconducting ferromagnet Ru-1212, in a way very similar to the proposed crypto-ferromagnetism in a ferromagnetic superconductor [14]. For instance, superconductivity may exist between the ferromagnet-domain boundaries where the magnetic field can be smaller than $H_{c2}$ and the magnetic scattering is suppressed. The 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 in the closely related highly correlated colossal magnetoresistance manganites [15]. Such a superconducting structure is expected to display a very small condensation energy associated with the superconducting transition at $T_s$. This proposed structure is consistent with the zero $\rho$ observed and with our preliminary results suggesting a negligible condensation energy determined by the magnetization method [13].

While the large $\lambda$ suggested by our $\chi_{ac}$-$H_{ac}$ results can be explained in terms of the possible appearance of crypto-superconductivity, we would also like to address the other possible cause, i.e. the presence of a minor superconducting impurity phase in the otherwise non-superconducting ferromagnet Ru-1212. RSr$_2$Cu$_3$O$_7$ (Cu-1212) with $R = Y$ or a rare-earth element is known to form at ambient pressure by slight doping with a high valence element [16] or under high pressure without doping [17]. For example, the Cu-1212 with its chain-Cu partially replaced by Ru has been reported [18] to form at ambient pressure and has a $T_s$ of $\sim 20$–65 K. A small amount of the slightly Ru-doped Cu-1212 present in an otherwise non-superconducting Ru-1212 may thus account for the observation of the large $\lambda$, the zero $\rho$, and the absence of a bulk Meissner state. However, more than $\sim 10\%$ of the minor phase of Ru-doped Cu-1212 is required to be present in order to account for the observed percolative path of zero $\rho$ in Ru-1212. Although the similar structures of Ru-1212 and Cu-1212 make the XRD less decisive in differentiating the two phases, the difference
between the Cu/Ru-ratios of the two phases (2/1 and 2.7/0.3 for the Ru-1212 and Ru-doped Cu-1212, respectively) can be easily detected by the microprobe for their separate presence. Unless the slightly Ru-doped Cu-1212 or other unknown superconducting impurity phase is finely dispersed to a scale below one micrometer or is deposited in the grain boundaries of the sample, our microprobe data suggest the unlikely presence of such superconducting impurities, in agreement with previous reports [6].

In conclusion, we have measured the electrical and magnetic properties of both bulk and powdered Ru-1212 of different particle sizes in various dc and ac fields. The XRD and microprobe data show that the Ru-1212 samples examined are chemically pure to a few percent and uniform to a scale of 1–2 µm. The reversible magnetization as a function of field clearly demonstrates the absence of a bulk Meissner state in Ru-1212. The $-4\pi\chi_{ac}$ decreases as the particle size decreases and remains constant initially as the ac field increases, but decreases rapidly, independent of the particle size, as the ac field increases to above $\sim 0.5$ Oe. Several possible scenarios have been considered and discussed. While a spontaneous vortex state may exist in a bulk superconducting ferromagnet Ru-1212, we also propose that the superconducting state in a superconducting ferromagnet is more likely to have modified itself to a sponge-like non-uniform superconducting fine (crypto-superconducting) structure to fit the ferromagnetic state in the chemically uniform Ru-1212. While the spontaneous vortex lattice shows a reduced condensation energy as the compound undergoes the superconducting transition, the crypto-superconducting structure is expected to display a negligible condensation energy. Further experiments to determine the condensation energy and the spontaneous vortex lattice in superconducting ferromagnets are needed to differentiate the above suggestions.

