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Spin glass behavior in $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$

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The dynamics of the magnetic properties of polycrystalline $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) have been studied by ac susceptibility and dc magnetization measurements, including relaxation and ageing studies. Ru-1222 is a reported magnetosuperconductor with Ru spins magnetic ordering at temperatures near 100 K and superconductivity in Cu-O_2 planes below $T_c \sim 40$ K. The exact nature of Ru spins magnetic ordering is still being debated, and no conclusion has been reached yet. In this work, a frequency-dependent cusp was observed in χ_{ac} vs T measurements, which is interpreted as a spin glass transition. The change in the cusp position with frequency follows the Vogel-Fulcher law, which is commonly accepted to describe a spin-glass with magnetically interacting clusters. Such an interpretation is supported by thermoremanent magnetization (TRM) measurements at $T=60$ K. TRM relaxations are well described by a stretched exponential relation, and present significant aging effects.

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The coexistence of superconductivity and magnetic order in ruthenium copper oxides $RuSr_2(Gd,Sm,Eu)_2Cu_2O_{10-\delta}$ (Ru-1222) (Refs. 1–6) and $RuSr_2(Gd,Sm,Eu)Cu_2O_{10-\delta}$ (Ru-1212) has recently attracted considerable attention from the scientific community.[7–19] However, there still remain some unresolved questions about the exact type of magnetic order in these compounds. To understand the magnetic ordering in these systems is not trivial, since different techniques like muon spin rotation (μSR),[9] magnetic resonance,[12] neutron powder diffraction (NPD),[13,16–18] magnetization,[14,19] and nuclear magnetic resonance[15] are not in full agreement. However, all them indicate the presence of canted antiferromagnetic ordering with a ferromagnetic component. This situation is especially unclear for the Ru-1222 family. For Ru-1222, though NPD results were recently reported,[20] the magnetic structure has not been unveiled. Although the magnetic behavior of Ru-1222 has been considered to be analogous to the magnetic response for Ru-1212 samples, some recent results point towards various differences between them.[3]

The $RuSr_2Gd_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ru-1222) sample studied in this work was synthesized through a solid-state reaction route from RuO_2, SrO_2, Gd_2O_3, CeO_2, and CuO. Calcinations were carried out on the mixed powder at 1000, 1020, 1040, and 1060°C each for 24 h with intermediate grindings. The pressed bar-shaped pellets were annealed in a flow of high-pressure oxygen (100 atm) at 420°C for 100 h and subsequently cooled slowly to room temperature.[21] X-ray diffraction patterns were obtained at room temperature [MAC Science: MXP 18 VAHF[22]; CuK_α radiation]. Resistivity measurements were made in the temperature range of 5–300 K using a four-point-probe technique. All ac susceptibility measurements were performed in a commercial PPMS (Physical Properties Measurement System), while for the dc measurements a Superconducting quantum interference device magnetometer MPMS-5 were employed, both equipments made by Quantum Design company.

The Ru-1222 copper oxide sample crystallizes in a tetragonal structure of space group $I4/mmm$ with $a=b=3.8327(7)$ Å and $c=28.3926(8)$ Å. The x-ray- diffraction pattern, (Fig. 1), shows a single phase material, without any detectable impurity peak. The compound exhibited superconductivity ($R \approx 0$) below 40 K in electrical transport measurements,[21] as shown in the inset of Fig. 1. To recall the characteristic magnetic behavior of $Ru-1222$, Fig. 2 displays the temperature dependence of both zero field cooled (ZFC) and field cooled (FC) dc magnetization measured at $H=50$ Oe. The ZFC branch presents a pronounced peak at $T_p=68$ K, just below the temperature where the ZFC and FC curves separate. The freezing temperature T_f, extracted from ac susceptibility measurements, is also indicated and

