Evidence for Possible Phase-Separations in
$\text{RuSr}_2(\text{Gd,Ce})_2\text{Cu}_2\text{O}_{10-\delta}$

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Abstract

An unusual thermal-magnetic hysteresis was observed between a minor magnetic transition around 120 K and the main one at 80 K in superconducting RuSr$_2$(R,Ce)$_2$Cu$_2$O$_{10-\delta}$ (Ru1222R) samples, where R = Gd or Eu, down to a submicron length-scale. The observation suggests a possible phase-separation and is consistent with the very small but universal demagnetizing factor observed, which is difficult to reconcile with the canted spin-structure previously proposed. In such a scenario, the unusual superconducting properties of the Ru-based cuprates can also be understood naturally.

75.60.-d,75.70.Cn,74.72.Jt
The neutron-powder-diffraction (NPD) observation that the Ru-spins in RuSr$_2$GdCu$_2$O$_8$ (Ru1212), which is superconducting below 20–40 K, are antiferromagnetically (AFM) aligned below a magnetic transition-temperature $T_M \approx 133$ K makes its physics more complicated. Although canted Ru-spins have been proposed, the interpretation seems to be debatable. On one hand, the macroscopic moment of ceramic Ru1212 samples appears as that of a ferromagnet with a remnant moment of $m_r \approx 0.14 \mu_B$/cell. On the other hand, the NPD sets an upper limit of only 0.1 $\mu_B$/cell for the ferromagnetically (FM) aligned spins, $M$. Since $M$ should be larger than 2$m_r$ in a ceramic, the two measurements are difficult to reconcile with each other as canted spins. A possible way to accommodate these conflicting values is the existence of mesoscopic phase-separations. Previously, such a possibility has been disregarded based on a $\mu$SR measurement. We would like to point out, however, that the volume-fraction $\approx 2m_r/m_o$ of the possible FM species may be well below the experimental uncertainty of 20% with the Ru moment $m_o > 3 \mu_B$/cell. A similar debate in manganites further demonstrates that it is difficult to rule out phase-separations with only a few measurements. A re-examination of the Ru-based cuprates, therefore, is warranted. It should be noted that the magnetic configuration of Ru1212 is directly related to its superconductivity (SC). While “ordinary” SC may coexist with canted AFM, a phase-separation will result in the appearance of Josephson-junction arrays as previously proposed. The severe granularity of Ru1212 could thus be understood similar to the heterogeneous magnetic structure of ErRh$_4$B$_4$.

As part of our effort, the thermal-magnetic hysteresis of superconducting RuSr$_2$R$_{2-x}$Ce$_x$Cu$_2$O$_{10-\delta}$ (Ru1222R) with R = Gd or Eu and $x$ between 0.6 and 0.7, whose magnetic structure is expected to be similar to that of Ru1212, is studied. Our data confirm that there are minor weak-ferromagnetic transitions at $T_{M2} \approx 120$ K and $T_{M3} \approx 140$ K above the main transition at $T_{M1} \approx 80$ K, as reported previously. A dipole-dipole AFM interaction is further detected between the $T_{M1}$ and the $T_{M2}$ FM-species with a universal strength down to a length scale far smaller than the grain size, i.e. these two FM-species should coexist in a single structural grain. Furthermore, the strength, measured as the effective demagnetizing factor of the dipole field, is too small to be accommodated with a homogeneously canted-spin structure. A spatial correlation between the two species is needed. The observation, therefore, suggests a possible phase-separation between the FM species and a possible AFM matrix. Such a scenario can naturally account for many unusual superconducting properties previously reported in Ru1212/Ru1222.