ACKNOWLEDGMENTS

The work 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.
REFERENCES

[1] For a review, see L. N. Bulaevskii, A. I. Buzdin, M. L. Kulić and S. V. Panjukov, Advances in Physics 34, 175 (1985).
[2] S. K. Sinha, H. A. Mook, D. G. Hinks and G. W. Crabtree, Phys. Rev. Lett. 48, 950 (1982).
[3] W. Thomlinson, G. Shirane, J. W. Lynn and D. E. Moncton, Superconductivity in Ternary Compounds II, Topics in Current Physics, vol. 34, ed. M. B. Maple and Ø. Fischer (Berlin: Springer-Verlag, 1982), p. 99.
[4] J. W. Lynn, J. A. Gotaas, R. W. Erwin, R. A. Ferrel, J. K. Bhattacharjee, R. N. Shelton and P. Klevins, Phys. Rev. Lett. 52, 133 (1984).
[5] R. A. Ferrel, J. K. Bhattacharjee and A. Bagchi, Phys. Rev. Lett. 43, 154 (1979); H. Matsumota, H. Umezawa and M. Tachiki, S. S. Comm. 31, 157 (1979); and H. S. Greenside, E. I. Blount and C. M. Varma, Phys. Rev. Lett. 46, 49 (1981).
[6] C. Bernhard, J. L. Tallon, Ch. Niedermayer, Th. Blasillo, A. Golnik, E. Brcker, K. K. Kremer, D. R. Noakes, C. E. Stronack and E. J. Ansaldo, Phys. Rev. B 59, 14099 (1999).
[7] I. Felner, U. Asaf, Y. Levi and O. Millo, Phys. Rev. B 55, R3374 (1997).
[8] E. B. Sonin and I. Felner, Phys. Rev. B 57, R14000 (1998).
[9] C. W. Chu, Y. Y. Xue, R. L. Meng, J. Cmaidalka, L. M. Dezaneti, Y. S. Wang, B. Lorenz and A. K. Heilman, cond-mat/9910056 5 October 1999.
[10] J. R. Clem and Z. D. Hao, Phys. Rev. B 48, 13774 (1993).
[11] A. Knigavko and B. Rosenstein, Phys. Rev. B58, 9354 (1998).
[12] J. L. Tallon, J. W. Loram, G. V. M. Williams and C. Bernhard, to appear in Phys. Rev. Lett.
[13] Y. Y. Xue, S. Tsuei, J. Cmaidalka and C. W. Chu, to be published.
[14] P. W. Anderson and H. Suhl, Phys. Rev. 116, 898 (1959).
[15] J. Goodenough and J. S. Zhou, Nature 386, 229 (1997).
[16] C. Greaves and P. R. Slater, Physica C 180, 245 (1989); T. E. Dann, M. S. Thesis, Tankung University, Taiwan (1990); and B. Debrowski, K. Rogack, J. W. Koenitzer, K. R. Peopelmeir and J. D. Jorgensen, Physica C 277, 24 (1997).
[17] B. Okai, Jpn. J. Appl. Phys. 29, L2180 (1990); and Y. Cao, T. L. Hudson, Y. S. Wang, J. H. Xu, Y. Y. Xue and C. W. Chu, Phys. Rev. B 58, 11201 (1998).
[18] D. H. Chen, Ph.D. Thesis, National Tsing Hua University, Taiwan (1995).
FIGURES

FIG. 1. $4\pi\chi_{dc}$ vs $T$ for Ru-1212 at 5 Oe. Inset: $M_r$ vs $H$ at 2 K for Ru-1212 bulk ($\nabla$) and 50 $\mu$m particles ($\bigcirc$).

FIG. 2. $\rho$ vs $T$ for Ru-1212 at 0 (solid) and 9 T (dashed).

FIG. 3. $M_r$ and $dM_r/dH$ vs $H$ for Ru-1212 at 2 K.

FIG. 4. The formation of the spontaneous vortex state (SVS) and Meissner state (MS) in superconducting ferromagnets, in which $T_m > T_s$, when a) $H_{c1}$ always smaller than $4\pi M$; b) $H_{c1} > H_{c1}$ below $T_{so}$; c) $T_s = T_m$ and $H_{c1} < 4\pi M$ always; and d) $T_s = T_m$ and $H_{c1} > 4\pi M$.

FIG. 5. $\chi_{ac}$ vs $H_{ac}$ for bulk and powdered samples of different particle sizes: $\bigtriangleup$ — bulk; $\Box$ — 820 $\mu$m; $\nabla$ — 110 $\mu$m; $\bigtriangledown$ — 50 $\mu$m; and $\bigcirc$ — 20 $\mu$m. The arrows represent the $H'_{ac}$ based on the Bean model.
This figure "fig1.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0002212v1
This figure "fig2.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0002212v1
This figure "fig3.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0002212v1
This figure "fig4.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0002212v1
This figure "fig5.png" is available in "png" format from:

http://arxiv.org/ps/cond-mat/0002212v1