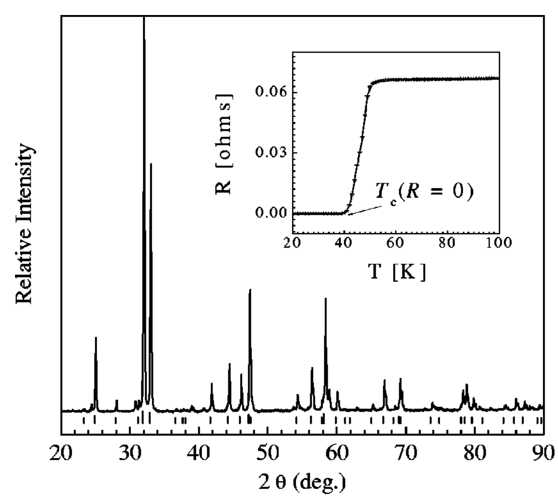

FIG. 1. Powder x-ray-diffraction pattern for the Ru-1222 sample. Inset: $R(T)$ measurement at $H=0$ showing the superconducting transition.

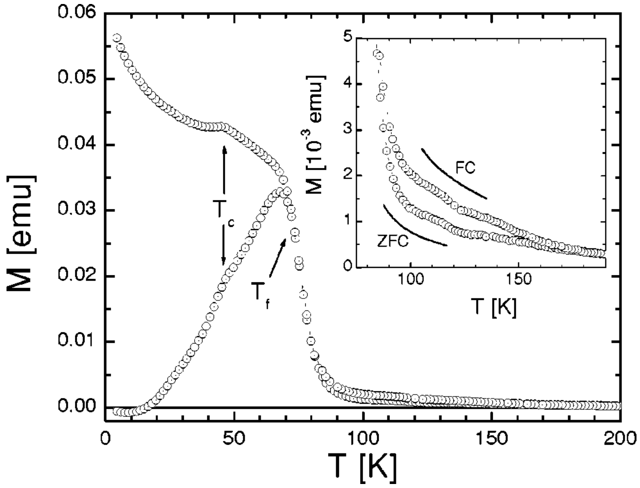

FIG. 2. Field-cooled and zero-field-cooled temperature dependences of the magnetization for $H=50$ Oe. Inset: amplification of the $M(T)$ curves showing the small hysteresis at high temperatures.

will be discussed later. At $T_c=45$ K is observed a kink in both ZFC/FC curves as the Ru-1222 goes through its superconducting transition. The steady increase of the FC branch at low temperatures is interpreted as being caused by the paramagnetic response of the Gd ions. It is important to notice that some magnetic ordering starts to occur at a temperature $T^*=160$ K much higher than T_p. This can be observed in the inset of Fig. 2, which shows an enlarged view of the magnetization curve at temperatures above T_p revealing a small hysteresis at these temperatures. Interestingly, both curves merge together again at a temperature around 80 K. The anomaly observed at T^* was previously reported to be associated with an antiferromagnetic transition.[5] In the same temperature region we observed a small bump in $\rho\times T$ measurements (not shown). We speculate that this anomaly indicates the appearance of spin clusters which at a lower temperature would have the magnetic moments frozen to originate a spin-glass system. In Fig. 3 we present a magnetization curve measured as a function of field, $M(H)$. The magnetization does not saturate even at the highest field of

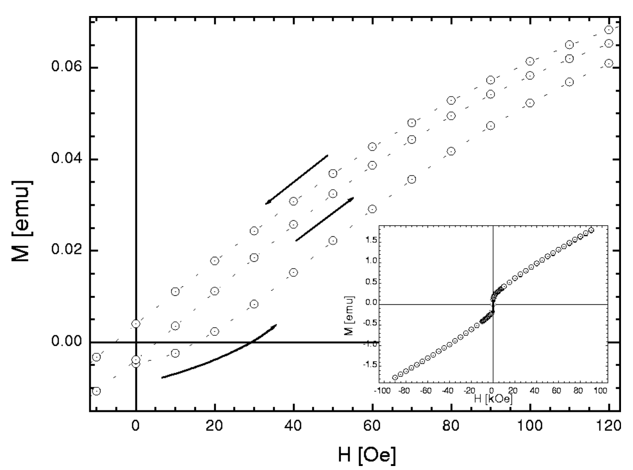

FIG. 3. Low-field portion of the $M(H)$ curve at $T=60$ K. Inset: entire $M(H)$ curve for fields up to 90 kOe.