Ceramic Ru1222 samples were synthesized following the standard solid-state-reaction procedure. Raw oxide powders were first prepared by calcination at 400–900 °C under flowing O$_2$. Mixed powder with a proper cation ratio was then pressed into pellets and sintered at 900 °C in air for 24 hr. The final annealing was done at 1090 °C for 60 hr after repeatedly sintering at 1000 °C and regrinding. Pulverized samples of Ru1222R with different particle sizes sorted by the descending speeds in acetone were prepared. The structure was determined by powder X-ray diffraction (XRD) using a Rigaku DMAX-IIIIB diffractometer. There are no noticeable impurity lines in the X-ray diffraction pattern within a resolution of a few percent. The grain sizes of the ceramic samples, the particle sizes of the powders, and the composition were measured using a JEOL JSM 6400 scanning electron microscope (SEM) and a JEOL JXA 8600 electron microprobe with attached Wavelength Dispersive Spectrometers (WDS). The cation-composition is homogeneous within our experimental
resolution (≈ 1–2%). The magnetizations were measured using a Quantum Design SQUID magnetometer.

The field-cooled magnetization, \( M_{FC} \), at 5 Oe is shown in the inset to Fig. 1 for a Ru1222Gd powder sample with a particle size of ≈ 1 µm and diluted with a large amount of epoxy. The particle size was far smaller than the grain size (≈ 2–20 µm) of the initial ceramic sample, and the powder should be regarded as a collection of single grains with negligible inter-particle (grain) interactions. Two additional transitions at \( T_{M2} \) and \( T_{M3} \) can be seen above the main transition at \( T_{M1} \). Below 35 K, the zero-field-cooled magnetization, \( M_{ZFC} \), becomes negative (not shown) and \( M_{FC} \) shows a diamagnetic drop, indicative of a superconducting transition (inset, Fig. 1). All of these observations are in qualitative agreement with the data previously reported.

To determine whether the different transitions are associated with different structural grains, we examined the thermal-magnetic hysteretic effects; the spin-alignment of the \( T_{M1} \) species in highly diluted powder should not depend on their history above \( T_{M1} \) if one grain contains only one type of species. A procedure was thus designed as A (field-cooled under a fixed field of 10 Oe from 200 K to a temperature \( T_S \)) - B (swapping field from 10 Oe to a lower field of \( H_S \) at \( T_S \)) - C (field-cooled under \( H_S \) from \( T_S \) to 60 K) - D (raising the temperature under \( H_S \) to 200 K) - E (field-cooled under \( H_S \) from 200 K to 60 K) (Fig. 1). It should be noted that the \( H_S \) was exactly the same between steps C and E and was measured using a Hall sensor with a resolution of 0.005 Oe. Additional tests that were performed demonstrated that the SQUID magnetometer is suitable to measure ferromagnets down to \( 10^{-2} \) Oe if precautions are taken.

The \( M_{FC} \)-jump across \( T_{M1} \), \( \Delta M_{FC} (H_S, T_S) \equiv M_{FC} |_{at \ 60 \ K} - M_{FC} |_{at \ 95 \ K} \), and the magnetization just above \( T_{M1} \), \( M_{FC} (H_S T_S) \equiv M_{FC} |_{at \ 95 \ K} \), were used here to measure the spin alignments of the \( T_{M1} \) species and the \( T_{M2} \) species, respectively. Both use a unit of emu per cm³ Ru1222, i.e. a “nominal” moment without considerations of the epoxy-filling. During the \( T_{M1} \) transition, the spins of a \( T_{M1} \) species should be ordered under both \( H_S \) and interaction with the neighboring \( T_{M2} \) species. For a dipole-dipole interaction, the interaction should be proportional to the magnetization of the \( T_{M2} \) species around \( T_{M1} \). However, \( M_{FC} |_{at \ 95 \ K} \), i.e. the nominal moment at a slightly higher temperature, was used as an approximation to avoid interferences from the \( T_{M1} \) species. A correlation between \( \Delta M_{FC} \) and \( M_{FC} (H_S T_S) \) was indeed observed. The \( \Delta M_{FC} \) in step C, for example, is systematically lower than that in step E. In particular, the jump \( \Delta M_{FC} \) in step C can even be negative under a positive \( H_S \) up to 0.5–0.6 Oe. It should be noted that this memory effect at low fields is qualitatively different from the well-known coercive-hysteresis of ferromagnets. For example, the observed \( \Delta M_{FC} \) at a fixed \( H_S = 0.05 \) Oe changes sign when \( T_S \) crosses \( T_{M1} \approx 80 \) K (triangles in inset, Fig. 1). While the positive \( \Delta M_{FC} \) at \( T_S < 70 \) K represents a typical coercive-hysteresis of the FM \( T_{M1} \) domains, the \( \Delta M_{FC} < 0 \) observed between 80 and 130 K demonstrates an AFM interaction between the \( T_{M1} \) and the \( T_{M2} \) domains. This sign change across \( T_{M1} \) demonstrates that the \( T_{M1} \) and \( T_{M2} \) species involve different spins and interactions.

