# Spin-Glass Behavior in $La_{1.96}Sr_{0.04}CuO_4$

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We report magnetization measurements in $La_{1.96}Sr_{0.04}CuO_4$, which has neither antiferromagnetic long range order nor superconductivity. All the features that characterize a canonical spin-glass transition are seen: irreversibility, remnant magnetization, and scaling behavior. The magnetic moment arises from a small density of effective free spins.

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The phase diagram of $La_{2-x}Sr_xCuO_4$ is quite rich, including the antiferromagnetic phase for $x \leq 0.02$, an intermediate region for $0.02 < x < 0.05$ characterized by 2D weak localization and unusual short range 2D magnetism, and the high $T_c$ superconducting phase for $x > 0.05$ [1]. Each of these ranges contains new and important physics issues. Further, because the magnetic and electronic properties evolve continuously as a function of doping, a thorough characterization of the entire phase diagram may provide clues about the origin of the superconductivity. We focus here on $La_{1.96}Sr_{0.04}CuO_4$, which is in the intermediate region with neither long range antiferromagnetic order nor superconductivity. Aharony *et al.* [2] predicted a novel spin-glass (SG) phase at such intermediate $x$. However, although experimental evidence for slowing down of the spin fluctuations has been found in neutron [3], muon spin relaxation ($\mu$SR) [4–6], and nuclear quadrupole resonance (NQR) [7] measurements, there has been no report of the magnetization behavior typical of canonical SGs: irreversibility and remnant magnetization below the glass transition and scaling behavior above and below it [8]. We report here measurements of the dc magnetization of a single crystal of $La_{1.96}Sr_{0.04}CuO_4$ that show all these features. Notably, although neutron measurements show that there is a staggered magnetization corresponding to one spin per Cu atom, the system has a uniform magnetization characterized by a very low density of effective free spins that undergo a conventional three-dimensional SG transition.

The single crystal used for this experiment was a small piece ($2 \times 2 \times 4$ mm$^3$ with the $c$ axis normal to the largest face) cut from the same crystal used for the neutron scattering and conductivity measurements of Keimer *et al.* [3]. It was grown by the top-seeded solution method using CuO as a flux [9]. The neutron results show short range antiferromagnetic order with a correlation length that is about 40 Å and independent of $T$ below 250 K. There is indirect evidence [3] that, although the spins behave like three-component Heisenberg ones at high $T$, they may cross over to $XY$-like behavior at $T \sim 20$ K. This is also the temperature below which a central (near zero-energy transfer) peak begins to grow with decreasing $T$, showing that the spin fluctuations slow down on the time scale of picoseconds, determined by the resolution of the neutron spectroscopy. Magnetization measurements were made with a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer at fields between 0.02 and 5.5 T applied parallel ($H\|ab$) and perpendicular ($H\|c$) to the $CuO_2$ planes.

The zero-field-cooled (ZFC) and field-cooled (FC) magnetizations $M$ at $H = 0.02$ T for the two field directions are plotted in Fig. 1. History dependence sets in at the irreversibility temperature, identified by the splitting of the ZFC and FC curves. This irreversibility temperature is the same for $H\|ab$ and $H\|c$. A peak is evident

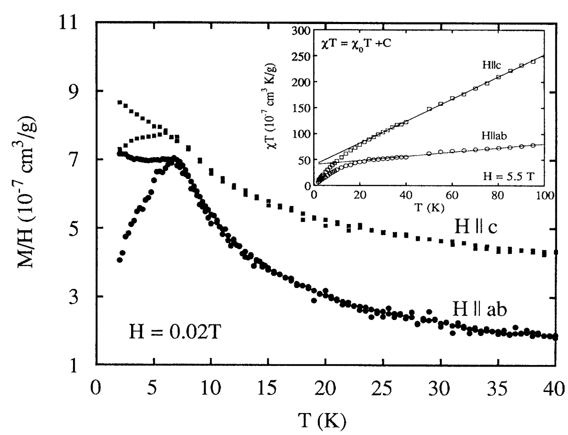


FIG. 1. Magnetization versus temperature for a field of 0.02 T applied perpendicular ($H\|c$) and parallel ($H\|ab$) to the $CuO_2$ plane. The field-cooled (FC) data deviate from the zero-field-cooled (ZFC) data at low $T$ indicating irreversibility. The data for $H\|c$ have been shifted by $10^{-7}$ cm$^3$/g. Inset: A plot of $\chi T$ vs $T$ at $H = 5.5$ T demonstrates the Curie behavior.

