

Observation of incommensurate magnetic correlations at the lower critical concentration for superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.05$)

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(Received 8 April 1999)

Neutron-scattering experiments have been performed on lightly doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ single crystals in both the insulating ($x=0.03,0.04,0.05$) and superconducting ($x=0.06$) regions. Elastic magnetic peaks are observed at low temperatures in all samples with the maximum peak linewidth occurring at the critical concentration $x_c=0.05$. Incommensurate peaks are observed only at $x=0.05$, the positions of which are rotated by 45° in reciprocal space about (π, π) from those observed for $x \geq 0.06$ in the superconducting phase. [S0163-1829(99)50126-4]

The interplay between magnetism and superconductivity has been a central issue in research on high- T_c superconductivity for over a decade. Recently Yamada *et al.*¹ carried out a systematic series of neutron-scattering experiments on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) over a wide range of Sr compositions to study the evolution of the dynamical spin fluctuations in the presence of a varying hole concentration. In these experiments the fluctuations appear as four incommensurate (IC) inelastic magnetic peaks centered on the reciprocal lattice position (π, π) (square lattice notation, unit lattice constant). Indexed on a tetragonal unit cell, the positions of the four IC peaks are $(\frac{1}{2} \pm \delta, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2} \pm \delta)$.² [See Fig. 1(a).] The results of Yamada *et al.*¹ have clarified how the incommensurability δ changes with hole concentration x after the onset of superconductivity above the critical concentration $x_c \sim 0.05$ shown in Fig. 1(a). Motivated by the pioneering work of Tranquada *et al.*³ in which elastic magnetic peaks were observed in Nd-doped LSCO, Suzuki *et al.* and Kimura *et al.*⁴ performed neutron-scattering measurements on $\text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4$ [$T_c(\text{onset})=31$ K] and also found sharp elastic magnetic peaks at these same IC positions with the magnetic transition temperature T_m equal to T_c . Kimura *et al.*⁴ also found that the sharp elastic IC peaks were very weak in a sample with $x=0.10$ and not observable at all in an optimally doped sample with $x=0.15$, implying that the magnetic long-range order exists only in a very narrow concentration range near $x=0.12$. Analogous behavior has been seen in the system $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$. In that case, for hole concentrations $n_h = x + 2y \geq 0.11$, dynamic incommensurate peaks are also observed, albeit at the positions $(\frac{1}{2} \pm \epsilon/2, \frac{1}{2} \pm \epsilon/2)$, that is, rotated by 45° with respect to those in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$. Static order, either short or long range, is also observed at these positions at low temperatures in the

nickelates.⁵ Notably, the Ni system is insulating in both the commensurate and incommensurate magnetic phases.⁵

The magnetic properties of lightly doped ($0.01 < x < 0.07$) LSCO have been studied by various techniques⁶ including neutron scattering,^{7,8} μSR (Refs. 7 and 9), and conventional magnetic measurements.^{10,11} Keimer *et al.*⁸ reported that at temperatures $T \leq 20$ K, $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_4$ exhibits a broad commensurate (C) elastic peak centered at $(\frac{1}{2}, \frac{1}{2})$, which they ascribed to spins freezing into a spin-glass (SG) phase. Chou *et al.*¹⁰ studied the same sample using a superconducting quantum interference device (SQUID) magnetometer and confirmed that the sample indeed exhibited all the features expected for a canonical SG transition at $T_g = 7.2$ K. The same SG behavior is observed in the crystals used in the present study ($x=0.03,0.04,0.05$).¹¹ Niedermayer *et al.*⁹ performed a systematic μSR study over a wide range of x and found a magnetic transition to a SG-like state for $0.02 \leq x \leq 0.10$, which extends well into the superconducting regime.

What is the relationship between the broad C elastic peak at $x \sim 0.04$ observed by Keimer *et al.*⁸ and the sharp IC elastic peaks observed by Kimura *et al.*⁴ that appear to exist only in the vicinity of $x=0.12$? In this paper, we try to develop a connection between these two important regions by performing comprehensive neutron-scattering experiments on single crystals of LSCO with $x=0.03, 0.04, 0.05$, and 0.06 , that bracket the lower critical concentration for superconductivity, $x_c \sim 0.05$. Our most important and surprising result is that in the sample with $x=0.05$, which is insulating at low temperatures, we observe sharp elastic magnetic peaks, albeit at the positions $(\frac{1}{2} \pm \epsilon/2, \frac{1}{2} \pm \epsilon/2)$, that is, like those in insulating $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$ (Ref. 5) rather than those in superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.⁶ Thus, the commensurate-

