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Coexistence of ferromagnetism and cluster glass state in superconducting ferromagnet $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$

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Systematic dc and ac magnetic susceptibility measurements performed on $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru1222) demonstrate a paramagnetic to ferromagnetic transition around 95 K. The third harmonic of the ac susceptibility reveals that the system undergoes a spin glass transition below 75 K. The features of the zero-field cooled and field cooled dc magnetization curves of Ru1222 material resemble those of a cluster glass state, rather than those of a canonical spin glass state. The magnetization versus applied field loops do not saturate, even at very high applied fields, resulting in the short range magnetic order in the system, which facilitates the formation of clusters that freeze at low temperature. The temperature dependence of the second and third harmonic ac susceptibilities further confirms the coexistence of a cluster glass state and ferromagnetic order in the Ru1222 system. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3063069]

The unusual coexistence of superconductivity and ferromagnetism (FM) in ruthenocuprates: $RuSr_2RE_{1-x}Ce_xCu_2O_{10-\delta}$ (Ru1222)[1,2] and $RuSr_2RECu_2O_{8-\delta}$ (Ru1212)[3,4] where (RE=Gd, Eu, and Sm) has been under investigation for over a decade. So far, the magnetic behavior of the Ru1222 system could not be unambiguously understood, which is likely to be due to sophisticated materials aspects in these Ru-based systems.[2] A drawback in one of the most effective techniques for studying magnetism is the non-feasibility of neutron diffraction studies on the Ru1222 system with Eu, Gd, and Sm substitutions due to the very high neutron absorption and the very high cost of low-neutron absorbent rare earth isotopes. In addition, the synthesis of single crystal and superconducting thin films of Ru1222[5] has not achieved the desired success. Hence, the nonlinear susceptibility can serve as an effective tool to investigate the complex magnetic properties. The magnetization measured in the presence of an excitation field H can be written as[6]

$$M = M_0 + \chi_1 H + \chi_2 H^2 + \chi_3 H^3 + \dots, \quad (1)$$

where χ_1, χ_2, and χ_3 are the first-, second-, and third-order harmonics of the susceptibility, respectively. The third-order harmonic (χ_3) has been explored in depth in order to study the vortex dynamics and the pinning mechanisms in the high temperature superconductors,[7] where changes in the sign of χ_3 as a function of temperature within the superconducting state provide information regarding the type of flux flow mechanism. χ_3 is also used to distinguish various magnetic phases in the material.

In our recent work[2] we have shown that $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ undergoes a paramagnetic (PM) to FM transition at the Curie temperature (T_C), and at slightly lower temperature the system starts exhibiting features of a spin glass (SG) state so that the SG state coexists with the FM order. At an even lower temperature, the Ru1222 exhibits its characteristic superconducting transition at T_C. Note that the upper case subscript notation is used for the Curie temperature, whereas the lower case subscript notation is for the superconducting transition.

Although SG behavior has been proposed for Ru1222,[2,8] the nature of the glassy behavior is still not clear. The appearance of the glassy state in the vicinity of the FM transition gives rise to two possible types of SG behavior: reentrant SG (RSG)[6] or cluster glass (CG).[9] RSG systems undergo PM to FM ordering at T_C and the SG transition takes place much below the FM transition, developing a plateaulike feature in the zero-field cooled (ZFC) and field cooled (FC) curves. On the other hand the CG state can be considered as a set of clusters formed around T_C due to short range FM ordering. The freezing of the assembly of clusters takes place at a low temperature by overcoming the energy barrier induced by local anisotropy. In this paper, we present a detailed investigation of ZFC and FC dc magnetization behavior, including $M(H)$ magnetization loops, as well as the temperature dependence of χ_1, χ_2, and χ_3 of the ac susceptibility measured at different applied ac fields. These measurements suggest that Ru1222 is a CG system instead of a RSG system.

