Evidence for stripe correlations of spins and holes in copper oxide superconductors

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ONE of the long-standing mysteries associated with the high-temperature copper oxide superconductors concerns the anomalous suppression[1] of superconductivity in $La_{2-x}Ba_xCuO_4$ (and certain related compounds) when the hole concentration x is near $\frac{1}{8}$. Here we examine the possibility that this effect is related to dynamical two-dimensional spin correlations, incommensurate with the crystal lattice, that have been observed in $La_{2-x}Sr_xCuO_4$ by neutron scattering[2–4]. A possible explanation for the incommensurability involves a coupled, dynamical modulation of spin and charge in which antiferromagnetic 'stripes' of copper spins are separated by periodically spaced domain walls to which the holes segregate[5–9]. An ordered stripe phase of this type has recently been observed in hole-doped La_2NiO_4 (refs 10–12). We present evidence from neutron diffraction that in the copper oxide material $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, with $x = 0.12$, a static analogue of the dynamical stripe phase is present, and is associated with an anomalous suppression of superconductivity[13,14]. Our results thus provide an explanation of the '$\frac{1}{8}$' conundrum, and also support the suggestion[15] that spatial modulations of spin and charge density are related to superconductivity in the copper oxides.

To clarify the nature of the correlations with which we are concerned, we begin by describing the stripe modulation that has been observed[10–12] in nickel oxide analogues of the copper oxides, $La_2NiO_{4.125}$ and $La_{1.8}Sr_{0.2}NiO_4$. The spatial correlations of spins and holes in an NiO_2 plane are illustrated schematically in Fig. 1*a*. The magnetic moments on Ni atoms are locally antiferromagnetic. For a two-dimensional square lattice, antiferromagnetic order is characterized by the wave vector $(\frac{1}{2}, \frac{1}{2})$ (where we specify coordinates in terms of reciprocal lattice units, $2\pi/a$). In the case of the modulated spin structure, the characteristic wave vectors are $(\frac{1}{2} \pm \varepsilon, \frac{1}{2} \pm \varepsilon)$ and $(-\frac{1}{2} \pm \varepsilon, \frac{1}{2} \pm \varepsilon)$, where, for the case shown, $\varepsilon = \frac{1}{8}$. One might imagine that higher harmonics should be important for describing the spin structure; however, even for the extreme case of sharp domain walls shown in the figure, Fourier analysis shows that the only other distinct harmonic is the third [wave vectors $(\frac{1}{2} \pm 3\varepsilon, \frac{1}{2} \pm 3\varepsilon)$], and its intensity is only 3% of the first harmonic. The experimentally observed third-harmonic intensities are somewhat smaller than this, indicating a more sinusoidal modulation of the domains.

The period of the charge modulation is only half that of the spins, and as a result corresponding diffraction peaks appear at second-harmonic positions. Of course, the charge distribution cannot be detected directly by neutrons; instead, we measure the modulation of atomic positions associated with the charge modulation (a charge-density wave). The characteristic three-dimensional wave vectors for the atomic displacements are $(h, k, l) = (\pm 2\varepsilon, 0, 1)$. The requirement that $l = 1$ is related to the presence of two NiO_2 layers per unit cell, and indicates that the displacement pattern in one layer is exactly opposite to that in the layer just above (and below) it. This result is consistent with a staggering of the hole stripes from one layer to the next, as one would expect because of Coulomb repulsion. A quantitative analysis[12] of the observed superlattice intensities measured in the oxygen-doped crystal has verified that the positions of the Ni and O atoms in the planes are sinusoidally modulated along the direction perpendicular to the stripes, as expected for a charge-density wave. Although it is not possible to infer the charge distribution directly from the atomic displacements, the observations are generally consistent with recent multiband Hubbard model calculations by Zaanen and Littlewood[16].

The spin and hole ordering in the nickel oxides described above occurs for temperatures near 100 K. A striking feature of the ordering is its cooperative nature: the charge and spin order parameters show similar temperature dependences[10,11]. The ordered magnetic moments are found to be quite large, with a maximum moment (in the oxygen-doped crystal[12]) of approximately 85% of that found in the undoped antiferromagnetic-insulator phase. Because a hole has its own magnetic moment which will tend to couple to a Ni moment in a way that reduces the ordered value, the large observed moments indicate that the hole density is strongly modulated, as assumed in the domain-wall/stripe picture. The localization of the holes in domain walls increases the kinetic energy of the holes, while decreasing the potential energy of the Ni spins. The competition between these energies drives the density modulation.

