Anelastic spectroscopy study of the spin-glass and cluster spin-glass phases of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($0.015 < x < 0.03$)

A. Paolone$^1$, F. Cordero$^2$, R. Cantelli$^1$, M. Ferretti$^3$

1 Università di Roma “La Sapienza”, Dipartimento di Fisica, P.le A. Moro 2, I-00185 Roma, and INFM, Italy
2 CNR, Area di Ricerca di Tor Vergata, Istituto di Acustica “O.M. Corbino”, Via del Fosso del Cavaliere 100, I-00133 Roma, and INFM, Italy
3 Università di Genova, Dipartimento di Chimica e Chimica Fisica, Via Dodecanneso 31, I-16146 Genova, and INFM, Italy

The anelastic spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have been measured at liquid He temperatures slightly below and above the concentration $x_c \simeq 0.02$ which is considered to separate the spin-glass phase from the cluster spin-glass (CSG) phase. For $x \leq x_c$ all the elastic energy loss functions show a step below the temperature $T_g (x = 0.02)$ of freezing into the CSG state, similarly to what found in samples well within the CSG phase, but with a smaller amplitude. The excess dissipation in the CSG state is attributed to the motion of the domain walls between the clusters of antiferromagnetically correlated spin. These results are in agreement with the recent proposal, based on inelastic neutron scattering, of an electronic phase separation between regions with $x \sim 0$ and $x \sim 0.02$, at least for $x > 0.015$. 
I. INTRODUCTION

The magnetic properties of the High $T_c$ Superconductors (HTCS) have attracted much interest also because these compounds are experimental realizations of a 2D Heisenberg antiferromagnet. In undoped La$_2$CuO$_4$ the Cu$^{2+}$ spins order into a 3D antiferromagnetic (AF) state below $T_N \approx 315$ K with the staggered magnetization in the $ab$ plane. When doping by substituting Sr for La, the long range AF order is rapidly suppressed and around $x_c \approx 0.02$ the Néel temperature drops to 0 K. In the long range AF region $T_N(x)$ follows a power law relationship with $x$, interpreted as an indication that the holes introduced by doping form walls separating domains of undoped material. Later work indicated that the spin degrees of freedom associated with the doped holes are distinct from the in-plane Cu$^{2+}$ spin degrees of freedom that order themselves below $T_N$, and the localization of the doped holes allows the associated spins to progressively slow down and freeze. The state in which the doped spins freeze is usually referred to as a spin glass (SG) state, and occurs below $T_f(x) \approx (815 \text{ K}) x$. For $x > x_c$, there is no long range AF order, but approaching $T_g \approx 0.2 \text{ K}/x$ AF correlations develop within domains separated by charge walls, with the easy axes of the staggered magnetization uncorrelated between different clusters. This picture corresponds to a cluster spin-glass (CSG) state. The formation of the SG and CSG states are inferred from sharp maxima in the $^{139}$La NQR and $\mu$SR relaxation rates, which indicate the slowing of the AF fluctuations below the measuring frequency ($\sim 10^7 - 10^8$ Hz in those experiments), and from the observation of irreversibility, remnant magnetization, and scaling behavior in magnetic susceptibility experiments. Also anelastic spectroscopy can provide useful information about the magnetic properties of high HTCS. Above $x_c$, the elastic energy loss coefficient shows a rise below a temperature close to the $T_g(x)$ for freezing into the CSG state. The absorption is not peaked near $T_g$, but is step-like or at least displays a plateau, and therefore does not directly correspond to the peak in the dynamic spin susceptibility due to the spin freezing; rather, it has been attributed to the stress-induced changes of the sizes of the spin clusters, or equivalently to the motion of the domain walls.

Recently, Matsuda et al. reported a neutron scattering study of the magnetic correlations in La$_{2-x}$Sr$_x$CuO$_4$ for $x < x_c$, which suggests a different picture of the spin glass phase. In fact, they found that also at $x < x_c$ the 3D AF ordered phase coexists below $\sim 30$ K with domains of "diagonal" stripe phase (with the hole stripes at $45^\circ$ with respect to the Cu-O bonds), as observed for $x > x_c$. According to these authors, the hole localization starting around 150 K involves an electronic phase separation into regions with $x_1 \sim 0$ and $x_2 \sim 0.02$. The volume fraction of the $x_2 = 0.02$ phase changes as a function of the Sr doping, in order to achieve the average $x$.

In the following we will report on anelastic spectroscopy measurements of lightly doped La$_{2-x}$Sr$_x$CuO$_4$, where the anelastic spectra for $x < x_c$ present the same features attributed to the domain wall motion into the CSG phase, although attenuated. The step-like rise of dissipation occurs near 10 K, as for $x \approx 0.02$, supporting the view of an electronic phase separation, at least for $0.015 < x < 0.02$.