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in the ZFC magnetization near 7 K at low field, especially for $H \| ab$. Such a sharp peak in the ZFC magnetization, which broadens with increasing field, is one identifying feature of a spin glass.

Before discussing other aspects of the SG behavior we examine the magnetization at high $T$. Between ~20 and ~100 K the Curie form, $\chi = \chi_0 + C/T$, provides an excellent fit to the $T$ dependence of $M = \chi H$ for fields between 0.02 and 5.5 T [10]. A fit by the Curie-Weiss form gives a Curie-Weiss temperature $\Theta = 0$ within experimental error. We find $\chi_0 = 0.4 \times 10^{-7}$ and $2.1 \times 10^{-7}$ $cm^3/g$ for $H \| ab$ and $H \| c$, respectively. $\chi_0$ contains a diamagnetic contribution from the ion cores, and a paramagnetic contribution from the $Cu^{+2}$ $d$ electrons. The Van Vleck susceptibility of the latter is the origin of the large anisotropy of $\chi_0$. The inset of Fig. 1 shows a plot of $\chi T$ vs $T$ at 5.5 T illustrating that $C$, which has the value $(4.7 \pm 0.05) \times 10^{-6}$ $cm^3$ K/g, is isotropic. Using $g = 2$ and $S = 1/2$, this value corresponds to only 0.5% of the Cu spins or ~10% of the Sr atoms. Thus, the moment apparently arises from a small density of weakly interacting spins with an isotropic $g$ tensor.

Because it is so small, the Curie contribution has often been attributed to impurities or defects [11]. The starting materials contain less than 0.1 at. % of paramagnetic impurities. We have prepared a number of single crystal and sintered powder samples with $x$ in the range 0.03 to 0.04. Typically, we find an effective spin density ($S = 1/2$, $g = 2$) of ~0.5%. However, two of the samples had effective spin densities of ~0.2% and ~5%, respectively. There is no obvious correlation of these varying spin densities with the purities of the starting materials or the method of preparation. In spite of these variances, all samples exhibit the same basic magnetic behavior. Thus, the results we discuss in this paper are almost certainly intrinsic to the doped $CuO_2$ layers.

As is typical of spin glasses [12], the magnetization for $T < T_g$ remains after the field is turned off. Figure 2 shows the magnetic moment measured 1 h after setting the field to zero. For the ZFC case the field was applied for 5 min at 2.2 K and then turned off. The behavior of this remnant magnetization is typical of canonical spin glasses such as Cu:Mn and $Eu_{1-x}Sr_xS$ [8]. The time decay of the magnetization can be well described by the standardly used stretched exponential form, $M(t) = M_0 \exp(-\alpha t^{1-n})$. From a fit with the latter (see inset of Fig. 2), we find $1 - n = 0.31 \pm 0.07$. Although the data are not sufficient to prefer uniquely this functional form (one can also fit with $M \sim M_0 - a \ln t$), it is encouraging to note the consistency of $n$ with theoretical predictions [13] and with experiments on traditional spin glasses [14,15], which also give $1 - n \sim 1/3$.

