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Static and dynamic spin fluctuations in superconducting $La_{2-x}Sr_xCuO_4$

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We report a neutron scattering study of the spin fluctuations in samples of $La_{1.89}Sr_{0.11}CuO_4$ which are ~80% superconducting with $T_c=10$ K. The structure factor $S(\mathbf{Q})$ reflects three-dimensional modulated spin correlations with an in-plane correlation length of order 18 ± 6 Å. The fluctuations evolve with temperature from being predominantly dynamic at high temperatures to mainly quasielastic ($|\Delta E|<0.5$ meV) at low temperatures. No significant differences are observed in the normal and superconducting states.

A variety of experiments has indicated that the CuO_2 lamellar superconducting materials exhibit novel but complicated magnetic effects.[1-3] Recent neutron experiments in $La_{2-x}Sr_xCuO_4$ with $0.02\leq x\leq 0.14$ show that as x increases the Cu^{2+} moment is preserved but the basic antiferromagnetic state becomes progressively shorter ranged.[1] These experiments, however, are not definitive vis-a-vis the nature of the magnetism in the superconducting state since the samples studied there exhibit a Meissner fraction of at best 15%. Recently, however, two of us (Y.H. and T.M.) have made significant progress in the growth of single-crystal $La_{2-x}Sr_xCuO_4$ of high crystalline perfection and with a large Meissner fraction (~80%).[4]

In this note we report a neutron scattering study of samples of $La_{2-x}Sr_xCuO_4$ with $T_c=10$ K and an 80% Meissner fraction. The high quality of the samples has allowed a much more thorough study of the spin correlations than was possible previously. We find a number of new results. First, the static factor $S(\mathbf{Q})$ exhibits a complicated three-dimensional incommensurate structure with a characteristic two-dimensional (2D) correlation length of order 18 ± 6 Å. The low-energy ($|\Delta E|<0.5$ meV) part of $S(\mathbf{Q})$ exhibits pronounced *three-dimensional* correlations at all temperatures (5 to 350 K). The response function evolves with temperature from being predominantly inelastic ($|\Delta E|>0.5$ meV) at high temperatures to mainly quasielastic ($|\Delta E|<0.5$ meV) at low temperatures, $T\leq 50$ K. The integrated intensity is, however, preserved; further it is close to that observed under identical spectrometer conditions for pure La_2CuO_4.[5]

The experiments were carried out on the H7 and H4M triple-axis spectrometers at the Brookhaven High Flux Beam Reactor. As will be discussed below, the experiments proved to be rather difficult and, thus, required a novel approach to data collection. Specifically, it was discovered early in the experiments that there was a striking thermal evolution in the distribution in energy of the scattering so that it was essential to separate the quasielastic ($|\Delta E|<0.5$ meV) and integrated inelastic ($|\Delta E|>0.5$ meV) contributions to $S(\mathbf{Q})$. Data were obtained primarily using neutrons with energy $E_i=14.7$ meV and collimations 40′-40′-40′-80′; the monochromator and analyzer were pyrolytic graphite (PG) (002) and the incoming beam passed through two PG filters in order to eliminate completely any $\lambda/2$ neutrons. The spectrometer was set up in the triple-axis mode and all scans were carried out twice, first detecting neutrons scattered off the PG analyzer so that $|\Delta E|<0.5$ meV and second detecting neutrons passing straight through the analyzer. The effective reflectivity of the analyzer was measured to be 78% so that by subtracting 29% of the first scan from the second scan, one obtained precisely in the latter scan the intensity integrated over all energies with $|\Delta E|>0.5$

meV since the absorption by the analyzer is negligible. These latter data turn out to be particularly clean, with little contamination scattering.

