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Bulk superconductivity in $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$

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An $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ sample synthesized by high-pressure high-temperature solid-state reaction underwent (weak) ferromagnetic transition at ~150 K followed by a bulk superconducting transition at ~30 K. It showed a clear Meissner signal in the field-cooled process up to external magnetic field of a few hundred Oe (~300 Oe). These results appear to indicate coexistence of bulk superconductivity and ferromagnetism. At the same time, both magnetic-susceptibility and hysteresis data can be interpreted as mere superimposition of superconducting diamagnetic and (weak) ferromagnetic responses without any anomalous behavior. The genuine coexistence of bulk superconductivity and ferromagnetism in this compound might not yet be conclusive.

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Recent discovery of the ‘‘superconducting ferromagnet’’ of $RuSr_2LnCu_2O_8$ (Ln/Ru-1212, $Ln=$Gd, Eu, Y) is of tremendous interest.[1] In these compounds, ordering of Ru spins occurs at $T_N=120-150$ K followed by the superconducting transition at $T_c=10-40$ K. A similar phenomenon was also observed in $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10}$ (Gd/Ru-1222).[2] The bulk nature of the ferromagnetic order parameter in Gd/Ru-1212 was evidenced from muon-spin-resonance (μSR) and electron-spin-resonance experiments.[1,3] However, there are still serious discrepancies among magnetic properties obtained by different experimental tools. Neutron-diffraction experiments for Ln/Ru-1212 indicated that they have a G-type antiferromagnetic structure with $\mu_{Ru}\sim 1\mu_B$ and ferromagnetism in these phases is due to canting of the Ru moments.[4–7] Recent dc magnetic measurements for Gd/Ru- and Eu/Ru-1212 have cast doubt on the model proposed by the neutron studies from various points of view.[8]

The bulk nature of superconductivity was initially criticized due to a lack of Meissner signal in Gd/Ru-1212 and instead a cryptosuperconducting phase was proposed.[9,10] Recently, however, Bernhard *et al.* reported a sizable Meissner signal in a field-cooled (fc) process for a Gd/Ru-1212 sample as a evidence of a bulk Meissner phase.[11] According to them, the bulk Meissner phase develops below a certain temperature T^{ms}, which is substantially lower than the superconducting transition temperature T_c, and a spontaneous vortex phase exists in the intermediate-temperature region $T^{ms}<T<T_c$. Quite a similar picture regarding the coexistence of superconductivity and magnetism has been proposed for the Gd/Ru-1222 phase.[12]

As far as the phase purity is concerned, a good amount of work has been done on Gd/Ru-1212, including synchrotron x-ray (Ref. 13) and neutron powder[6] diffractions, and high-resolution transmission-electron microscopy.[13] Yet the question of phase purity has not been resolved to a satisfactory level.[14] Not only do various phase pure nonsuperconducting samples exist,[15] but also the reproducibility of superconducting compounds with the same heat treatments is reported to be in doubt.[9] Some of these puzzles are due to the fact that solid solutions of $Ru_{1-x}Cu_x$-1212, which can be superconducting with $x>0.5$, but not necessarily magnetic, may precipitate within the stoichiometric Ru-1212 composition.[16] Because Ru and Cu have close scattering cross sections for neutrons, neutron-diffraction study is not very helpful for such a problem.

It seems that we still need fundamental data, in particular, on magnetic properties, to determine a final conclusion on the coexistence of superconductivity and magnetism. To observe the magnetic behavior, Gd/Ru-1212 is not an appropriate system because of the presence of magnetic Gd ions ($8\mu_B$), which limit knowledge of the exact magnetic contributions from the Ru ions and from superconductivity. Ru-1212 can be formed for nonmagnetic Y instead of Gd, but only using a high-pressure high-temperature (HPHT) synthesis technique.[5,17,18] It is our aim here to study the magnetic properties of a superconducting Y/Ru-1212 sample prepared with the HPHT method. We observe the Meissner signal in the fc process up to a few hundred Oe external fields for this sample. This result presents a striking contrast to Gd/Ru-1212, for which a fc diamagnetic signal was seen up to only a few Oe fields or even without a signal.

A sample with the composition $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ was synthesised through a HPHT solid-state reaction with ingredients of Y_2O_3, SrO_2, $SrCuO_2$, RuO_2, and CuO. Details of the sample synthesis are given elsewhere.[17,18] A slightly Ru-poor starting composition was selected because a single-phase sample may be obtained from this composition without the contamination of $SrRuO_3$.[17] X-ray powder-diffraction patterns were obtained by a diffractometer (Philips-PW1800) with Cu K_α radiation. dc susceptibility data were collected by a superconducting quantum interference device magnetometer (Quantum Design, MPMS).

$Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ crystallized in an essentially single-phase form without any contamination from $SrRuO_3$ or YSr_2RuO_6, in space group $P4/mmm$ with lattice parameters $a=b=3.818(1)$ and $c=11.522(3)$ Å.[17,18] Any extra x-ray peaks were not observed indicating that the impurity content, if any, was less than ~3%. Figure 1 shows both zero-field-cooled (zfc) and fc magnetic susceptibility versus temperature (χ vs T) plots for the $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ sample, in various external fields H of 50, 70, 100, 300, and 1000 Oe. As seen from this figure the zfc and fc magnetization curves show a rapid increase near 150 K followed by a significant branching at around 145 K. The branching is indicative of the long-range magnetic order of the Ru moments. Neutron-diffraction studies revealed that the Ru moments order anti-

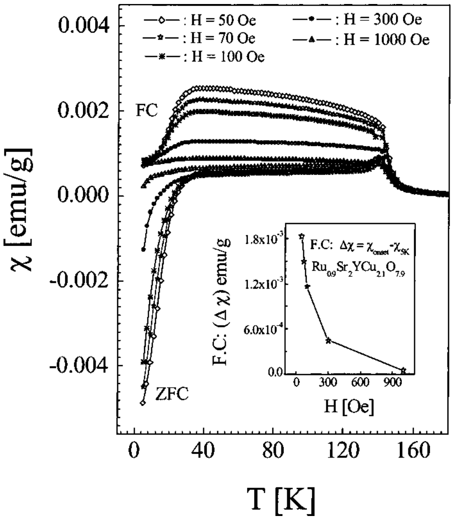

FIG. 1. Magnetic susceptibility versus temperature (χ vs T) plots for a $\mathrm{Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}}$ sample, in various applied fields of 50, 70, 100, 300, and 1000 Oe; inset shows the difference of magnetic susceptibility ($\Delta\chi$) between T_c (onset) and 5 K for field-cooled (fc) transitions in various fields.

ferromagnetically at $T_N = 133$ and 120 K, in Gd/Ru-1212 and Eu/Ru-1212, respectively.[4,6,7] In a recent neutron study on Y/Ru-1212 prepared by the HPHT process, similar magnetic order was observed at $T_N = 149$ K,[5] which is in close agreement to the current value. With an increase in applied field ($10\ \mathrm{Oe} < H < 1\ \mathrm{kOe}$) basically no change is observed in the magnetic transition temperature.

The zfc part of magnetic susceptibility at low T below 30 K shows clear diamagnetism up to $H \sim 300$ Oe. The diamagnetism is field dependent, and almost disappears at $H = 1000$ Oe. The diamagnetic signal onset temperature is described as the superconducting transition temperature (T_c) although the transition is rather broad. Worth noting is the fact that the diamagnetic signal observed in the zfc process does not saturate down to 5 K.

The fc part of the magnetic susceptibility remains positive down to 5 K. However, the Meissner signal is observed clearly as a dip below $\sim$30 K. The dip in the fc susceptibility is dependent on the external field; the higher the field and the lower the dip. For applied magnetic field of 1000 Oe, the dip disappears almost completely. The dip in the fc curve corresponds well to the decrease of the susceptibility in the zfc curve with almost the same onset temperature. Though a negative susceptibility is not observed in the fc process, the observation of the clear dip guarantees the bulk nature of superconductivity in the sample. We roughly evaluate the dip by defining $\Delta\chi$ as the difference of susceptibility between T_c (onset) and 5 K, which is plotted in the inset of Fig. 1. It is clear that $\Delta\chi$ decreases with an increase in H. However, $\Delta\chi$ has a nonzero value even at $H = 300$ Oe. At $H = 50$ Oe, $\Delta\chi$ is 1.8×10^{-3} emu/g, which is converted to 1.1×10^{-2} emu/cm^3 using the calculated density of 6.02 g/cm^3. This value gives nearly 14% of the Meissner superconducting volume fraction compared with the perfect diamagnetic susceptibility of $-1/4\pi$. At $H = 300$ Oe, on the other hand, $\Delta\chi = 4.6\times10^{-4}$ emu/g $= 2.8\times10^{-3}$ emu/cm^3 gives nearly 4% of the Meissner fraction. The fc susceptibility is almost saturated below about 10 K. In contrast to the nonsaturated zfc one resulting in an increase of the difference between the fc and the zfc values with decreasing temperature. This probably reflects the effect of pinning of vortexes, i.e., we have to suppose fairly strong pinning for the present system.