The last feature that is used to identify spin-glass ordering involves the nonlinear susceptibility $\chi_{\rm nl} = \partial^3 M/\partial H^3|_{H=0}$. More generally, a spin glass is expected to show scaling behavior, one manifestation of which is the divergence of $\chi_{\rm nl}$ as $H \to 0$ and $T \to T_g$, where $T_g$ is

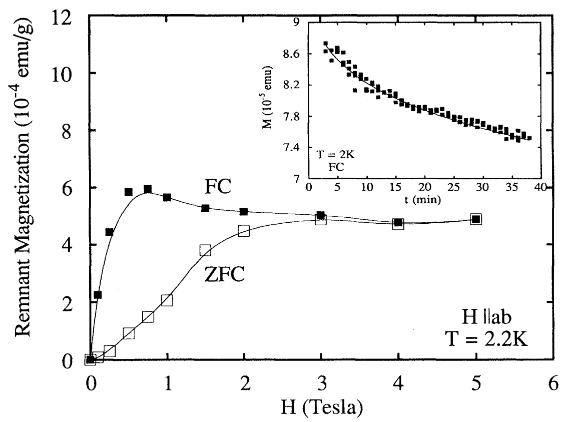


FIG. 2. The remnant magnetization is plotted versus applied magnetic field. The moment is measured 1 h after setting the field to zero. The inset shows the time dependence of the moment immediately after the field is set to zero. The line in the inset is a stretched exponential (see text).

the SG transition temperature. $\chi_{\rm nl}$ is usually measured by an ac susceptibility technique, which was not available to us, or by measuring $M$ vs $H$ at low field. Unfortunately, since the effective spin density is so low in our material, a very small contaminant moment [10] makes it impossible for us to measure $M(H)$ at very low field. Therefore, we have explored the scaling behavior in a different way.

Scaling theory predicts that

$$\chi - \chi_0 = \frac{C}{T}(1 - q) = \frac{C}{T}[1 - |t|^{\beta} f_{\pm}(H^2/|t|^{\beta+\gamma})], \quad (1)$$

where $t$ is the reduced temperature $t = (T - T_g)/T_g$, $q$ is the SG order parameter, and the scaling functions $f_+$ and $f_-$ apply for $t > 0$ and $t < 0$, respectively [16]. This expression reduces to the Curie form at high $T$ where $q = 0$. Equation (1) also predicts that $\chi_{\rm nl}$ diverges as $H \to 0$ and $T \to T_g$; in particular, an expansion of $M$ for small $H$ using Eq. (1) gives coefficients of $H^3$ and $H^5$ that are predicted to follow $\chi_3 \sim |t|^{-\gamma}$ and $\chi_5 \sim |t|^{-(\beta+2\gamma)}$. For $t < 0$, Eq. (1) predicts that $q \sim |t|^{\beta}$ for $H = 0$, that is, $f_-(0)$ is nonzero, while $f_+(0) = 0$.

Using our measured values of $C$ and $\chi_0$ we extract $q(T)$ from the FC measurements of $\chi$ and plot it for various fields as shown in Fig. 3. For $H \| ab$, $q$ shows evidence for a phase transition at 7 K, which broadens with increasing $H$. For $H \| c$, $q$ appears to grow with decreasing $T$ between ~20 and 7 K even at $H = 0.02$ T. This behavior is seen in several samples prepared in different ways. Above ~1 T $q$ becomes isotropic. To emphasize this we have fit a polynomial to the data for $H \| ab$ at 5.5 T and have plotted the same curve without adjustment with the $H \| c$ data.

Equation (1) describes an equilibrium phase transition, but neither FC nor ZFC data represent equilibrium measurements for $t < 0$. Nonetheless, the FC and ZFC values

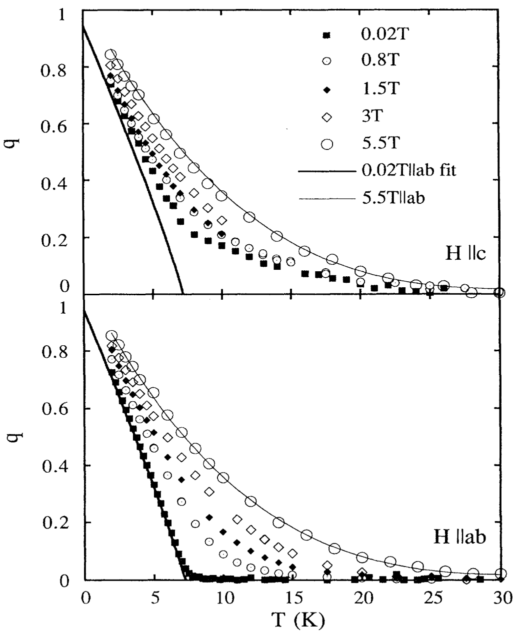


FIG. 3. The SG order parameter $q(T)$ versus temperature for fields applied in the two directions. The thick line is $q(T) \sim (T_g - T)^\beta$ with $T_g = 7.2$ K and $\beta = 0.9$. The thin lines are the results of a polynomial fit to the $H = 5.5$ T $(H \| ab)$ data.

