Separation between antiferromagnetic and ferromagnetic transitions in Ru\(_{1-x}\)Cu\(_x\)Sr\(_2\)EuCu\(_2\)O\(_{8+\delta}\)

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The macroscopic magnetizations of Ru\(_{1-x}\)Cu\(_x\)Sr\(_2\)EuCu\(_2\)O\(_{8+\delta}\) with \(x\) between 0 and 0.15 were investigated. A ferromagnetic transition as well as an antiferromagnetic transition appear around \(T_M\) in the low-field magnetization and around \(T_{AM}\) in the high-field differential susceptibility, respectively. The separation between them, which is accompanied by a flat plateau in the magnetic \(C_p\), increases with \(x\). Superparamagnetic \(M(H)\) and slow spin dynamics, i.e., characteristics of nanomagnetic clusters, were observed far above \(T_M\). A comparison with RuSr\(_2\)(Eu\(_{1-x}\)Ce\(_x\))Cu\(_2\)O\(_{10+\delta}\) and some manganites further suggests that a phase separation occurs, which can describe well the conflicting magnetic-superconductivity data previously reported.

The puzzling bulk, yet granular, superconductivity (SC) in ruthenocuprates Ru\(_2\)Sr\(_2\)RuCu\(_2\)O\(_{8+\delta}\) (Ru1212R) and RuSr\(_2\)(R, Ce)\(_2\)Cu\(_2\)O\(_{10+\delta}\) (Ru1222R) with \(R\) = Gd, Eu, or Y\(_{1-x}\) which coexist with weak ferromagnetism, is closely related to their magnetic structure. While a homogeneous canted antiferromagnetic (CAFM) spin order may coexist with more or less ordinary superconductivity, such as the proposed Meissner state or the with more or less ordinary superconductivity, such as the

The inflection point \(T_M\) of Ru1212Gd already suggest that its magnetic transition is far from simple; the spin correlations may exist up to 2 \(T_M\) with a significant entropy and a correlation size as large as \(10^2 \mu_B\)–\(10^3 \mu_B\), both characteristic of phase separation. It is interesting to note that both \(T_M\) and \(T_{AM}\) of Ru1212R can be tuned by Cu doping. The evolutions of \(M\), \(\chi_{\text{Ru, only}}\), and \(C_p\) of Ru\(_{1-x}\)Cu\(_x\)Sr\(_2\)EuCu\(_2\)O\(_{8+\delta}\) with \(0 < x < 0.15\), therefore, were measured. The \(T_M\) drops more than 25 K with \(x\) while the variation in \(T_{AM}\) is negligibly small. A separation between \(T_M\) and \(T_{AM}\) is developed with \(x\). This separation is further accompanied by a magnetic \(C_p/T\) with a flat plateau between \(T_M\) and \(T_{AM}\). Hence, a mesoscopic phase separation is suggested.

Ceramic Ru\(_{1-x}\)Cu\(_x\)Sr\(_2\)EuCu\(_2\)O\(_{8+\delta}\) samples with \(x\) between 0 and 0.15 were synthesized following a standard solid-state-reaction procedure. Precursors were first prepared by calcinating commercial oxides at 600–900 °C under flowing \(O_2\) at 1 atm. Mixed powder with a proper cation ratio was then pressed into pellets and sintered at 960 °C. The final heat treatment was done at 1065–1070 °C for 7 d in oxygen after repeatedly sintering and regrinding. The structure of the samples was determined by powder x-ray diffraction using a Rigaku DMAX-IIIIB diffractometer. The \(x\) dependence of the lattice parameters, i.e., the \(c=11.553(2)\) to \(11.550(2)\) Å for \(x=0\) and 0.15, respectively, is slightly weaker than that reported for Ru\(_{1-x}\)Cu\(_x\)Sr\(_2\)GdCu\(_2\)O\(_{8+\delta}\). Minor impurity phases, likely SrRuO\(_3\) or oxides of (Sr,Cu), are below 5% at \(x\leq 0.15\) (Fig. 1). The composition was measured by a JEOL JXA 8600 electron microprobe with attached wavelength-dispersive spectrometers. The local inho-
mogeneity of $1-x$ is within experimental resolution of \( \pm 0.05 \). The magnetizations were measured using a Quantum Design superconducting quantum interference device (SQUID) magnetometer with an ac attachment and the specific heat was measured in a Quantum Design physical property measurement system with a specific-heat attachment.