Bernhard *et al.* also reported a dip in the fc process for a Gd/Ru-1212 sample.[11] According to their scenario on the coexistence of superconductivity and ferromagnetism, a spontaneous vortex phase (SVP) is formed when the spontaneous magnetization $4\pi M$ exceeds the lower critical field H_{cl} (i.e., $4\pi M > H_{cl}$). On the other hand, the Meissner phase will become stable if $4\pi M < H_{cl}$. Since H_{cl} depends on the temperature being zero at T_c while $4\pi M$ is practically constant for temperatures near or below T_c, the Meissner state will develop below a certain temperature T^{ms}, which is substantially lower than T_c, and a SVP exists in the intermediate-temperature region $T^{ms} < T < T_c$. When the external magnetic field is applied, the Meissner phase will occupy a narrower area with $4\pi M + H < H_{cl}$. For the Gd/Ru-1212 sample, Bernhard *et al.* estimated $4\pi M$ of the order of 50–70 Oe and $H_{cl}(T=0)$ of the order of 80–120 Oe. The difference between the two values (30–50 Oe) is not very large, and this was claimed to be a reason for the Meissner signal disappearing under a higher external magnetic field $H_t > 35$ Oe (here, it is implied that the SVP phase has a minimal Meissner effect, although its reason has not yet been clarified). A similar picture was proposed for the Gd/Ru-1222 phase.[12]

Bernhard *et al.* observed a clear dip in the fc process only at very low applied fields (<10 Oe). In our case for the Y/Ru-1212 compound the dip in the fc process is observed up to 300 Oe. Moreover, it should be noted that if we subtract the ferromagnetic contribution in Fig. 1, the remaining magnetic-susceptibility curve looks very normal compared with those of high-T_c oxides without any anomalous behavior pertaining to microscopic coexistence of superconductivity and ferromagnetism. Although the superconducting transition is rather broad in the present sample, such a broadening often occurs in an inhomogeneous system. As far as the compositional variation is concerned, a lot of discussion has already been reported in the literature regarding similar compounds, namely, the intermixing of Ru and Cu.[9,10,14,16,17] Interestingly even microprobe analysis was proved to be inconclusive.[9,10] As far as thermal neutrons (used widely for fixing the various cationic positions in a cell) are concerned they cannot distinguish with certainty between the Ru and Cu atoms due to their very close thermal scattering factors. In such a situation, the compound is left to be judged based on its various bulk physical properties.

It is worth discussing here that the dc electric resistivity of the present Y/Ru-1212 sample is quite high and zero resistivity was not usually attained even when the sample showed a large diamagnetism in a low-temperature region. Although zero resistivity was attained after high-oxygen-pressure postannealing,[5,17] it resulted in decomposition of the Y/Ru-1212 phase and the superconducting volume fraction was not increased at all after the postannealing.[17] This fact may have an origin related to the possible phase separation. In some

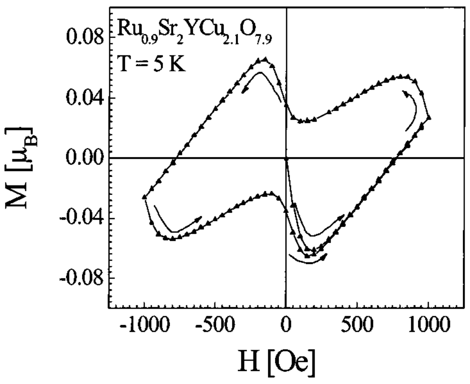

FIG. 2. M vs H plot for the $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ compound at 5 K. The applied field H is in the range of $0 = H = 1000$ Oe.

high-temperature superconductor cuprates, however, the superconducting volume fractions are not high (~20%) and the weak links, etc. can affect the electrical conduction process in polycrystalline samples. What is clear from our results in Fig. 1 is that our Y/Ru-1222 compound possesses both bulk superconductivity below 30 K and weak ferromagnetism above 150 K. But their coexistence on a microscopic scale cannot yet be conclusive, because a phase-separated state of a superconductor and a ferromagnet can also account for the susceptibility data in Fig. 1.

Figure 2 depicts the magnetization loop for the $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ sample at 5 K with the applied fields in the range of $1000 < H < 1000$ Oe. At the present stage, it is not known exactly what kind of anomaly is expected in the magnetization curve for the coexistence system of superconductivity and magnetism, i.e., for SVP and the Meissner phase. Sonin and Felner carried out a theoretical analysis and proposed an equilibrium magnetization curve expected for the system in question.[12] However, as the clear magnetic hysteresis is seen in Fig. 2, the present system is far from the equilibrium state (it is also worth noting that a fairly strong pinning effect is suggested from the magnetic-susceptibility data). The experimental hysteresis loop in Fig. 2 can be again interpreted both ways, such as the mere superimposition of superconducting and ferromagnetic hysteresis or the Sonin and Felner model with an appropriate pinning for the ferromagnetic superconductor. The H_{cl} value estimated from Fig. 2 is reasonable within the order of 100 Oe.