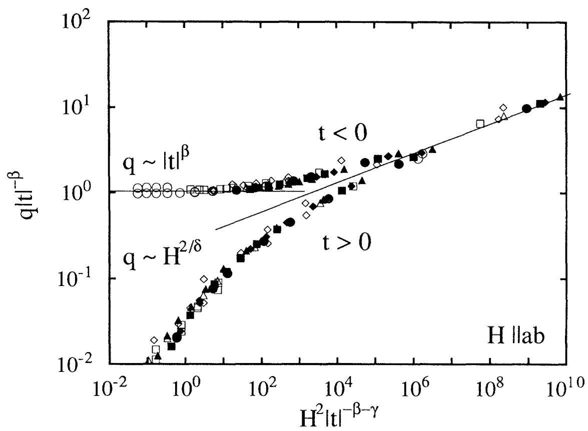


FIG. 4. Log-log plot of $q|t|^{-\beta}$ vs $H^2|t|^{-(\beta+\gamma)}$. Different symbols represent different fields: ○ 0.1 T, □ 0.5 T, ◇ 1 T, △ 1.5 T, ● 2 T, ■ 3 T, ◆ 4 T, ▲ 5.5 T. All data in the ranges $2 < T < 30$ K and $0.1 < H < 5.5$ T collapse, demonstrating the scaling described by Eq. (1).

of $q$ differ only slightly, even at the lowest $H$. The differences in $\chi$, seen clearly in Fig. 1, correspond to much more subtle differences in $1 - q \sim T(\chi - \chi_0)$. To determine $T_g$ and $\beta$, we have fit the FC data and ZFC data separately by the form $q \sim |t|^\beta$. Averaging $\beta$ and $T_g$ from the two fits we find $\beta = 0.9 \pm 0.1$ and $T_g = 7.2 \pm 0.1$ K. The heavy curve in Fig. 3 is given by $B|t|^{-\beta}$ with $T_g = 7.2$ K and $\beta = 0.9$, with the amplitude $B$ adjusted to match the $H = 0.02$ T data. From Eq. (1) we expect $q \sim H^{2/\delta}$ for $H^2 \gg |t|^{(\beta+\gamma)}$, where $\delta = 1 + \gamma/\beta$. This form describes the data near $T_g$ well, and the fit gives $\delta = 5.9 \pm 0.6$, which, with $\beta = 0.9 \pm 0.1$, gives $\gamma = 4.3 \pm 1.1$.

Using these values we plot the data for all fields and temperatures in Fig. 4, using the variables $q|t|^{-\beta}$ vs $H^2|t|^{-(\beta+\gamma)}$. The data for $t < 0$ are FC data, but the ZFC data are indistinguishable in a plot of this kind. It would be interesting to compare FC and ZFC data in other SG systems. All of the data collapse onto two curves, that is, $f_-(x)$ for $t < 0$ and $f_+(x)$ for $t > 0$. Note that for these data the quantity $H^2|t|^{-(\beta+\gamma)}$ varies over 11 decades. As noted above, the magnetization is isotropic for $H > 1$ T so the data collapse for $H\|c$ as well as for $H\|ab$ at high fields. The line $q \sim H^{2/\delta}$ with $\delta = 5.9$ is drawn in the figure to illustrate the asymptotic behavior for $t \to 0$. The observation that $q|t|^{-\beta}$ approaches a constant for small $H^2|t|^{-(\beta+\gamma)}$ for $t < 0$ is consistent with the observed scaling $q \sim |t|^\beta$ discussed above.