Superconductivity appears in all the samples below a critical temperature \( T_c \approx 20-30 \) K. A single-step jump of \( M_{FC} \) also appears with cooling at a higher temperature [Fig. 2(a)]. According to the scaling correlation \( \frac{H M_0}{|MH_0|^1} = t + (\frac{M}{M_0})^{1/2} \), the \( \partial M / \partial T \) of an ideal ferromagnet should decrease with \( t = (T - T_M)/T_M \) as \( 1/t^{y+1} \) above \( T_M \), but increase as \( (-t)^{1-\beta} \) below, where \( 0 < \beta < 1 \), \( \gamma > 0 \), \( H_0 \), and \( M_0 \) are two critical exponents and two critical amplitudes, respectively. The situation for a CAFM magnet should be similar. Therefore, the inflection point of \( M_{FC}(T) \) at 5 Oe, i.e., the temperature at which \( \partial M_{FC} / \partial T \) peaks, is used as \( T_M \) [Fig. 2(a)]. The well defined \( T_M \) and the large FM component below \( T_M \) are in rough agreement with those reported for Ru1212Eu, but rather different from those of Ru1-xCuSr3GdCu4O8+\( \delta \), where no clear FM transition can be identified with \( x \approx 0.1 \). Differences in both the rare-earth elements and the synthesis procedures may contribute to the variation. It should be pointed out that the well defined \( T_M \) and the large \( M_{FC} \) of our samples make the analysis of \( M_{FC} \) and \( C_p \) easier and without significant interference from the minor impurities. A systematic decrease of \( T_M \) with \( x \) is observed, e.g., \( T_M \approx 134 \) K and 117 K at \( x = 0 \) and 0.1, respectively [Fig. 2(a)]. It is also interesting to note that the reported bifurcation point between \( M_{ZFC} \) and \( M_{FC} \), which should be very close to \( T_M \) if the domain pinning is strong, in Ru1-xCuSr3GdCu4O8+\( \delta \) shows almost the same \( x \) dependence, i.e., down to \( \approx 115 \) K and 100 K with \( x = 0.1 \) and 0.2, respectively.

The \( \chi = M/H \) of a simple AFM magnet, which will be \( H \) independent far above its AFM transition, should have a maximum slightly above the Neél temperature, \( T_{AM} \). It has been suggested, in fact, that the magnetic energy, \( E_m \), and \( \chi \) should both depend on the pair-correlation functions \( \Gamma (r) = 3S(S)S(r)S(S+1) \) as \( E_m \approx \Gamma_1 \) and \( \chi \approx [1 + \Sigma \Gamma (r)/T]^{1+[1+f(T)]} \), where \( \Gamma (r) \), \( \Gamma_1 \), and \( f(T) \) are the pair correlation with the pair distance \( r \), the correlation with the nearest neighbor, and a slowly varying function of \( T \), respectively. This leads to an approximation of \( C_p \propto \partial (T\chi)/\partial T \) if the short-range correlation \( \Gamma_1 \) is dominant. \( T_{AM} \), therefore, can be defined as the temperature of the \( \partial (T\chi)/\partial T \) peak, which is observed close to the \( \chi \)-maximum temperature in three dimensions (3D) but much lower in 2D. For CAFM magnets, an FM-like \( M_{FC} \) step may coexist with a \( \partial (T\chi)/\partial T \) peak. However, \( T_{AM} \approx T_M \) is expected, except for the possible \( H \)-induced transition shifts.

To analyze the magnetization of Ru1-xCuSr3EuCu4O8+\( \delta \), the Eu/CuO2 contributions were first eliminated using the procedure previously proposed, i.e., with a Van Vleck susceptibility of free Eu3+ and a T independent \( \chi_0 \) of \( 8.7 \times 10^{-4} \) emu/mole for CuO2. For the undoped sample with \( x = 0 \), the Ru contribution is \( H \) independent and follows a Curie-Weiss (C-W) fit only above 250 K with a C-W constant \( \approx 2.6 \mu_B/\text{Ru} \) and a Curie temperature of 127 K. Deviation from the C-W fit and large superparamagnetic \( M(H) \), however, develop at lower temperatures [Fig. 2(a)]. The Ru contribution to \( \chi \) at 1 T, for example, is more than 10% higher than that expected between 180 K and \( T_{AM} \) [Fig. 2(a)], indicating a dominant FM interaction.
5-T differential Ru susceptibility after subtracting the Eu/CuO₂ contributions ($\chi_{Ru\ only}$), however, shows an opposite downturn, suggesting significant AFM interactions [Fig. 2(a)]. In particular, a minimum of $1/\chi_{Ru\ only}$ and a $\partial(T\chi)/\partial T$ peak appear around 157 K [Fig. 2(a)] and $T_{AM}\approx138$ K [Fig. 2(b)], respectively, for the $x=0$ sample. Undoped Ru1212Eu, therefore, might be interpreted as a simple canted antiferromagnetic by either ignoring the 4-K difference between $T_M$ and $T_{AM}$, or by regarding it as a small $H$-induced transition shift.