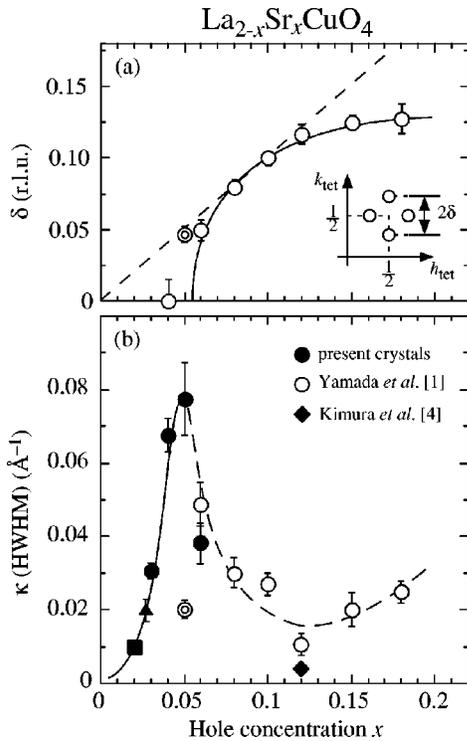


FIG. 1. Hole concentration dependence of (a) the incommensurability δ of the spin fluctuations, and (b) the neutron-scattering linewidth of the magnetic IC or C peaks around $(\frac{1}{2}, \frac{1}{2}, -0.3)$. In (a), the dashed line corresponds to $\delta=x$, whereas the solid line is a guide to the eye. The inset shows the IC peak positions in the superconducting phase. For $x=0.05$, the IC peak positions are rotated, as described in the text, however δ still represents the magnitude of the IC wave vector from $(\frac{1}{2}, \frac{1}{2})$. In (b), the solid and dashed lines are guides to the eye. In both figures, the closed symbols represent the elastic components (Refs. 6 and 8). The open circles correspond to the widths of 2–3.5 meV excitations at $T=T_c$ (Ref. 1). The double circles at $x=0.05$ denote the new IC elastic peaks.

incommensurate transition in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which coincides with the onset of superconductivity, proceeds via a more elaborate route than previously assumed. This manifestly represents a major challenge for all theories of high- T_c superconductivity.

Single crystals of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x=0.03, 0.04, 0.05$, and 0.06 , which were typically 6 mm in diameter and 30 mm in length, were grown by the traveling-solvent floating-zone method. The as-grown crystals were annealed in flowing argon to reduce the excess oxygen. We performed x-ray and neutron-diffraction measurements on powdered and single crystal samples, respectively. The results show the presence of no secondary phases and a good mosaic spread [0.3° – 0.5° full width at half maximum (FWHM)], indicating a high sample quality. Measurements of the lattice constants¹ and the structural phase-transition temperatures T_s (Ref. 6) as well as direct iodometric titration all confirm that the effective x values are essentially the same as the nominal ones.

The magnetic susceptibilities of the $x=0.03, 0.04$, and 0.05 samples were fitted to the canonical model of the SG order parameter. From this we determined T_g to be 6.3, 5.5,