This AFM interaction can be seen more clearly in the inset of Fig. 2. The data of step E fall into a straight line through the origin as expected, while the data of step C show a molecular field of −0.6 Oe. We interpret the interaction as a demagnetizing field with or without additional interface interaction. It is difficult, unfortunately, to distinguish
between these two cases, and we will first discuss a pure dipole-dipole interaction. In such a case, the demagnetizing field can be written as $-f \cdot 4\pi M_{FC}(T_S, H_S)$, where $f$ is a constant. Indeed, good linear correlation between the $\Delta M_{FC}$ and $M_{FC}(T_S, H_S)$ was observed in all powder/ceramic samples examined, supporting the dipole-dipole model (Fig. 2). An almost universal $f = 0.36 \pm 0.1$ was obtained by fitting $\Delta M_{FC} \propto [H - f \cdot 4\pi M_{FC}(T_S, H_S)]$ for all cubic-shape ceramic samples and unaligned powder samples with different Ru1222/epoxy ratios. This universal $f$ is a surprise since the demagnetizing factor $4\pi f$ is expected to be $4\pi f_o V_R/(V_R + V_E)$ in the “nominal” magnetization-unit used if the $T_{M1}$ and the $T_{M2}$ species form separated grains, where $f_o$, $V_R$, and $V_E$ are the geometric demagnetizing factor and the relative volumes of Ru1222 and epoxy, respectively. A dilution-independent $f$ demonstrates that the $T_{M1}$ and $T_{M2}$ species coexist as nanodomains in the same structural grain, an indication of possible phase-separations.

It should be noted that geometric corrections are needed to convert the $f$ observed in randomly oriented powders to that (identified as $g$ in the discussion below) in a single grain with $H$ along its easy-axis. In Ru1212, an easy axis has been suggested along the $(a, b)$ plane. The significant $M$-$H$ hysteresis of both the $T_{M1}$ and $T_{M2}$ species in Ru1222 suggests that a similar situation may exist. Below the coercive field, the only relevant components of both $H$ and $M_{FC}$ would be those along the easy axis. In such a case, the intragrain- and intergrain-contributions to $f$ would be weighted differently if a correlation exists between the easy axes of the $T_{M1}$ and the $T_{M2}$ species in the same grain. The $f$ of a thin ceramic disk with a diameter-to-thickness ratio of 5 was measured to verify that. The $f$ observed was 0.25 and 0.5 with $H$ perpendicular and parallel to its axis, respectively. The values, however, still differ significantly from the geometric factor of $f_o = 0.125$ and 0.75 expected for a homogeneous disk, i.e. the contributions from all neighboring grains are heavily suppressed. The suppression factor estimated is 2.5 based on above data, which is in rough agreement with the calculated value of 3 assuming that the intragrain $T_{M1}$ and the $T_{M2}$ species share the same easy axis but those in adjacent grains are random. It should be noted that the result is also in agreement with the universal $f$ observed. The observation, i.e. two types of magnetic species coexist and share a common easy axis in the same structural grain, will be another piece of evidence for the existence of a phase separation.