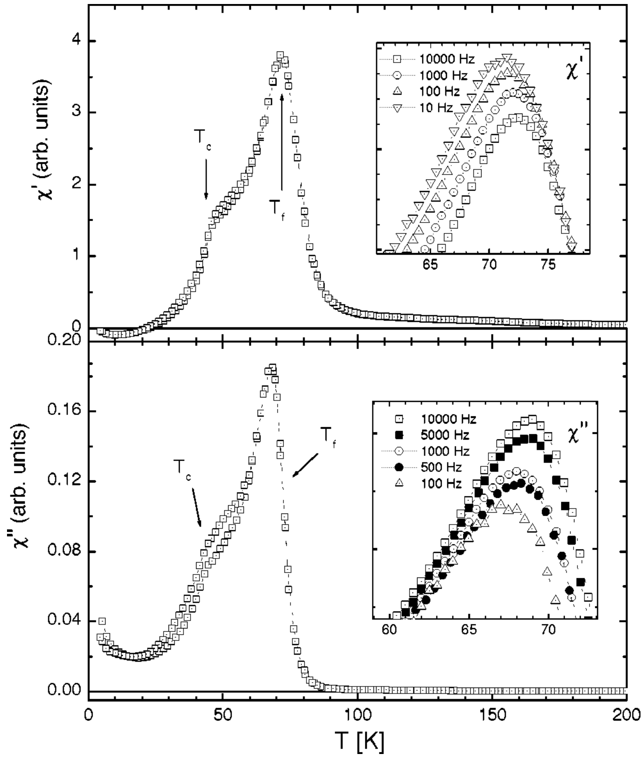

FIG. 4. Complex susceptibility as a function of temperature for $\nu=10$ kHz (main panel). The upper (lower) inset shows the frequency dependence of the peak in the real (imaginary) component at the freezing temperature T_f.

90 kOe, as shown in the inset of Fig. 3, which is consistent with the expected behavior of a spin glass. The low field portion of the virgin branch of the hysteresis loop at 60 K displays an S shape, with a positive curvature at low fields, which is a typical characteristic of spin-glass systems. It is important to notice that $T=60$ K$\gg T_c=45$ K; thus this positive curvature at low field is not due to a superconductor contribution superimposed with a magnetic loop. Another striking characteristic of the virgin branch is that it stays outside the hysteresis loop. This unusual behavior was previously reported for cluster glasses with magnetic interacting clusters.[22–24] It seems to be related to the displaced loop frequently observed when the sample is field cooled.[22,23,25,26] Recently, it has been considered that it may be due to a strong increase of the local surface anisotropy when the sample is cooled below a certain characteristic temperature, for a system of nanosized antiferromagnetic particles in an amorphous matrix.[24]

The ac susceptibility (χ_{ac}) technique is a powerful method which has been used to study spin systems. In the case of a spin-glass, both components χ' and χ'' of χ_{ac} present a sharp, frequency dependent cusp. The position of the cusp in χ' defines the freezing temperature T_f, which is coincident with the temperature of the inflection point in χ''. It is also well known that dc magnetic fields as low as a few hundreds of oersteds can round this cusp up. In Fig. 4 we present the ac susceptibility for our sample measured at $H_{dc}=50$ Oe. The main frame of Fig. 4 presents the ZFC/FC temperature dependence of both χ' and χ'' for the frequency

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$\nu = 10000$ Hz. χ' presents a sharp drop at the superconducting transition temperature T_c and a sharp, frequency dependent peak at $T_f \approx 72$ K. The peak shifts to lower temperatures and its intensity increases as the frequency of the excitation field is decreased (see the upper inset of Fig. 4). For the χ'' peak we observe the shift to lower temperatures as well as a decrease of its intensity with decreasing frequency (see the lower inset of Fig. 4). The frequency dependence of both components is a typical feature of the dynamics of spin-glass systems. The coincidence of the temperature of both, the peak in χ' and the inflection point in the χ'' curve, is also verified in our data. The χ' component present a double anomaly in the 110–170 K range, but neither frequency nor thermal-magnetic history dependencies are observed. The imaginary component does not present any significant feature in this temperature range. On the other hand, for temperatures below 60 K a clear separation of the ZFC/FC curves is observed in both components, although it is more prominent in χ''.