As noted above, we studied two crystals of $La_{2-x}Sr_xCuO_4$; we label these NTT-30 and NTT-35; the samples were $\sim 2\times 2\times 0.2$ cm^3 in volume with the thin direction along the orthorhombic **b** perpendicular to the CuO_2 planes (**a**$-$**c**). For both crystals the tetragonal-orthorhombic structural phase transition occurred at 265 ± 10 K; from Fig. 3 of Ref. 1 this implies $x=0.11\pm 0.02$, close to, but slightly less than, the chemical analysis value of $x=0.14\pm 0.02$. Our new crystal-growth technique is described elsewhere;[4] as discussed there, this technique produces large single crystals with an 80% Meissner fraction. As a check, the Meissner fraction was measured via both the zero-field and field-cooled susceptibility in fields of order 10 Oe on a piece $6\times 6\times 2$ mm^3 broken off of NTT-35, the sample was found to be at least 80% superconducting with $T_c=10$ K. These data will be discussed in more detail in Ref. 6. We also confirmed directly using a neutron depolarization technique that both samples become superconducting at 10 K. We suspect that this low T_c is due to oxygen vacancies, and, indeed, these presumed vacancies may play an important role in the spin fluctuation spectrum.

Closely similar results were obtained in both samples; however, our data for NTT-30 are much more extensive so we present only those results in this paper. The sample was mounted with the orthorhombic **a** (or **c** because of twinning) axis vertical (see Refs. 1 and 5 for diagrams of the real space lattice) first in a closed cycle refrigerator (12 K $\leq T \leq$ 350 K) and second in a pumped helium cryostat (1.9 K$\leq T \leq$ 20 K). The sample was masked very carefully in order to minimize parasitic peaks from the sample container, multiple scattering, etc. Fortunately, the crystals themselves are of very high quality so that there is little or no contamination from powder lines, flux inclusions, or unreacted material.

Representative scans across the 2D magnetic ridge are shown in Figs. 1 and 2. As discussed extensively in Ref. 1 and 5 these scans are along the direction $(h,h-0.45,0)$ which for $E_i=14.7$ meV has the feature that the outgoing neutron direction $\mathbf{k}_f/|\mathbf{k}_f|$ is along $-\mathbf{b}$, that is, it is always perpendicular to the CuO_2 planes. The two-axis scan then automatically integrates over energy without varying the two-dimensional (2D) momentum transfer $\mathbf{Q}_{2D}$. For the total scattering the energy integration range is from $\sim -kT$ (neutron energy gain) to E_i (energy loss). This is illustrated in the uppermost panel of Fig. 3 which shows an integrated inelastic scan (with $|\Delta E|>0.5$ meV) with the 2D momentum transfer $\mathbf{Q}_{2D}$ held fixed at $1.05\mathbf{a}^*$ and $\mathbf{Q}_\perp = k\mathbf{b}^*$ varied; the scattering geometry is illustrated at the top of Fig. 3. This scan shows a well-defined peak at $\mathbf{Q}_\perp \simeq 0.6\mathbf{b}^*$ at which point $k_f \parallel -\mathbf{b}^*$ for $E_i=14.7$ meV. This verifies that there is a substantial inelastic 2D cross section at 350 K. As we shall discuss later, this is confirmed by direct inelastic measurements.

Figures 1 and 2 show the integrated inelastic ($|\Delta E|>0.5$ meV) quasielastic, ($|\Delta E|<0.5$ meV), and fitted total cross sections for the $(h,h-0.45,0)$ scans across the 2D ridge at a sequence of temperatures. Two features are

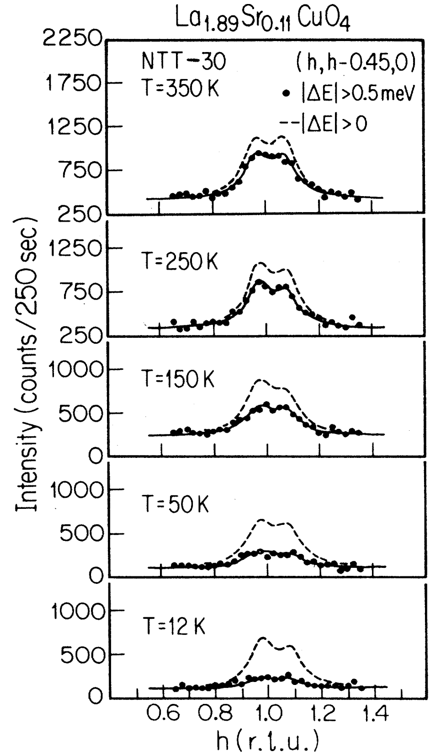

FIG. 1. Integrated inelastic ($|\Delta E|>0.5$ meV) scattering for scans across the magnetic ridge along $(h,h-0.45,0)$; $E_i=14.7$ meV and the collimator configuration is 40′-40′-40′-80′. The solid lines are the result of fits to two displaced 2D Lorentzians as discussed in the text. The dashed lines are the result of the best fits to the total scattering, elastic plus inelastic.