To further confirm the presumed $T_{AM}$, the magnetic specific heat was measured at zero field using a nonsuperconducting YBa₂(Cu₂₋ₓZn₀.27)O₇ (YBCO) ceramic as the reference [Fig. 2(b)]. The raw specific heat of Ru1212 is well above that of YBCO between 80 and 180 K, but the two merge outside this region, a situation similar to the data of Ru1212Gd.³ The magnetic $C_p/T$, i.e., the difference between Ru1212Ru and YBCO, shows a well-defined peak at 133 K, which is only slightly lower than the 138-K $\partial(T\chi)/\partial T$ peak observed. This agreement between the $C_p/T$ peak at zero field and the $\partial(T\chi)/\partial T$ peak at 5 T again demonstrates that the procedure of Fisher² works reasonably well and that the $H$-induced transition shift is small in our case. It is also interesting to note the high-$T$ tail of $C_p/T$ and the non-C-W magnetization up to 180 K or higher [Figs. 2(a) and 2(b)]. Significant short-range spin orders, therefore, should occur far above $T_M$ and $T_{AM}$.

With the Cu doping, however, the $T_M$ and the $T_{AM}$ evolve in different ways and the separation between them broadens. At $x=0.1$, for example, the $T_M$ is quickly suppressed to 117 K but the $\partial(T\chi)/\partial T$ peak remains at 138 K [Figs. 2(a) and 2(b)]. The accompanying $C_p/T$ appears to broaden with $x$ as well [Fig. 2(b)]. In particular, the well-defined peak evolves into a flat plateau between $T_M$ and $T_{AM}$ [Fig. 2(b)]. It should also be pointed out that the separation at $x=0.1$ is larger than the transition width in $M_{FC}$. Neither the sample inhomogeneity nor the experimental resolution, therefore, can account for the separation [Figs. 2(a) and 2(b)]. The AFM-like $\partial(T\chi)/\partial T$ peak and the FM-like $M_{FC}$ jump seem to carry distinct spin entropies of comparable strength.

It is therefore interesting to compare the data with that of Ru1222Ru, where two separate transitions have been observed in both magnetizations and Mössbauer spectra.¹ The $T_M$ and $T_{AM}$ of Ru₁₋ₓCuₓSr₂Eu₂CuₓO₈₊δ samples with $0≤x≤0.15$, the O₂/Ar-annealed Ru₁₋ₓCuₓSr₂Eu₂CuₓO₈₊δ, and two as-synthesized Ru1222Eu samples are shown in Fig. 2(c). The separation $T_{AM}-T_M$ increases systematically with decreasing $T_M$ in the Cu-doped Ru1222Eu: from an extrapolated zero separation at $T_{AM}\approx140$ K to 25 K at $T_{AM}\approx110$ K, where the data smoothly evolve into that of Ru1222Ru [Fig. 2(c)]. The observation of $T_{AM}=T_M$ in the Ru1222Eu sample,⁵ therefore, may be only a coincidence. Distinct AFM and FM transitions may coexist in both Ru1222Ru and Ru1222R.

These two transitions, as has been argued in the case of Ru1222Ru,¹⁶ may be due to either a mesoscopic phase separation or a multistage transition. The magnetic properties between $T_M$ and $T_{AM}$, however, will be different in these two scenarios: some parts of Ru1222Ru should be in superparamagnetic states during phase separation, but should stay in a long-range spin-order state during a multistage transition. Evidence for the possible phase separation in Ru1222Ru, for example, is found in both the superparamagnetic $M(H)$ with a magnetic cluster size of $10³µB$ and the slow spin dynamics far above $T_{FM}$.⁵ Similar properties were therefore tested in Cu-doped Ru1212Eu.