The exponents we find are similar to those found for conventional spin glasses. Our measured value of $\beta \approx 0.9$ is close to the mean field prediction $\beta = 1$ and to experimental values, 0.7 and 0.9, measured for Cu:Mn [17]. $\gamma$ values are found to be near $3 \pm 1$ in most of the SG systems but $\gamma = 4.5 \pm 0.2$ has been reported for the 2D Ising SG $Rb_2Cu_{1-x}Co_xF_4$ [18]. Our measurement $\gamma \approx 4.3$ is consistent with these. Because of the experimental uncertainties as well as the field and temperature ranges in which the exponents are derived, the experimental values of critical exponents vary even in the same SG system [19]. Despite this, our values of the critical exponents are close to those of the canonical SGs, suggesting that the spin freezing phenomenon near 7 K is truly a three-dimensional SG phase transition. The shapes of our scaling functions $f_\pm(x)$ are also very similar to those observed in more traditional spin glasses [8].

As mentioned above, neutron, $\mu$SR, and NQR measurements also provide evidence for the freezing of spins in $La_{2-x}Sr_xCuO_4$. Keimer *et al.* [3] observe slowing down of spin fluctuations below a neutron-measured freezing temperature $T_f^N \sim 20$ K in the same crystal studied here. Sternlieb *et al.* [5] find $T_f^N \sim 40$ K for $x = 0.06$, and their zero-field $\mu$SR experiments show the existence of a frozen local magnetic field below $T_f^\mu \sim 6$ K. They ascribe the different temperatures measured to the different frequency windows of the two measurements, $\sim 10^{12}$ Hz for neutrons and $\sim 10^6$ Hz for $\mu$SR. Harshman *et al.* [6] find $T_f^\mu \sim 10$ K for $x = 0.02$, so by interpolating between $x = 0.02$ and 0.06, it appears that $T_f^\mu$ is close to the $T_g$ we measure here. NQR experiments show the slowing down of Cu spin fluctuations through the enhancement of the $^{139}$La nuclear spin-lattice relaxation rate. The temperatures at which this happens are 10 K for $x = 0.02$, 7.4 K for $x = 0.03$, and 5.2 K for $x = 0.04$ [7]. The latter measurement, which like $\mu$SR has a frequency window of $10^6$ Hz, also gives a freezing temperature in reasonable agreement with the $T_g$ we measure.

We conclude that the apparently isotropic free spins that contribute to the magnetization undergo a canonical three-dimensional spin glass transition at 7 K in $La_{1.96}Sr_{0.04}CuO_4$. However, interesting questions remain to be elucidated. One such question concerns the low density of effective free spins. In the simple picture given by Aharony *et al.* [2], each Sr ion generates local frustration of the couplings among Cu spins. However, neutron measurements [3] show an antiferromagnetic correlation length of $\sim 40$ Å, so that a majority of the Cu spins are strongly antiferromagnetically correlated in domains, which freeze with random orderings. It is thus feasible that the spins we see in the magnetization are only those sitting near domain walls (which may indeed vary among samples). Although we cannot totally exclude the possibility that these spins come from defects, the agreement with $\mu$SR and NQR measurements as well as the universality of our basic results show that the free spins we measure reflect the freezing of the entire Cu spin system.

In addition, the anisotropy in the spin ordering at low field is very interesting. For $H \| c$, the SG order parameter at low fields appears to grow gradually below 20–30 K in all the samples we have studied, whereas at high fields (>1 T) the magnetization is completely isotropic. Keimer *et al.* [3] suggest that there is a crossover from Heisenberg to *XY* coupling of the Cu spins at about the same temperature. Clearly, the anisotropy of the spin-glass transition remains to be understood.

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*Note added.*—The data reported in this paper have been analyzed using the Curie form for the susceptibility. Reanalysis using the Brillouin function for $S = 1/2$ and $g = 2$ yields qualitatively similar results with only small quantitative differences at the highest fields and lowest temperatures. In particular, the scaling plot in Fig. 4 is not discernably altered. We are grateful to A. P. Ramirez for pointing out the possible importance of the latter analysis.

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