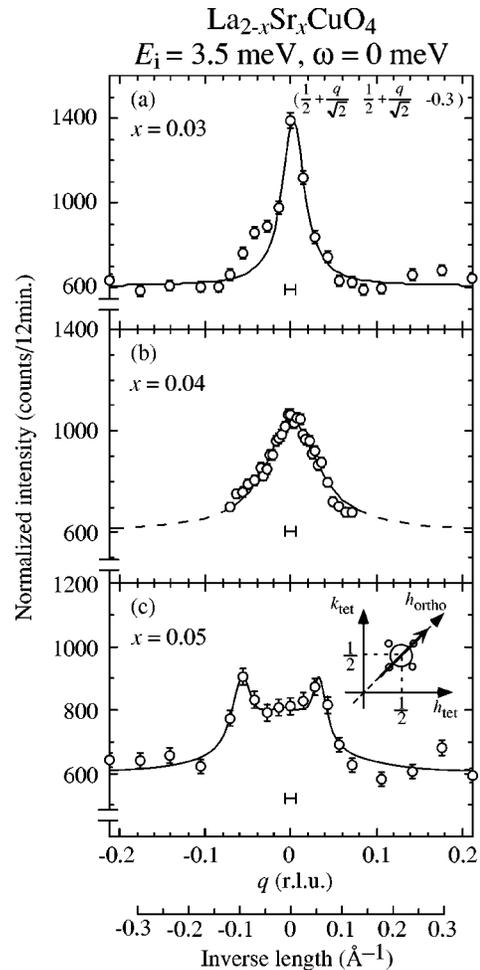


FIG. 2. Elastic peak profiles measured around $(\frac{1}{2}, \frac{1}{2}, -0.3)$ at $T=2$ K using the SPINS spectrometer. We use the $(\frac{1}{2}+q/\sqrt{2}, \frac{1}{2}+q/\sqrt{2}, -0.3)$ notation to allow a direct comparison of δ for $x=0.05$ with that for $x \geq 0.06$ in the tetragonal unit cell. The solid curves are the results of least squares fits assuming a single Lorentzian function for $x=0.03$ and 0.04 , and a triple Lorentzian function (two sharp incommensurate peaks and one broad commensurate peak) for $x=0.05$. The small horizontal bars indicate the instrumental resolution q width.

and 5.0 K for $x=0.03, 0.04$, and 0.05 , respectively. Combined with the T_g values of the powdered samples,¹¹ we have constructed a universal curve for T_g vs x . Using this universal curve, we infer that the actual hole concentration of the $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_4$ single crystal studied by Keimer *et al.*⁸ and Chou *et al.*¹⁰ is closer to $n_h=0.027$. In contrast to the other crystals, the $x=0.06$ sample shows superconductivity below $T_c=12$ K.

The neutron-scattering experiments were carried out on the SPINS cold neutron triple-axis spectrometer located at the NIST Center for Neutron Research, and on the HER cold neutron triple-axis spectrometer located at the JAERI JRR-3M reactor. Pyrolytic graphite crystals were used to monochromate and analyze the neutron energies, and a Be filter was used to remove contamination from higher-order neutron energies. The energy resolution was about 0.25 meV FWHM for both spectrometers. The crystals were oriented so as to give access to either the (hhl) or (hko) zone. Throughout this paper we will index reflections using the

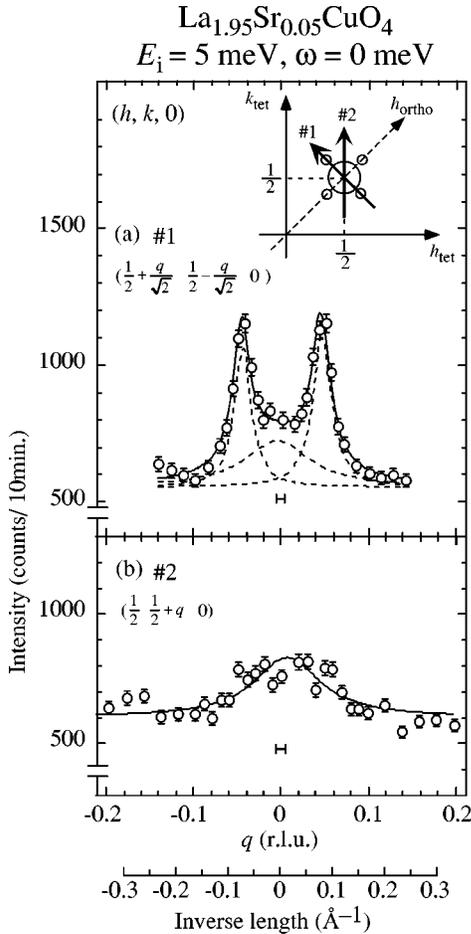


FIG. 3. Elastic peak profiles around $(\frac{1}{2}, \frac{1}{2})$ in the $(h k 0)$ zone measured in the $x=0.05$ sample at $T=2$ K using the HER spectrometer. In (a), we use the $(\frac{1}{2} + q/\sqrt{2}, \frac{1}{2} - q/\sqrt{2}, 0)$ notation. The solid lines are the results of least squares fits assuming a triple Lorentzian function for (a), and a single Lorentzian function for (b). The dashed lines in (a) show the individual peak components of the triple Lorentzian function. The small bars indicate the instrumental resolution q width.

tetragonal $I4/mmm$ crystallographic structure.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ exhibits superconductivity for $x \geq 0.06$. This concentration range is also where inelastic magnetic peaks appear at the incommensurate reciprocal lattice positions shown in Fig. 1(a).¹ For x less than the critical concentration $x_c \sim 0.05$ an elastic peak appears at the commensurate position $(\frac{1}{2}, \frac{1}{2})$ as shown in Figs. 2(a) and 2(b). We plot in Fig. 1(b) the half width at half maximum (HWHM) of the elastic and inelastic peaks. These widths are related to, but technically distinct from, the instantaneous inverse correlation length κ which is measured in an energy integrating neutron experiment.^{6,8} As may be seen in Fig. 1(b), the line widths are sharply peaked at x_c .