We estimated the $g$ in a local coordinate system with its $z$-axis being the common easy axis. The effective field $H^*$, the $M_{FC}$-jump across $T_{M1}$, $\Delta M_{FC}^*(H_S, T_S)$, and the magnetization just above $T_{M1}$, $M_{FC}^*(H_S T_S)$, will be $H \cos \theta_1$, $\Delta M_{FC}(H_S, T_S)/\cos \theta_1$, and $M_{FC}(H_S T_S)/\cos \theta_1$, respectively, where $\theta_1$ is the polar angle of $H$. For unaligned powders, therefore, $g = f/3 \approx 0.12 \pm 0.03$. To verify the conclusion that the $g$ is rather small, a Ru1222Eu sample was partially magnetically aligned by heating a mixture of the powder and wax to 400 K under a 5 T field. The $M_{FC}$ |at 5 K of the cubic sample at 10 Oe were 0.21 emu/g and 0.29 emu/g with $H \parallel$ and $\perp$ to its axis, respectively. The $f$ observed, on the other hand, were 0.37 and 0.29. Assuming an angular distribution of $1 - a \cdot \cos^2 \theta$, a $g \approx 0.1$ was extrapolated for $a = 0$.

The demagnetizing field of a dipole-array at $r$ is the summation of an average field $-4\pi h M$ and a nearest-neighbor term of $B_{near}$, where $h$ is the demagnetizing factor and $h \approx 1/3$ for a sphere. The $B_{near}(r)$ oscillates rapidly with $r$, but would be zero after averaging if there is no geometric correlations between $r$ and $r_i$, where $r_i$ is the position of the nearest dipoles. This can be easily understood since the average field of a dipole $m$ at the origin
is $\int [3(\mathbf{m} \cdot \mathbf{r})\mathbf{r} - \mathbf{m} | \mathbf{r} |^2]d^3\mathbf{r}$, which can be factorized as $\propto \int_0^\pi (3\cos^2\theta - 1) \sin \theta d\theta = 0$, where $\theta$ is the polar angle of $\mathbf{r}$. This average, therefore, will be only from the dipoles near the sample boundary where the factorization fails. Their contribution, however, is exactly the $-4\pi hM$ of the effective surface poles. In our case, the $h$ should be $\approx 1/3$ based on the more-or-less spherical grains observed under SEM. To confirm that, a sample was measured at different $H$ directions. Strong anisotropy is expected if the grains are far from spherical. The $g$ deduced, however, is isotropic within 10%. A significant and positive $B_{near} \approx (1/3 - g) \cdot 4\pi M = 0.21 \cdot 4\pi M$ at the positions of the FM $T_{M1}$ species, therefore, is required. That, as discussed above, can be true only if the FM $T_{M1}$ species occupy merely a small fraction of the samples, i.e. the nearest $T_{M1}$ and $T_{M2}$ species are aligned along their easy axis. A phase separation between FM nanodomains and an AFM matrix is suggested.

Additional interface interactions might also exist. However, the fact that the $g = 0.12$ observed is almost universal and far smaller than the geometric factor $1/3$ expected requires a sample-independent but delicate balance between the dipole field and the interface interaction. This is very unnatural unless both the $T_{M1}$ and $T_{M2}$ nanodomains are the products of phase-separations.

It might be possible that this phase separation has a chemical origin, i.e. due to the inhomogeneity in Ce doping. In our opinion, however, this is unlikely: the scenario is not supported by our microprobe data; and the memory effect is qualitatively the same in our samples with different $x$. To further probe the topic, the $M_{FC}$ at 1 T (solid diamonds) and the differential $ac\chi(T)$ at 5 T (open circles), as well as the intercept $M_o$ of the $M$-$H$ loops of a Ru1222Eu sample (Eu was used to reduce the paramagnetic background) were examined (Fig. 3 and its inset). It is interesting to note that these parameters, which may serve as a measure for the volume-fraction of the respective species, vary smoothly around $T_{M1}$ (Fig. 3), where a significant anomaly is expected if the $T_{M2}$ and $T_{M3}$ species were due to doping inhomogeneity (as demonstrated by the $M_{FC}$ of Ru1212 at 1–6 T). Instead, the ferromagnetic contribution $M_o$ shows a single transition at $140 K \approx T_{M3} >> T_{M1}$ (Fig. 3), as reported before. The $M_{FC}$ and the $ac\chi(T)$ show similar behavior. The minor $T_{M2}$ FM species observed, therefore, is unlikely to be merely due to the doping inhomogeneity.