In Fig. 3 is shown the magnetization curves at various temperatures of 5, 20, 50, 100, 120, and 150 K, in applied fields of $-70 < H < 70$ kOe. According to the neutron-diffraction experiments, Ln/Ru-1212 (Ln=Gd, Eu, Y) phases order below T_N in a G-type antiferromagnetic structure with $\mu_{Ru} \sim 1\mu_B$ along the c axis, and canting of the moments gives a small ferromagnetic component less than $0.3\mu_B$.[4–7] From Fig. 3, the magnetization at 70 kOe and 5 K is $1.17\mu_B$, and the extrapolation of the high magnetic-field data at 5 K to $H=0$ gives $M_0 \sim 1\mu_B$. These values are in good agreement with previous magnetization reports for the Ln/Ru-1212 phases.[1,5,7] M_0 is close to the μ_{Ru} proposed by the neutron-diffraction experiments. The agreement of the two values means that the Ru moments align parallel to the external magnetic field with an external field of ~40 kOe. However, this seems somewhat curious if we consider T_N as high as ~150 K. The antiferromagnetic correlation should be of the order of 150 K and it is natural to assume that a very high magnetic field with corresponding strength is needed in order to align the Ru moments completely parallel.

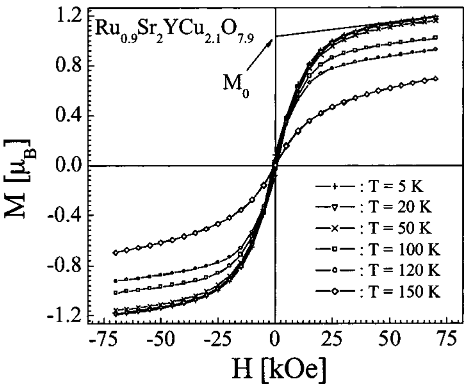

FIG. 3. M vs H plot for the $Ru_{0.9}Sr_2YCu_{2.1}O_{7.9}$ compound at T=5, 20, 50, 100, 120, and 150 K. The applied field H is in the range of $-70 < H < 70$ kOe.

According to a recent report for Gd/Ru-1212 and Eu/Ru-1212, high-temperature magnetic-susceptibility data gave $\mu_{Ru} \sim 2.5\mu_B$ for both phases which is 2.5 times larger than the neutron value. Using this value and considering this within the canted antiferromagnetism regime, the low-temperature magnetization curves in Fig. 3 may be divided into two parts $H < 40$ and $H > 40$ kOe. The data for $H < 40$ kOe mainly reflects the process in which the net ferromagnetic moment aligns parallel to the external magnetic field, changing its direction from the easy axis of magnetization (or easy plane of magnetization). According to the magnetic structure proposed by the neutron experiments, the easy plane of magnetization for the net ferromagnetic moment is the a-b plane, and this plane is not always parallel to the external magnetic fields in a polycrystalline ceramic sample. It may be worth noting here that a recent ferromagnetic-resonance study suggested an extremely large easy-plane anisotropy of ~110 kOe,[3] though that is much higher than the present value of ~40 kOe.

In the second process for $H > 40$ kOe, the canting angle of the Ru moment may increase exclusively, with H resulting in the linear increase of the magnetization. According to this scenario, M_0 is not the "saturation" magnetization but the spontaneous magnetization (the same interpretation has been made for Gd/Ru-1222 in Ref. 10), giving an internal dipolar magnetic field of ~700 Oe ($=4\pi M_0$). This value of the magnetic field is in good agreement with the result of the μSR measurement for Gd/Ru-1212,[1] but is one order-of-magnitude larger than that of the neutron-diffraction experiments, and in addition, it will require a large canting angle, which may be unusual.[6] At the present stage, it is very difficult to propose a definite model for the magnetism of Ru-1212 because of the serious discrepancies among the magnetic data obtained by different experimental tools. It seems that single-crystal measurements are needed for the final conclusion.

In summary, our Y/Ru-1212 sample prepared under high pressure appeared to undergo a (weak) ferromagnetic transition at ~150 K followed by a bulk superconducting transition at ~30 K. A clear Meissner signal was observed in the fc process up to $H=300$ Oe, in contrast to the earlier reports for various Ru-1212 samples, which showed a Meissner signal only under very low magnetic field or even without a signal. These results appear to indicate the genuine coexistence of bulk superconductivity and ferromagnetism. However, that is not yet conclusive because we did not observe any anomalous behavior in the magnetic-susceptibility and hysteresis data, and the data may be explained assuming a macroscopic mixing state of a superconductor and a ferromagnet. The ferromagnetic properties obtained by the dc magnetic measurements were also not fully consistent with the magnetic structure proposed by neutron-diffraction experiments.

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