immediately evident. First, the scattering is broad and flat topped with some indication of a two-peaked structure. This incommensurate two-peaked structure was suggested in previous experiments[1] but was not established definitively. Second, the total cross section as measured in this particular cut through reciprocal space varies only weakly with temperature from 350 to 12 K. However, the spin fluctuations change from being predominantly inelastic at 350 K to predominantly quasielastic at 12 K. We confirmed that the integrated intensity at room temperature is identical within the errors ($\sim$20%) to the integrated 2D magnetic cross section for a sample of pure La_2CuO_4 ($T_N=240$ K) measured under identical spectrometer conditions. Since the scattering near $h=1$ comes predominantly from low energies, this implies that the full Cu^{2+} moment or a significant part thereof is preserved in the superconducting samples. Figure 4 shows pure two-axis scans along $(h,h-0.4,0)$ across the ridge at $T=20$ K (normal) and $T=5$ K (superconducting) together with a background scan along $(h,-0.2,0)$. It is evident that any change in the static structure factor, $S(\mathbf{Q})$, between the normal and superconducting states is below our limit of detectability.

Before discussing quantitatively the data in Figs. 1, 2, and 4 we consider further the qualitative features of the low-energy spin fluctuations. The full Q dependence of

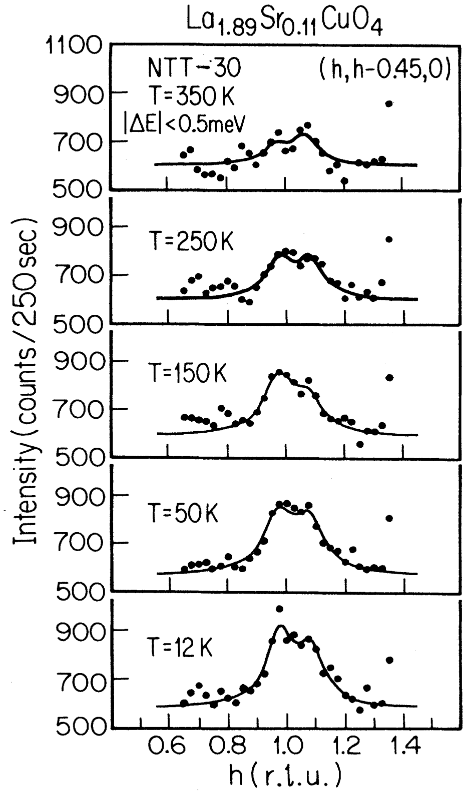

FIG. 2. Three-axis ($|\Delta E| < 0.5$ meV) scans across the magnetic ridge along $(h,h-0.45,0)$; $E_i = 14.7$meV and the collimator configuration is 40′-40′-40′-80′. The solid lines are the results of fits to two displaced 2D Lorentzians with width and positions held fixed at the values determined from fits to the total cross section, elastic plus inelastic.