To understand the nature of the $T_{M2}$ nanodomains (no comparable phenomena observed in Ru1212), a Curie-Weiss (C-W) fit (solid line) was calculated from $M_{FC}$ at 1 T and above 180 K. A Curie constant of $C = 1.03$ emuK/mole ($\approx 2.8 \mu_B$/Ru with $\mu$(Ce) = 2.54 $\mu_B$ and $\mu$(Eu) = 0 $\mu_B$) and a C-W temperature $T_{CW}$ of 84 K $\approx T_{M1}$ were obtained. The increase of the $\chi$ with cooling, however, significantly slows down below 1.5$T_{M1}$, and is even lower than the C-W fit below 1.25$T_{M1}$. These are in line with the observed $ac\chi(T)$ with a $dc$ bias of 5 T, which peaks around 120 K $>> T_{M1}$. All of these, however, are in great contrast with Ru1212Eu, whose $dc\chi(1 T)$ stays above the C-W and whose $ac\chi(T)$ increases with cooling down to its AFM transition temperature. A short-range AFM correlation, therefore, seems to exist far above $T_{M1}$ in Ru1222, and may be closely related to the $T_{M2}$ species observed. This is slightly different from Ru1212, but offers an opportunity to probe the magnetitic structures below $T_{M1}$.

It should be pointed out that a phase separation of Ru1222 into a FM species and an AFM species will offer a natural interpretation for many unusual superconductive properties of Ru1212/Ru1222, although a detailed structure study is needed to confirm our proposition.

In summary, several magnetic transitions and an unusual thermal-magnetic memory
effect between them were observed in Ru1222. Detailed analysis of the magnetization under different thermal-magnetic conditions led us to the suggestion of a phase separation of Ru1222 into FM and AFM nanodomains inside the crystal grains. Such a suggestion can also account for the unusual superconducting properties reported in the Ru-based cuprates. A direct detailed magnetic structure study is warranted to confirm our proposition.

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FIGURES

FIG. 1. $M(T)$ in a procedure discussed in text. From top to bottom: $H_S = 1.4, 1.02, 0.63, -0.04, -0.22,$ and $-0.6$ Oe. Solid symbols: data in steps B-C; open symbols: data in the section D-E. Inset: $\bigcirc - M_{FC}$ under 5 Oe; the four vertical arrows show $T_c, T_{m1}, T_{m2},$ and $T_{m3}$, respectively; $\blacksquare - \Delta M_{FC}$ at $H_S = 0.05$ Oe but with different $T_S$.

FIG. 2. $\Delta M_{FC} = M_{FC}(95 \text{ K}) - M_{FC}(60 \text{ K})$ against the effective field $H - f \cdot 4\pi M(105 \text{ K}, H_S)$ ($f = 0.36$ in this sample). Inset: $\Delta M_{FC}$ vs. $H$. Open symbols: data from steps D-E. Solid symbols: the data from steps B-C.

FIG. 3. The susceptibility $\chi'$ of a Ru1222Eu sample. $\bigtriangleup$: from $M_{FC}$ at 1 T; thin solid line: Curie-Weiss fit based on the $M_{FC}$ data between 180 and 350 K; $\bigcirc$: from ac susceptibility with a dc bias of 5 T; $-\triangle-$: the ferromagnetic contribution represented as the $M_o$ of the inset. Inset: the average $M_{ave} = (M_{inc} + M_{dec})/2$, where $M_{inc}$ and $M_{dec}$ are the magnetization in the $H$-increase branch and $H$-decrease branch of a $\pm 5$ T $M$-$H$ loop, respectively. The curves were measured at 60, 70, 80, 90, 100, 110, 120, 130, and 140 K (from top to bottom).
\[ \Delta M_{FC} (\text{emu/cm}^3) \]

\[ H_{S} (\text{Oe}) \]

\[ H - 0.36 \times 4\pi M(95 \text{ K}) (\text{Oe}) \]