To further verify the existence of a spin-glass behavior, we have studied the frequency dependence of χ_{ac} in more detail. A quantitative measure of the frequency shift is obtained from $\Delta T_f/[T_f \log(\omega)]$. This quantity varies in the range of 0.004–0.018 for spin-glass systems,[27] while for superparamagnets[27] it is of the order of 0.3. From a set of FC susceptibility measurements at different frequencies, presented in the upper inset of Fig. 4, we could estimate $\Delta T_f/[T_f \log(\omega)] \approx 0.005$ for our Ru-1222 sample. Therefore, our data are consistent with the spin-glass hypothesis. There are basically two different possible interpretations of the spin-glass freezing: the first one assumes the existence of a true equilibrium phase transition at a finite temperature (canonical spin glasses).[28] The second interpretation assumes the existence of clusters and, in this case, the freezing is a nonequilibrium phenomenon.[29] For isolated clusters (superparamagnets), the frequency dependence of their freezing temperature (in this context it is referred more correctly as *blocking* temperature) has been predicted to follow an Arrhenius law,

$$\omega = \omega_0 \exp[-E_a/k_B T_f], \qquad (1)$$

where E_a is the potential barrier which separates two easy orientations of the cluster and ω is the driving frequency of the χ_{ac} measurement. However, for magnetically interacting clusters, a Vogel-Fulcher law has been proposed,

$$\omega = \omega_0 \exp[-E_a/k_B(T_f - T_0)], \qquad (2)$$

where T_0 can be viewed as a phenomenological parameter which describes the inter-cluster interactions. Equation (2) implies a linear dependence of the freezing temperature with $1/\ln[(\omega\tau_0)^{-1}]$, $\tau_0 = 1/\nu_0 = 2\pi/\omega_0$. In Fig. 5 we present a Vogel-Fulcher plot, which shows that our data follows the expected linear behavior. From the best linear fit we obtained $\nu_0 \approx 1\times 10^{12}$ Hz, $T_0 = 66.92$ K, and $E_a = 76.92$ K.

Also, the existence of the spin-glass behavior has been checked through the time-dependent magnetic behavior of our sample. In this case, thermoremanent magnetization (TRM) measurements were performed. Since the behavior of a spin glass below T_f is irreversible and complicated by ageing processes, it is imperative to employ a well-defined H-T cycling procedure to obtain meaningful data. The precise procedure adopted in this work to measure the TRM relaxation was the following: the sample was field cooled ($H = 5000$ Oe) down from 200 to 60 K; after temperature stabilization we waited for a certain time t_w. Thereafter the field was reduced to zero and the magnetization was recorded as a function of the elapsed time. The results for different values of t_w ($100 < t_w < 1000$ s) are presented in Fig. 6. Among the various functional forms that have been proposed to describe the magnetic relaxation in spin glasses, one of the most popular is the so-called *stretched exponential*,

$$M(t) = M_0 - M_r \exp\left[-\left(\frac{t}{t_p}\right)^{1-n}\right], \qquad (3)$$

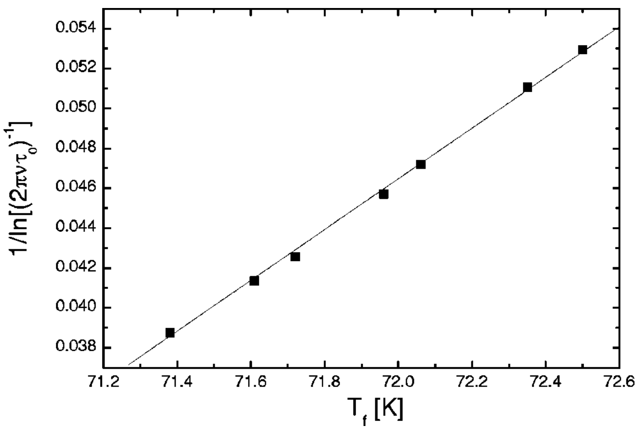

FIG. 5. Variation of the freezing temperature T_f with the frequency of the ac field in a Vogel-Fulcher plot. The solid line is the best fit of Eq. (2).