II. EXPERIMENTAL AND RESULTS

The samples were prepared by standard solid state reaction as described in Ref. [13] and cut in bars approximately $40 \times 4 \times 0.6 \text{ mm}^3$. In the as-sintered state all the samples contained small amounts of interstitial O, which was outgassed by heating in vacuum up to 790 K. The complex Young’s modulus $E(\omega) = E’ + iE''$, whose reciprocal is the elastic compliance $S^{-1} = E^{-1}$, was measured as a function of temperature by electrostatically exciting the flexural modes. The vibration amplitude was detected by a frequency modulation technique. The vibration frequency, $\omega/2\pi$, is proportional to $\sqrt{E}$, while the elastic energy loss coefficient (or reciprocal of the mechanical $Q$) is given by $Q^{-1} = E''/E' = S''/S'$, and was measured by the decay of the free oscillations or the width of the resonance peak. The imaginary part of the dynamic susceptibility $S''$ is related to the spectral density $J_\omega(T)$, while $\omega\tau = \int dt e^{i\omega t} \langle \mathcal{E}(t) \mathcal{E}(0) \rangle$ of the macroscopic strain $\mathcal{E}$ through the fluctuation-dissipation theorem, $S'' \propto (\omega/2\pi\tau)(J_\omega)$. Magnetoelastic coupling can couple strain to the spin degrees of freedom, so that pseudodiffusive spin excitations (with null characteristic frequency) or the motion of magnetic boundaries can contribute to $J_\omega$. An elementary relaxation process with a thermally activated relaxation time $\tau(T)$ contributes with $S'' \propto \omega\tau/\left[1 + (\omega\tau)^2\right]$, peaked at the temperature at which $\omega\tau = 1$ (which therefore increases with increasing $\omega$), while the relaxation of extended and interacting structures like domain walls generally gives rise to a broader dissipation curve.

The compositional jumps of the samples were: $x_{\text{nom}} = 0.015, 0.016, 0.018, 0.024$ and 0.030. The final Sr contents were checked from the temperature position of the step in the Young’s modulus $E$ due to the tetragonal (HTT) / orthorhombic (LTO) transition, which occurs at a temperature $T_i(x)$ decreasing with doping approximately as $T_i(x) = (535 - x/0.217) \text{ K}$ (Ref. [13]). The shape of the anomaly in $E$ cannot be completely fitted by a simple model, since it includes both contributions from the coupling of the spontaneous strain with the soft model, and from the domain wall motion, but its position in temperature provides information about the level of doping. Figure 1 presents the logarithmic derivative of the Young’s modulus with respect to temperature, $d\ln |E/E(0)|/dT$, so that the steps become peaks whose widths provide upper limits to the spread of the local Sr
concentration; the peaks are fitted with lorentzians. The Sr concentrations estimated from the peak positions and from \( T_1(x) \) are \( x = 0.0165, 0.0155, 0.0183, 0.0227 \) and 0.0273 respectively; the sample with \( x_{\text{nom}} = 0.016 \) results to be less doped than the one with \( x_{\text{nom}} = 0.015 \) and with a broader transition. There is considerable overlapping of the peaks of the samples with \( x_{\text{nom}} < 0.02 \), but this should not be simply interpreted as a distribution of local \( x \) spanning 0.015-0.018 for all these samples. In fact, the peaks in the derivative of \( E(T) \) cannot be interpreted as the distribution function of the local \( x \) after the \( T \) scale is converted into an \( x \) scale inverting \( T \), since the step of \( E(T) \) has an intrinsic width due to the progressive phonon softening above \( T_1 \) and to the relaxational character of the domain wall motion below \( T \). The undoped samples, for example, certainly do not have a spread of Sr concentration, but the widths of their lorentzians (not shown here) are 16 – 22 K, compared to 10 K of the sample with \( x_{\text{nom}} = 0.016 \). In the following we will refer to the doping level obtained from the position of the step in the Young’s modulus.