To examine the elastic peaks below x_c in more detail, we measured the peak profile for each crystal in the $(h h l)$ zone. As shown in Fig. 2, the C peaks at $T=2$ K for $x=0.03$ and 0.04 are reasonably well fitted with a single Lorentzian convoluted with the instrumental resolution function. For the $x=0.03$ sample there is a small shoulder visible on the low- Q side due to the orthorhombic splitting. We also confirmed that the C peak for $x=0.04$ shows only a weak l

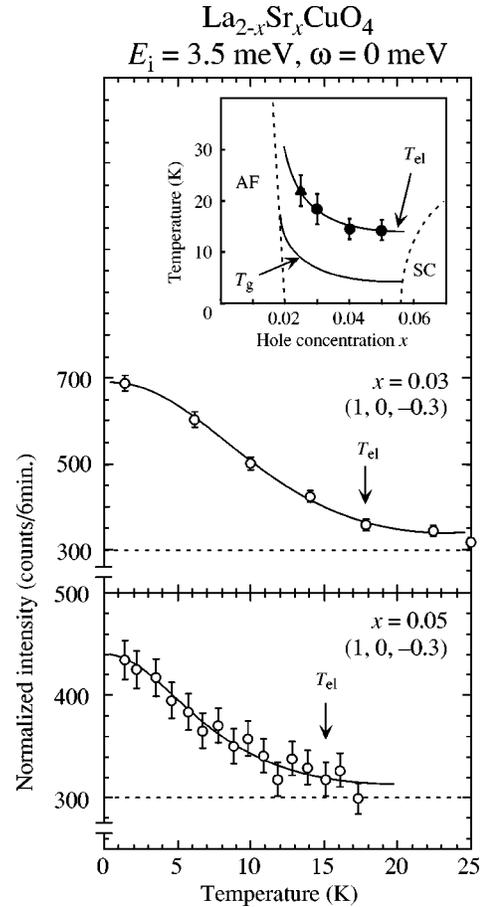


FIG. 4. Temperature dependence of the elastic peak intensity measured at $(\frac{1}{2}, \frac{1}{2}, -0.3)$. The dashed lines indicate background levels. The solid lines are guides to the eye. The estimated onset temperatures of the elastic peak are indicated by arrows. The universal curves for T_g and T_{el} are shown in the inset. The triangle in the inset represents the datum of Keimer *et al.* (Ref. 8).

dependence, indicating a predominantly two-dimensional (2D) magnetic character. To our surprise, however, the peak profile suddenly changes at $x=0.05$. Two new IC peaks appear in addition to the C one, all of which can be fitted to a sum of three Lorentzians. As may be inferred from the scan trajectory shown in the inset of Fig. 2(c), these new IC elastic peaks appear to be rotated by 45° in reciprocal space about $(\frac{1}{2}, \frac{1}{2})$ from those in $\text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4$. Moreover, they resemble the elastic peaks found in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$.⁵ None of the IC peaks, nor the C peak, shows any significant l dependence for $x=0.05$, that is, the scattering is purely 2D.

To verify the reciprocal space positions of these new IC peaks, we remounted the $x=0.05$ sample in the $(h k 0)$ zone. In this case, the long axis of the resolution ellipse is along the l direction, thence giving a cleaner signal from the incommensurate peaks. As is clearly shown in Fig. 3, the elastic signal consists of one broad C peak and two sharp IC peaks, the positions of which are indeed rotated by 45° about $(\frac{1}{2}, \frac{1}{2})$. The peaks are well fitted using a superposition of three Lorentzians for scan No. 1, and a single Lorentzian for scan No. 2. Here we define the incommensurability δ for $x=0.05$ as the distance from the IC peak position to $(\frac{1}{2}, \frac{1}{2})$ in reciprocal lattice units (r.l.u.) using the tetragonal notation to

maintain consistency with the prior definition of δ for $x \geq 0.06$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+y}$. The results so obtained are plotted in Fig. 1. The presence of a commensurate peak in the $x=0.05$ sample may be due to a slight inhomogeneity in the Sr concentration. We also carried out some brief elastic measurements on the $x=0.06$ crystal. We find weak and somewhat broad elastic scattering at low temperatures at the q positions which are identical to those shown for the inelastic scattering in Fig. 1(a). Thus, the new IC peaks observed in the $x=0.05$ sample are confined to a very narrow range in Sr concentrations, just at the insulator to superconductor transition.