The $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ powder sample was synthesized using the solid state reaction route from stoichiometric amounts of 99.99% pure RuO_2, $SrCO_3$, Eu_2O_3, CeO_2, and CuO. The powder was sintered in steps of 1000, 1020, 1040, 1060, and 1090 °C for 12 h for each sintering temperature with intermediate grinding. The powder was pressed into circular pellets. The pellets were then annealed at 600 °C in flowing oxygen for 48 h and subsequently cooled slowly over a span of another 24 h down to room temperature. X-ray diffraction revealed a phase pure sample with tetragonal structure belonging to the $I4/mmm$ space group. Lattice parameters are $a=b=3.845\,80$ Å and $c=28.5919$ Å. dc magnetic measurements were performed using a Magnetic Properties Measurement System (Quantum Design) over the

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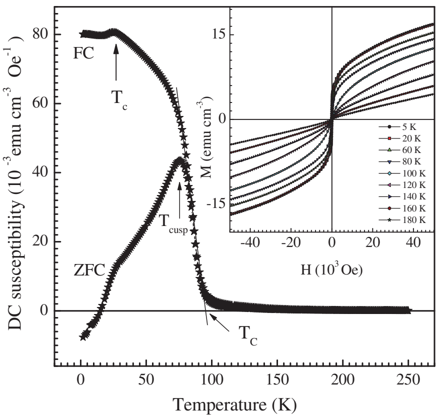

FIG. 1. (Color online) ZFC and FC dc susceptibility curves of $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ measured at the applied magnetic field, $H = 10$ Oe. The inset shows the magnetization (M) vs H curve at different temperatures in the range $-50\,000$ Oe$\leq H \leq +50\,000$ Oe.

temperature range of 1.9–300 K. The linear and nonlinear ac susceptibilities were measured using a Physical Properties Measurement System (Quantum Design).

Figure 1 shows ZFC and FC dc susceptibility curves of the $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ sample measured at 10 Oe. The sharp rise of both the ZFC and the FC curves at $T_C = 95$ K shows a PM to FM transition. Here, we have denoted T_C as the intercept of the straight line shown in the Fig. 1 the x-axis. At temperatures close to T_C, the ZFC and FC curves branch out, and the system enters into a glassy state. The ZFC curve has a peak at $T_{cusp} = 75$ K and the FC curve increases with decreasing temperature. The system undergoes a superconducting transition at $T_C = 27$ K (the kinks in both the curves). In our papers,[2] we show that Ru1222 undergoes the SG transition around the peak temperature of $\chi_1'(T)$, (see Fig. 2) resulting in the freezing spins. Therefore, the peak temperature is called the freezing temperature (denoted as T_f). This peak temperature corresponds to the peak in the

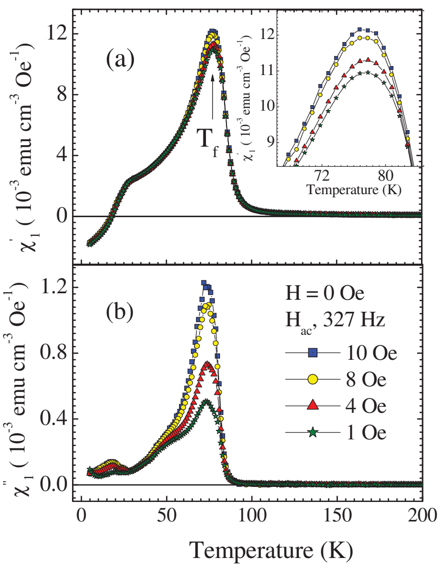

FIG. 2. (Color online) Temperature dependence of (a) the real part and (b) the imaginary part of first harmonic of the ac susceptibility, respectively, measured at different applied ac fields with zero dc bias. The inset of (a) shows an enlarged view of the real part of the first harmonic ac susceptibility.