Figure 2 presents the anelastic spectra of the five samples measured exciting the first flexural mode, around 1 kHz. The sharp rise of dissipation at the lowest temperatures is the tail of an intense peak attributed to the tunneling-driven tilt motion of a fraction of the O octahedra. The shift of the peak to lower temperature with increasing doping would be due to a direct coupling between the hole excitations and the tunneling-driven local tilts of the O octahedra; the more the hole excitations and the faster the local tilting. We are concerned with the steplike feature at \( T_g(x) \simeq 0.2/x \) for \( x > 0.02 \), and below \( \simeq 10 \text{ K} \) for \( x < 0.02 \). That such a dissipation rise occurs at \( T_g \) and is steplike or at least consists of a plateau rather than a peak is particularly evident at higher doping, when the influence of the tail of the peak at lower temperature is less important here only two curves with \( x \gtrsim 0.02 \) are presented. The dissipation rise has been attributed to the stress-induced movement of the boundaries between the clusters of quasi-frozen antiferroelectrically correlated spins which form the CSG phase. The main result is that also the samples with \( x < 0.02 \) present a similar feature around 10 K. With lowering \( x \) below 0.02, the position of the dissipation step remains unchanged, while its intensity decreases; this is more difficult to see for the sample with \( x = 0.0155 \), since the tail of the low temperature peak is shifted to higher temperature (consistent with the lowest doping in spite of the nominal \( x \)). Considering also previous data \( \cite{x} \), it appears that, starting from high doping and lowering it, the dissipation step first rises in temperature according to \( T_g(x) \) and increases in intensity down to \( x \simeq 0.02 \); below that doping its temperature remains unchanged and the intensity decreases.

III. DISCUSSION

One would expect that the dissipation rise near 10 K for \( x < 0.02 \) corresponds to the peak in the spin susceptibility occurring when the magnetic fluctuations slow down below the measuring frequency during the freezing process into the SG phase, as in the NQR measurements \( \cite{x} \). Also the temperature region would be as expected, since, according to the generally accepted phase diagram, at \( x = x_c \) both \( T_f(x) \) and \( T_g(x) \) merge at 10 – 15 K. However, there are two features signalling the different nature of the absorption rise below \( \sim 10 \text{ K} \): one is the shape, certainly different from the sharp peak of the NQR relaxation rate, and the other is the total absence of the expected linear shift toward lower temperature when the doping is reduced. This is better demonstrated by the derivatives of the \( Q^{-1}(T) \) curves in Fig. 3, where the negative peaks at high temperature, labelled with the estimated doping values, correspond to the steps in \( Q^{-1}(T) \). The three peaks with \( x < 0.02 \) even shift to higher temperature with decreasing \( x \), although the effect is very small and most likely attributable to the increasing influence of the tail of the peak at lower temperature. Instead, according to the generally adopted phase diagram with \( T_f(x) \simeq x \times (815 \text{ K}) \) the three peaks should display an overall shift by 2.3 K in the opposite direction; it is therefore clear from Fig. 3 that there is no relation between the acoustic dissipation step and \( T_f \propto x \).

The spectra of the samples with \( x < 0.02 \) strictly resemble those for \( x > 0.02 \), and the latter have been successfully interpreted in terms of onset below \( T_g \) of the motion of the domain walls between different spin clusters in the CSG phase. The decrease of the amplitude \( \Delta \) of the absorption step above \( x = 0.02 \) has been semiquantitatively explained considering a simple model of the CSG phase, with the Sr atoms acting as pinning points for the domain walls, which coincide with the hole stripes. The relaxation strength is expected to be of the form \( \Delta \propto n l^\alpha \), where \( n \) is the volume concentration of the domain walls, \( l \) is the distance between pinning points, and \( \alpha \) turns out \( \simeq 2.5 \), intermediate between the case of the motion of dislocations and of walls between ferromagnetic domains. It was also possible to observe the pinning of the walls by the low-temperature tetragonal lattice modulation in samples doped with Ba instead of Sr. The mechanism of dissipative motion of the domain walls is well known for ferromagnetic materials \( \cite{x} \) and is possible also for an AF state, if an anisotropic strain is coupled with the easy magnetization axis. In this case, the elastic energy of domains with different orientations of the staggered magnetization are differently affected by a shear stress, and the lower energy domains grow at the expenses of the higher energy ones providing the coupling between strain and domain wall motion. The same mechanism could not be applied to the SG state, even admitting the existence of hole stripes below 10 K, since
they would move into a uniform long-range ordered AF matrix, instead of separating inequivalent domains, and other more subtle mechanisms should be invoked.