The temperature dependences of the peak intensities for $x=0.03$ and 0.05 at $(\frac{1}{2}, \frac{1}{2}, -0.3)$ are shown in Fig. 4. Estimates for the onset temperatures T_{el} , where the elastic components first appear, are indicated by arrows. We have drawn a universal curve for the x dependence of T_g using all of the data available at present, and this is shown in the inset of Fig. 4. The “ $x=0.04$ ” sample of Keimer *et al.*⁸ actually sits at $x_{eff}=0.027$ on this universal curve as well as on the associated curves for the HWHM [see Fig. 1(b)] and T_{el} (see the inset of Fig. 4) as we already mentioned.

Our results show that fundamental changes in the magnetic properties of LSCO take place at $x_c=0.05$. This is most clearly demonstrated by the sudden appearance of new IC satellite peaks that are rotated by 45° with respect to those that exist for $x \geq 0.06$ about $(\frac{1}{2}, \frac{1}{2})$ at this critical concentration. There are two possible interpretations of this new diffraction pattern. The first is that $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ has a diagonal stripe pattern¹² identical to that in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$. In the notation where the peaks are at $(\frac{1}{2} \pm \epsilon/2, \frac{1}{2} \pm \epsilon/2)$, the measured incommensurability corresponds to $\epsilon \approx 0.06 \pm 0.005$,¹³ close to, but slightly larger than $n_h=0.05$. We note that $\epsilon \approx n_h$ is also observed in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$ in the incommensurate phase ($x \geq 0.11$).⁵ The second is that the stripes form a square grid; this will cause the magnetic but

not the charge peaks to rotate by 45° . Observations of either the associated charge peaks or a strong imbalance in the magnetic peak intensities would choose unambiguously between the diagonal stripe and grid models.

According to the μSR study by Niedermayer *et al.*,⁹ the dependence of T_g on hole concentration is almost the same as that of our crystals (shown in the inset of Fig. 4). However, they observed no clear signals at T_{el} . A possible explanation for this fact is that the observation time constant of μSR is much longer than that of neutron scattering. Thus, the “static” antiferromagnetic correlations reported here might exist instantaneously and be observable only by neutron scattering. If this speculation is correct, the elastic signals must be *quasielastic* rather than truly elastic.

We thank V. J. Emery, Y. Fujii, H. Fukuyama, S. Kawarazaki, P. A. Lee, K. Machida, K. Nemoto, M. Onodera, and J. M. Tranquada. The present work was supported by the U.S.-Japan Cooperative Research Program on Neutron Scattering. The work at Tohoku has been supported by a Grant-in-Aid for Scientific Research of Monbusho and the Core Research for Evolutional Science and Technology (CREST) Project sponsored by the Japan Science and Technology Corporation. The work at MIT was supported by the NSF under Grant No. DMR97-04532 and by the MRSEC Program of the National Science Foundation under Award No. DMR98-08941. The work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-98CH10886, Division of Material Science, U.S. Department of Energy. SPINS is supported by the NSF under Grant No. DMR94-23101.

Note added in proof. In recent work, we have found that there is a distinct imbalance in the relative intensities of the four incommensurate peaks. Specifically, our new data imply that $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ has a diagonal stripe structure. The two peaks characterizing the stripe structure appear as four incommensurate peaks because of the orthorhombic twin population.

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¹K. Yamada *et al.*, Phys. Rev. B **57**, 6165 (1998).

²S.-W. Cheong *et al.*, Phys. Rev. Lett. **67**, 1791 (1991).

³J. M. Tranquada *et al.*, Phys. Rev. B **54**, 7489 (1996).

⁴T. Suzuki *et al.*, Phys. Rev. B **57**, 3229 (1998); H. Kimura *et al.*, *ibid.* **59**, 6517 (1999).

⁵S. M. Hayden *et al.*, Phys. Rev. Lett. **68**, 1061 (1992); for a review, see J. M. Tranquada, Ferroelectrics **177**, 43 (1996).

⁶M. A. Kastner *et al.*, Rev. Mod. Phys. **70**, 897 (1998).

⁷B. J. Sternlieb *et al.*, Phys. Rev. B **41**, 8866 (1990).

⁸B. Keimer *et al.*, Phys. Rev. B **46**, 14 034 (1992).

⁹Ch. Niedermayer *et al.*, Phys. Rev. Lett. **80**, 3843 (1998).

¹⁰F. C. Chou *et al.*, Phys. Rev. Lett. **75**, 2204 (1995).

¹¹S. Wakimoto *et al.* (unpublished).

¹²An early theoretical prediction that a diagonal stripe structure is stabilized at low hole concentrations was given by M. Kato *et al.*, J. Phys. Soc. Jpn. **59**, 1047 (1990).

¹³Note that ϵ is larger than δ plotted in Fig. 1(a) by a factor of $\sqrt{2}$.