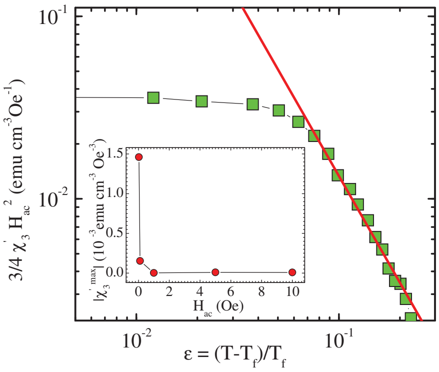

FIG. 3. (Color online) (a) Double logarithmic plot of real part of third harmonic susceptibility (χ_3') vs the reduced temperature. Inset: plot of the magnitude of the peak value of χ_3' denoted as $|\chi_3'^{max}|$ vs applied ac field.

ZFC curve with a few degrees of variation in the peak temperature because of the difference in the response of the system to dc and ac fields.

The temperature range of $70 \lesssim T \lesssim 100$ K is the critical region since the PM$\rightarrow$FM$\rightarrow$SG transitions take place in this region. SG behavior was confirmed by the typical features[6] observed in the χ_3(T) response of Ru1222: (i) the divergence of real part of χ_3 denoted as χ_3' as $T \rightarrow T_f$ according to the critical scaling law $\chi_3' \propto \varepsilon^{-\gamma}$, where $\varepsilon = (T - T_f)/T_f$ is the reduced temperature and γ is the susceptibility exponent, which comes out to be 1.94 in our case, (see Fig. 3); (ii) the divergence of the magnitude of the peak value of χ_3' denoted as $|\chi_3'^{max}|$ in the limit of $H_{ac} \rightarrow 0$ (see inset of Fig. 3); and (iii) the temperature dependence of χ_3, which exhibits a sharp negative peak at T_f.

However, certain features are observed in the ZFC and FC curves which indicate that the Ru1222 system does not possess canonical SG behavior. A canonical SG system develops irreversibility between the ZFC and the FC curves below T_f with the FC curve almost constant with decreasing temperature.[10] A true SG state is realized by the freezing of individual spins at low temperature in the direction of the applied field. With decreasing temperature the magnetic moments reduce their thermodynamic energy and the moments will not prefer to deviate from the direction of the applied field, hence resulting in a constant FC magnetization. In Fig. 1, we observe that the irreversibility between the ZFC and the FC curves starts at a temperature just above T_f with FC magnetization increasing with decreasing temperature. Such a behavior is observed in CG materials[10] where FM interactions within the cluster tend to align the moments in the direction of the applied field, resulting in increased magnetization and a large difference between the ZFC and FC curves. Another possibility is that, since Ru1222 undergoes a PM to FM transition at T_C followed by a SG transition, this system may also be classified as RSG, however, this possibility is ruled out since RSG materials show irreversibility far below T_C and the ZFC curve develops a plateau rather than the sharp peak.

The inset of Fig. 1 shows magnetization (M) versus applied field (H) curves of Ru1222 measured at different temperatures. At low temperatures M-H loops show a pronounced S-shaped curve that is characteristic of SG, which

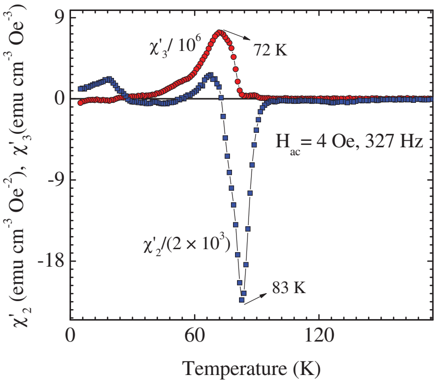

FIG. 4. (Color online) The real parts of the second harmonic and the third harmonic of ac susceptibility as a function of temperature measured at an applied ac field of 4 Oe.

dissolves into a linear curve with increasing temperature. The S-shaped curve also exhibits hysteresis and coercivity at low fields,[2] indicating coexisting SG and FM states. Also, it can be observed that even under the highest magnetic field of 50 000 Oe the magnetization remains unsaturated, indicating that no canonical long range order exists in the Ru1222 system.[11] This suggests that the formation of clusters is due to short range order and resulting in the CG state in this system.