It has to be concluded that the anelastic spectra for $x < 0.02$ (Fig. 2a) cannot be justified in terms of the spin-glass phase with $T_f(x)$ increasing linearly with $x$; rather, they can be explained in a straightforward way within the physical picture derived from the inelastic neutron scattering measurements. According to these observations, there is an electronic phase separation below $x = 0.02$, where domains with fixed $x_2 = 0.02$ coexist with regions of undoped material with $x_1 = 0$. Such domains have sizes estimated in several hundreds of Å within the CuO$_2$ planes, and display the same "diagonal stripe" correlations which are observed in the CSG state for $x > 0.02$. The volume fraction of these domains has also been verified to increase linearly with $x$, as expected. In this phase separation picture, the elastic energy dissipation curves for $x < 0.02$ simply contain the step-like increase due to the motion of the hole stripes within the $x_2 \simeq 0.02$ domains, whose sizes are sufficiently large that they appear as the homogeneous phase $x = 0.02$ with the same $T_F \simeq 10$ K. The reduced volume fraction at lower doping simply results in a reduced amplitude of the elastic energy absorption.

The fact that the temperature at which our measurements reveal the presence of spin domains is much lower than the temperature of 30 K reported by Matsuda et al. also agrees with what is observed in the CSG state. In fact, the onset temperature for freezing toward the glass state, $T_{on}$, depends on the time scale at which the experimental technique probes the system, and decreases as the angular frequency $\omega$ of the probe decreases. In neutron scattering experiments $\omega$ is of the order of $4 \cdot 10^{11}$ s$^{-1}$, whilst for the anelastic spectroscopy $\omega \sim 10^3 \div 10^5$ s$^{-1}$, resulting in a factor 2.5 between the two $T_{on}$, at $x \sim 0.03$. This is consistent with the $T_{on} = 10 \div 15$ K deduced from the curves of Fig. 2a.

The dissipation curves of Fig. 2a clearly indicate that the same dissipation mechanism of the CSG phase is operative also at $x < 0.02$, and therefore are in good agreement with the phase separation picture from the neutron scattering experiments. However, these curves alone are not sufficient for clearly discriminating between a neat phase separation into $x_1 \sim 0$ and $x_2 \sim 0.02$ or a situation with a smooth transition from the CSG to the SG state over a wide concentration range around 0.02. For example, according to the theoretical model proposed by Gooding et al. at low temperature the holes localize near the Sr dopants and circulate over the four Cu atoms neighbors to Sr, inducing a distortion of the surrounding Cu spins, otherwise aligned according to the prevalent AF order parameter. The spin texture arising from the frustrated combination of the spin distortions from the various localized holes produces domains with differently oriented AF order parameters, which can be identified with the frozen AF spin clusters. In this model there is no clear boundary between the SG and CSG state, and the present data could also fit into such a description.

The possibility has also to be considered that the discrepancy between the present results below $x \approx 0.02$ and the canonical phase diagram is due to inhomogeneous doping of the samples at a microscopic level. Errors in evaluating the actual doping and inhomogeneous doping would produce particularly large shifts and uncertainty in the determination of $T_f$ and $T_g$, since these temperatures appear to merge around the value $10 - 15$ K at $x = x_c = 0.02$, where they strongly depend on doping. Indeed, there is a wide scattering of experimental data in that region of the phase diagram, which can be due to uncertainties in $x$, but also to the fact that the transition between SG and CSG is not as sharp as supposed. The present data support the second explanation. In fact, we cannot exclude the possibility of inhomogeneous doping of our samples with certainty, only based on the width of the HTT/LTO phase transition, because we are not able to carry out a rigorous analysis of the curves of Fig. 1. Still, we note that if the high temperature of the step of samples with average $x < 0.02$ is due to regions with $x > 0.02$, then we should expect a similar spread of the local doping also for the samples with $x > 0.02$, since all the samples have been prepared in the same way. Then, the sample with $x = 0.0273$ should exhibit a partial onset of dissipation already above 10 K, due to regions with $x \approx 0.02$. The sample with $x = 0.0273$, instead, displays a neat rise below 8 K, excluding the presence of regions with $x \approx 0.02$. It can be concluded that the present measurements demonstrate the presence of CSG domains also for $x < 0.02$, and the insensitivity of the temperature of the acoustic anomaly on doping supports the proposal of an intrinsic phase separation at $x < 0.02$.

IV. CONCLUSION

We measured the anelastic spectra of La$_{2-x}$Sr$_x$CuO$_4$ for both $x < 0.02$ and $x > 0.02$, spanning the region of the phase diagram where the transition from the SG to the CSG phase is expected. The same step-like feature in the elastic energy loss function that has been attributed to the domain wall motion in the CSG state is also found for $0.015 < x < 0.02$. The step cannot be related to the SG phase whose onset is usually assumed to be $T_f \propto x$, since its temperature remains locked at the value found for $x = 0.02$. The present data clearly show that CSG regions exist also for $x < 0.02$ and therefore there is no neat separation between the SG and CSG regions. They can be naturally interpreted in the framework of the phase separation model for $x < 0.02$, recently proposed by Matsuda et al. to explain their inelastic neutron scattering measurements.
ACKNOWLEDGMENTS

The authors thank Prof. A. Rigamonti for useful discussions. This work has been done in the framework of the Advanced Research Project SPIS of INFM.