the quasielastic scattering is experimentally accessible albeit with considerable uncertainty in the background. As is evident in Fig. 2, the quasielastic scattering intensity increases gradually with decreasing temperature. Further, the quasielastic line shape for the $(h,h-0.45,0)$ scan across the ridge is closely similar if not identical to that for the total cross section and thence $S(\mathbf{Q})$. The overall geometry in **Q** space, however, turns out to be quite elaborate. Figure 3 shows quasielastic scans at 12 and 350 K in which $\mathbf{Q}_{2D}$ is held fixed at the peak position, $1.05\mathbf{a}^*$, and the momentum transfer perpendicular to the CuO_2 planes, $\mathbf{Q}_\perp = k\mathbf{b}^*$, is varied. As is evident in Fig. 3, the quasielastic peak intensity exhibits a sinusoidal modulation perpendicular to the CuO_2 sheets at both 12 and 350 K. The period of the modulation is about two La_2CuO_4 unit cells. Thus, even at temperatures as high as 350 K the low-energy spin fluctuations in $La_{1.89}Sr_{0.11}CuO_4$ are fully three dimensional in character. This contrasts markedly with the fluctuations in pure La_2CuO_4 which are essentially 2D above the Néel temperature.[5] Scans with $\mathbf{Q}_\perp \sim 0.5\mathbf{b}^*$ and $\mathbf{Q}_{2D}$ varied typically give either a flat-topped or a double-peaked structure with the incommensurability varying from $\sim 0.05\mathbf{a}^*$ to $\sim 0.2\mathbf{a}^*$ depending on the exact value of $\mathbf{Q}_\perp$. On the other hand, scans of

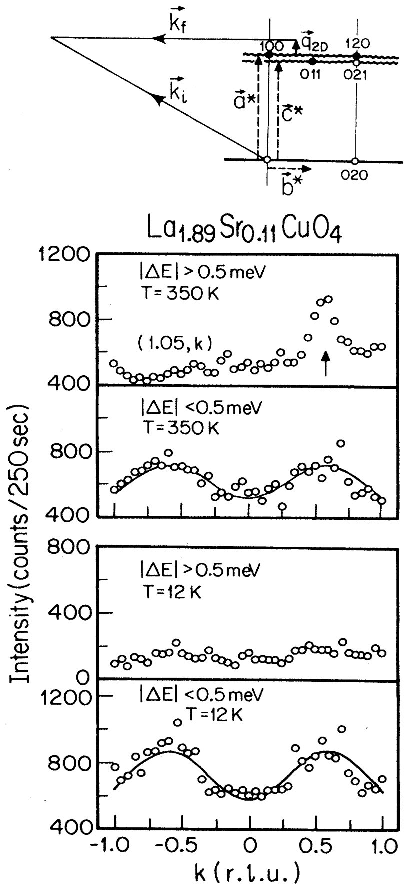

FIG. 3. Top: Superposition of $\mathbf{a}^* - \mathbf{b}^*$ and $\mathbf{c}^* - \mathbf{b}^*$ reciprocal lattice planes together with a representative scattering diagram for $E = 14.7$ meV neutrons. Bottom: Elastic ($|\Delta E| < 0.5$ meV) and integrated inelastic ($|\Delta E| > 0.5$ meV) scans perpendicular the CuO_2 sheets for $\mathbf{Q}_{2D} = 1.05\mathbf{a}^*$. The arrow gives the position at which the outgoing neutron wave vector $\mathbf{k}_f$ is perpendicular the CuO_2 sheets, that is along $-\mathbf{b}^*$.

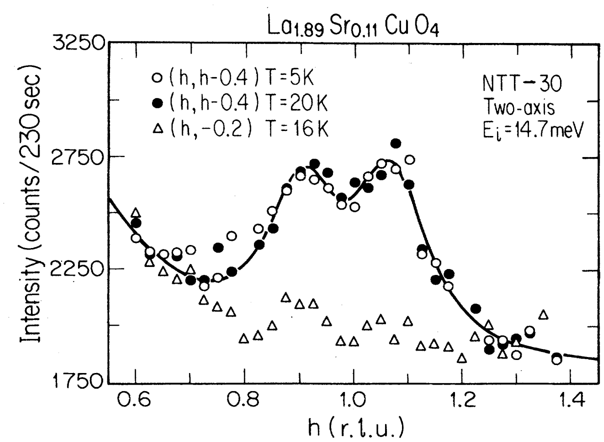

FIG. 4. Pure two-axis scans along $(h,h-0.4,0)$ at $T=5$ and 20 K and along $(h,-0.2,0)$ at $T=16$ K. The spectrometer had one PG filter and no analyzer. The solid line is the result of fits to two displaced 2D Lorentzians together with a background function determined from the $(h,-0.2,0)$ scan.