To investigate this further, we have performed nonlinear ac susceptibility studies on our Ru-based system. Figure 2 shows the real and imaginary parts of the first harmonic of the ac susceptibility, denoted as χ_1' and χ_1'', respectively, as functions of temperature, which were measured at different ac fields with zero dc bias. Figure 2(a) shows that the peak temperature of χ_1' is field independent whereas the peak height increases with increasing ac field. This is an unusual feature since it has been observed that χ_1' decreases with increasing ac field.[6] This is because with an increase in the applied magnetic field, the magnetic energy associated with the external field becomes large enough compared to the thermodynamic energy of the magnetic moments to make it difficult for the magnetic moments to freeze in the direction of the applied field, and as a result χ_1' is reduced with increasing applied field. The unusual field dependence of χ_1' shows discrepancies from the canonical SG state in this system.

As discussed above, SG and FM coexist in Ru1222. This is confirmed by the appearance of an even harmonic (χ_2') signal around the SG transition temperature. Figure 4 shows that χ_2' develops in the form of a sharp negative peak close to the peak temperature of χ_1', where the SG transition is supposed to occur, demonstrating the coexistence of SG and FM ordering. The magnetization is represented by Eq. (1). On the other hand, if there were a direct PM to SG transition, M would be expressed as an odd power series,[11]

$$M = M_0 + \chi_1 H + \chi_3 H^3 + \ \dots \ . \tag{2}$$

Moreover, as can be observed in Fig. 4, χ_3' shows a nondiverging broad positive peak close to the temperature where χ_2' shows a peak. A similar feature is observed in other CG systems.[9,12] In Fig. 2(b), χ_1'' shows a kink (change in slope) around 64 K. With increasing applied ac field the kink shifts slightly toward the lower temperature, which suggests that the freezing of clusters is taking place at a temperature just below the CG transition (T_f=75 K). A similar change in slope around 60 K is also visible in χ_3' (see Fig. 4). This can explain the sudden rise in the temperature dependence of the coercivity, $H_C(T)$ around 60 K in Ref. 2. The small peak adjacent to the main peak in χ_3' and the change in the sign of χ_2' from negative to positive at the main peak temperature of χ_3' are unusual features observed for the first time. They may arise due to the field dependent dynamic response of intercluster or intracluster FM interactions. However, a further discussion on this issue is beyond the scope of this paper.

The dc and ac susceptibility studies presented in this paper suggest that a CG state exists in the Ru1222 system. Along with the short range FM order resulting in the formation of clusters, there are various other factors that support the presence of cluster formation in Ru1222. First, the Ru1222 system exhibits oxygen nonstoichiometry, which leads to the reduction of Ru^{5+} to Ru^{4+}, resulting in cluster formation.[13] Hence the random distribution of clusters with $Ru^{5+}-Ru^{4+}$, $Ru^{5+}-Ru^{5+}$, and/or $Ru^{4+}-Ru^{4+}$ exchange interactions may lead to CG state. Second, the synthesis of Ru1222 is always accompanied by the presence of clusters of minority $RuSr_2EuCu_2O_8$ and $SrRuO_3$ phases, which affect the magnetic and transport properties of the Ru1222 system.[2,14]

In conclusion, dc magnetization and nonlinear ac susceptibility measurements have revealed that the Ru1222 system undergoes PM to FM ordering, followed by a SG transition. However, the system does not possess a canonical SG state, rather a CG state is observed, which bears similar features to those of SG and RSG. At low temperature a clusterlike glassy state coexists with FM ordering. Superconductivity in Ru1222 is not affected by the cluster SG state or the FM ordering, so as a result, these three phenomena coexist. This is because superconductivity resides in CuO_2 plane, whereas magnetism originates from RuO_2 plane, and these are partially decoupled.[1]

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