1 A. Rigamonti, F. Borsa and P. Carretta, Rep. Prog. Phys. 61, 1367 (1998).
2 D. Vaknin, S.K. Sinha, D.E. Moncton, D.C. Johnston, J.M. Newsam, C.R. Safinya and H.E. King, Jr. H.E. King, Jr., Phys. Rev. Lett. 58, 2802 (1987).
3 J.H. Cho, F.C. Chou and D.C. Johnston, Phys. Rev. Lett. 70, 222 (1993).
4 F.C. Chou, F. Borsa, J.H. Cho, D.C. Johnston, A. Lascialfari, D.R. Torgeson and J. Ziolo, Phys. Rev. Lett. 71, 2323 (1993).
5 J.H. Cho, F. Borsa, D.C. Johnston and D.R. Torgeson, Phys. Rev. B 46, 3179 (1992).
6 M.-H. Julien, F. Borsa, P. Carretta, M. Horvatic, C. Berthier and C.T. Lin, Phys. Rev. Lett. 83, 604 (1999).
7 Ch. Niedermayer, C. Bernhard, T. Blasius, A. Golnik, A. Moodenabaugh and J.I. Budnick, Phys. Rev. Lett. 80, 3843 (1998).
8 F.C. Chou, N.R. Belk, M.A. Kastner, R.J. Birgeneau and A. Aharony, Phys. Rev. B 46, 3179 (1992).
9 S. Wakimoto, S. Ueki, Y. Endoh and K. Yamada, Phys. Rev. B 62, 3547 (2000).
10 F. Cordero, A. Paolone, R. Cantelli and M. Ferretti, Phys. Rev. B 62, 5309 (2000).
11 R.S. Markiewicz, F. Cordero, A. Paolone and R. Cantelli, Phys. Rev. B 64, 54409 (2001).
12 M. Matsuda, M. Fujita, K. Yamada, R.J. Birgeneau, Y. Endoh and G. Shirane, cond-mat/0111228 (2001).
13 M. Daturi, M. Ferretti and E.A. Franceschi, Physica C 235-240, 347 (1994).
14 A.S. Nowick and B.S. Berry, Anelastic Relaxation in Crystalline Solids. (Academic Press, New York, 1972).
15 D.C. Johnston, Handbook of Magnetic Materials. ed. by K.H.J. Buschow, p. 1 (North Holland, 1997).
16 J.L. Sarrao, D. Mandrus, A. Migliori, Z. Fisk, I. Tanaka, H. Kojima, P.C. Canfield and P.D. Kodali, Phys. Rev. B 50, 13125 (1994).
17 W.-K. Lee, M. Lew and A.S. Nowick, Phys. Rev. B 41, 149 (1990).
18 F. Cordero, C.R. Grandini, G. Cannelli, R. Cantelli, F. Trequattrini and M. Ferretti, Phys. Rev. B 57, 8580 (1998).
19 F. Cordero, R. Cantelli and M. Ferretti, Phys. Rev. B 61, 9775 (2000).
20 F. Cordero, A. Paolone, R. Cantelli and M. Ferretti, Phys. Rev. B 64, 132501 (2001).
21 R.S. Markiewicz, F. Cordero, A. Paolone and R. Cantelli, Phys. Rev. B 64, 54409 (2001).
22 R.J. Gooding, N.M. Salem, R.J. Birgeneau and F.C. Chou, Phys. Rev. B 55, 6360 (1997).

23 A. Campana, R. Cantelli, F. Cordero, M. Corti, A. Rigamonti, E. Phys. J. B 18, 49 (2000).

FIG. 1. Derivatives of the logarithm of the Young’s modulus with respect to temperature at the HTT/LTO transformation for the five samples here studied. The inset reports the nominal doping and the doping level deduced from the temperature of the transition.

FIG. 2. Elastic energy loss coefficient of La_{2-x}Sr_{x}CuO_{4} with x = 0.0173 (1.35 kHz), x = 0.0192 (1.05 kHz), x = 0.0198 (0.76 kHz) in the part (a) of the figure and with x = 0.0227 (0.97 kHz) and x = 0.0313 (1.72 kHz) in part (b).

FIG. 3. Derivative of the elastic energy loss with respect to temperature for the five samples here studied.
La_{2-x}Sr_{x}CuO_{4}
(a) $x = 0.0165$

(b) $x = 0.0155$

$x = 0.0183$

$T (K)$

$0.0273$