$\mathbf{Q}_\perp$ at varying $\mathbf{Q}_{2D}$ all give the sinusoidal variation discussed above. Thus, at low temperatures the Cu^{2+} structure factor in superconducting $La_{1.89}Sr_{0.11}CuO_4$ corresponds to a slowly fluctuating ($<10^{-11}$ sec) 3D modulated spin fluid. We note that recent μSR studies[2] on a sample prepared identically to ours indicate that the entire volume freezes magnetically below $T \sim 4$ K. Similar results in $YBa_2Cu_3O_{6.4}$ had been inferred earlier but could not be established definitely.[2]

In order to compare these results with previous measurements[1] we have fitted the data to several simple cross sections. The solid lines in Figs. 1, 2, and 4 are the results of fits to two displaced 2D Lorentzians. Clearly, this simple model works well although it certainly is not unique. For the total scattering, the peak positions, intensities, and width as well as the background were all varied. For the quasielastic and integrated inelastic components the peak positions and widths were fixed at the values determined from the fits to the total scattering and only the intensities and background were allowed to vary. The quasielastic and integrated inelastic components turn out to be well described separately by the parameters characterizing the total cross section. The 2D instantaneous spin-spin correlation length is of order 18 ± 6 Å independent of temperature from 350 to 5 K. The 2D incommensurability from these fits is of order 0.05 $Å^{-1}$ (Fig. 2) to 0.08 $Å^{-1}$ (Fig. 4), although, as noted above, larger values are obtained from quasielastic scans perpendicular to the rod so the exact value of the incommensurability should be treated cautiously. At 350 K the total cross section, which corresponds to an integral from $\sim -kT$ to $+14.7$ meV, is predominantly ($\sim 75\%$) inelastic while at 12 K the $|\Delta E| < 0.5$ meV component accounts for $\sim 75\%$ of the observed scattering. We should note that all of the data reported in Ref. 1 are also well described by the two-Lorentzian line shape. Further, the 2D correlation lengths so-deduced agree well with the average separation of the O^- holes as suggested in Ref. 1.

Finally, as will be discussed in more detail in Ref. 6, we have carried out some preliminary direct inelastic measurements of the spin excitations. The inelastic line shape is closely similar to that obtained in the energy-integrated scans. Further, from both the temperature dependence and the dispersion we have confirmed that the scattering is indeed magnetic rather than lattice dynamical in origin. We have not, however, proven that the quasielastic scattering shown in Figs. 2 and 3 is magnetic and there remains the possibility that it actually arises from complicated multiple-scattering events. However, the continuous trade-off in intensity evident in Fig. 1 between the dynamic and static fluctuations with decreasing temperature as well as the closely similar line shapes is strongly suggestive. Certain theories such as that of Ref. 7 require a gap in the spin excitation spectrum in the superconducting state. Our results seem to contradict these predictions. However, the low value of T_c of 10 K in our samples implies considerable disorder in the CuO_2 planes probably due to oxygen vacancies. It is possible that the quasielastic scattering originates from this disorder. Only future experiments on more perfect samples with T_c near 40 K can remove this ambiguity.

Clearly, the magnetism in these samples of superconducting $La_{1.89}Sr_{0.11}CuO_4$ with $T_c = 10$ K is quite elaborate. The superconductivity occurs in the presence of a 3D-correlated, modulated, slowly fluctuating Cu^{2+} spin fluid; the 2D correlation length is of order 18 ± 6 Å while the 3D correlations are sinusoidal in character with a period of ~ 2 La_2CuO_4 unit cells. It seems clear heuristically that this novel spin state is generated by the O^- holes[8-10] which also carry the supercurrent. We have not succeeded in observing a direct manifestation of the superconductivity in the spin fluctuations. The gradual freezing of the Cu^{2+} spin fluid as the temperature is decreased from 350 to 5 K is, in our view, one of the most remarkable features of our results. Of course, these experiments have also confirmed unambiguously that there is a substantial Cu^{2+} moment is superconducting samples thence strengthening the case for a magnetic mechanism for the superconductivity in the lamellar CuO_2 superconductors.

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