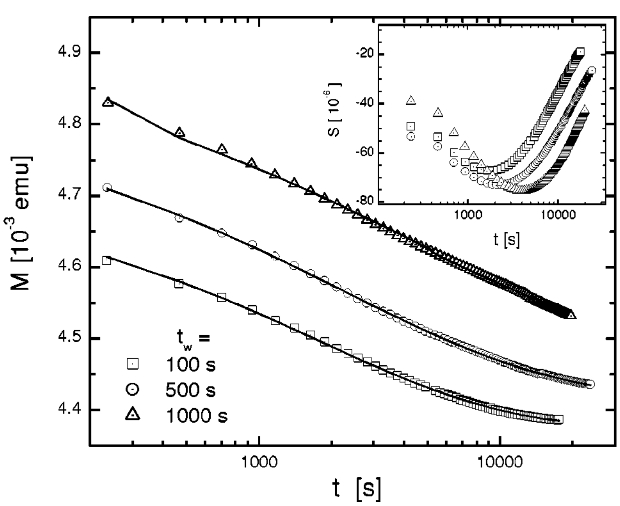

FIG. 6. Thermoremanent magnetization relaxation for $T = 60$ K and t_w ranging from 100 s to 1000 s. The solid lines are the best fits of Eq. (3). Inset: relaxation rate $S(t) = \partial M/\partial \ln(t)$ for the measurements presented in the main panel.

where M_0 relates to an intrinsic ferromagnetic component and M_r to a glassy component mainly contributing to the relaxation observed effects. Both M_r and t_p (the time constant) depend upon T and t_w, while n is only a function of T. If $n=0$ one has the Debye, single time-constant, exponential relaxation. On the other hand, for $n=1$, one does not have any relaxation at all. The solid lines in Fig. 6 are the best fits of Eq. (3) to our experimental data, with parameters $4.38\times10^{-3}<M_0<4.49\times10^{-3}$ emu, $3.3\times10^{-4}<M_r<3.7\times10^{-4}$ emu, and $n=0.45$ (fixed for all fittings). The single parameter which presents a large variation with changes in the wait time is the time constant t_p, which goes from $t_p=1749$ s for $t_w=100$ s to $t_p=5214$ s for $t_w=1000$ s. The changes observed in $M(t)$ measured for different values of t_w demonstrate the occurrence of aging effects, what means that the physical system is in a metastable state. In the inset in Fig. 6 this point is emphasized by showing the relaxation rate $S(t)=\partial M/\partial \ln(t)$. The shift in the minimum position of $S(t)$, expected to occur for a spin-glass system, is clearly observed.

In conclusion, the frequency-dependent peak observed in the temperature dependence of the ac susceptibility χ_{ac}, combined with magnetic relaxation results, provides strong evidence of the important role of magnetic frustration in polycrystalline Ru-1222 to establish the existence of spin-glass properties over a significant temperature range. This is to be contrasted with the usual interpretation of the existence of long-range antiferromagnetic order with spin canting for both Ru-1222 and Ru-1212 samples. The microscopic reason why Ru-1212 may present a long-range order while Ru-1222 does not is not clear at this time. However, our results come in line with the recent findings of Živković *et al.*, (Ref.3), who pointed out significant differences in the magnetic behavior of these two families of ruthenocuprates. Also, their results indicated the existence of a metastable magnetic state below the magnetic transition at T_f, which is in agreement with our interpretation of a spin glass freezing at T_f.

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