The Langevin function with an additional linear term, $a·H+m·[c\ tanh(\mu H/k_B T)−k_BT/\mu H]$, was used to fit the average magnetization in a $M−H$ loop [inset, Fig. 3(a)].⁶ The fit is reasonably good with the deduced $\mu$ between 100$µ_B$ and 700$µ_B$/cluster [closed symbols in Fig. 3(a)], which is four to five times smaller than those deduced in Ru1222Ru, but still far larger than that expected based on the spin fluctuations. A cluster of 400$µ_B$≈200 Ru ions, for example, would be 4–5 nm or larger in an RuO layer. It should be further noted that $\mu$ so deduced may be only a lower limit of the actual cluster/spin-correlation length.¹⁵ The existence of such large clusters at $T/T_M>1.1$ will be difficult to be interpreted as a simple fluctuation. This deduced size, on the other hand, appears to be too small for a crystalline magnet, as is suggested in the multistage transition model.

The dynamic spin response was also studied. The logarithmic increase of $M_{ZFC}$ at 5 Oe with time is almost unobservable, with the deduced rate of $d\ln M/d\ln t<10^{-3}$ well

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**FIG. 3.** (a) Cluster sizes for samples with $\bullet$: $x=0$; $\nabla$: $x=0.05$; $\blacksquare$: $x=0.10$; and $\large\bullet$: $x=0.15$ and for $O$: as-synthesized Ru1222Eu (×4). Inset: The isothermal $M(H)$ of the $x=0$ sample. (b) Relaxation of the remnant magnetizations at 160, 150, 140, and 130 K (from top to bottom) after field cooling at 50 Oe.
within our experimental resolution, where $60 \text{s} < t < 3600 \text{s}$ is the time after the field switch. This is rather different from that of Ru1222Eu, but in agreement with the unobservable relaxation of Ru1212R ac susceptibility reported between 1 s and 100 s. The lack of relaxations under the above conditions is apparently related to the cluster size in Ru1212R [Fig. 3(a)], which is four to five times smaller and leads to quicker equilibrium. The slow spin dynamics, therefore, should either be explored in a shorter time window or after an enhancement of the energy barriers. Several different experimental conditions were then tested, and significant non-logarithmic relaxations were observed in the remnant magnetization after a 50-Oe field cooling [Fig. 3(b)]. It is interesting to note that the energy barriers are $\propto KV_c - \mu H$ and $KV_c$, respectively, for the $M_{ZFC}$ and the remnant magnetization, where $K$ and $V_c$ are the magnetic anisotropy and the coherent volume, respectively. This may make the remnant magnetization a more favorable candidate for investigating the slow dynamics. The strong $T$ dependence of the relaxation observed [Fig. 3(b)] suggests, in our opinion, that the relaxation observed is unlikely an artifact of the SQUID magnetometer, but supports the existence of superparamagnetic clusters.

As pointed out earlier, the phase-separation model may also offer a consistent interpretation for the conflicting NPD/ NMR and superconductivity data reported previously. The conflict between the NPD and NMR data for the magnetic structure, for example, may be attributed to the fact that the two probes have different sensitivities to various magnetic species, such as those well documented in manganites. Similarly, the spatial separation between AFM and FM species offers a natural mechanism for the unusual superconductivity observed. Superconductivity can coexist with the AFM matrix. The finely dispersed FM clusters, on the other hand, depress the local SC order parameter and serve as tunnel barriers for the Cooper pairs. The superconductivity, therefore, may retain a significant part of the condensation energy, but appears only as a Josephson-junction array. Similarly, the critical temperature observed in the transport will naturally be much lower than that associated with the corresponding $C_p$ anomaly, and can be easily suppressed by external fields. The intragrain penetration depth will also be much larger than those expected based on the proposed universal $1/\lambda_s(T_c)$. In summary, a systematic separation between $T_M$ and $T_{AM}$ is observed in Ru1212Eu with Cu doping, suggesting the coexistence of FM and AFM orders and the occurrence of a mesoscopic phase separation in the compound. The super-paramagnetic $M(H)$ as well as the slow spin dynamics further support the interpretation.

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14. This is true below a critical field $H_c$, since $\partial(T_X)/\partial H$ and $\partial M_{FC}/\partial T$ have similar $T$ dependencies. Above $H_c$, however, the field may break the AFM spin correlations and a magnetization jump appears. H. Herweijer, W.J.M. de Jonge, A.C. Botterm, A.L.M. Bongaarts, and J.A. Cowen reported in Phys. Rev. B 5, 4618 (1972), for example, that the magnetizations of CsCoCl$_3$·2H$_2$O (a one-dimensional CAFM) are linear in $H$ below 0.3 T with identical $T_{AM}$ and $T_M$.