What has the above to do with the copper oxides? After all, the nickel oxides remain insulating up to rather high dopant concentrations. One reason for considering a connection comes from mean-field analyses of the single-band Hubbard model[5–7], a simple model believed to contain the basic physics of a CuO_2 plane. If electron–electron interactions are assumed strong and spatial modulation of the spin and charge densities is allowed, stripe phases involving charged domain walls are commonly found. Another reason is the observation of incommensurate magnetic peaks in inelastic neutron scattering studies[2–4] of super-

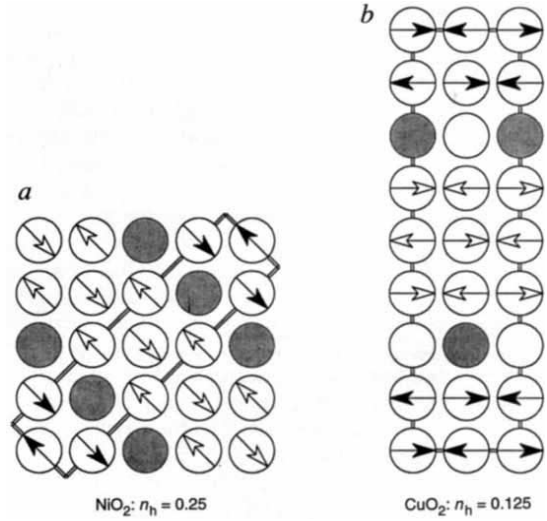

FIG. 1 *a*, Idealized diagram of the spin and charge stripe pattern within a NiO_2 plane observed in hole-doped La_2NiO_4 with a hole density of $n_h = \frac{1}{4}$. *b*, Hypothesized stripe pattern in a CuO_2 plane of hole-doped La_2CuO_4 with $n_h = \frac{1}{8}$. In both, only the metal atoms are represented; the oxygen atoms, which surround the metal sites in a square planar array (as shown in Fig. 2), have been omitted. Arrows indicate the orientation of magnetic moments on metal atoms, which are locally antiparallel; the spin direction rotates by 180° (relative to a simple antiferromagnetic structure) on crossing a domain wall, as emphasized by the change in filling of the arrow heads. The doubled lines outline the magnetic unit cell in each case. Holes are located at the anti-phase domain boundaries, which are indicated by the rows of circles without arrows. A filled circle denotes the presence of one hole, centred on a metal site. For the present analysis, the hole density is assumed to be uniform along a domain wall; the ordering of holes along stripes suggested in *b* has not been tested experimentally, but serves as a reminder that the hole per Cu ratio is $\frac{1}{2}$.

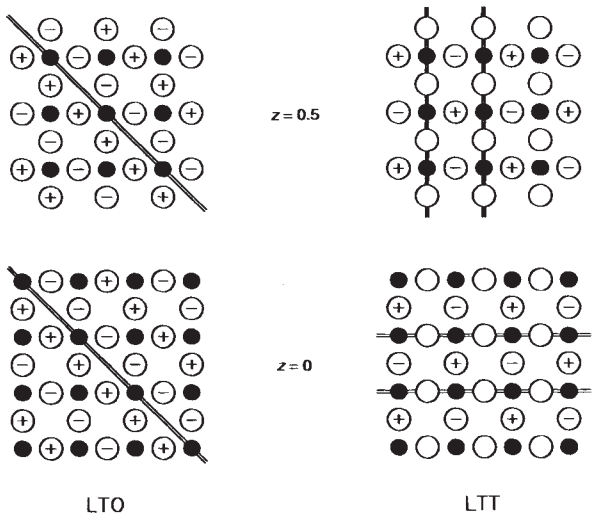

FIG. 2 Displacement patterns within the two CuO_2 layers of a unit cell for the LTO and LTT structures. Open (solid) circles represent oxygen (copper) atoms. The oxygen atoms are displaced out of the plane (+ or −) by local rotations of square planar CuO_4 units about tilt axes shown by the doubled lines. In the LTT structure the tilt axes rotate by 90° from $z=0$ to $z=0.5$, where z is the height along the c axis in lattice units.

conducting $La_{2-x}Sr_xCuO_4$. Those peaks are characterized by the two-dimensional wave vectors $(\frac{1}{2}\pm\varepsilon, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}\pm\varepsilon)$ with $\varepsilon\approx x$ (previous authors[2-4] have used the parameter $\delta=2\varepsilon$ to describe the splitting). Although no static component is observed, those peaks are consistent with instantaneous correlations of the type shown in Fig. 1*b*, with horizontal, rather than diagonal, domain walls. Besides the orientation of the stripes, another difference from the nickel oxides is the hole concentration in the domain walls, corresponding to only one hole for every two Cu sites. This constraint conflicts with the strong-interaction mean-field analyses, which predict[7] one hole per site ($\varepsilon=\frac{1}{2}x$), and led initially to rejection[2] of the stripe interpretation. (A related problem is that the domain wall solutions are insulating[7].) An alternative approach[17-19] that assumes weak correlations leads to incommensurate spin modulations with a period determined by the shape and size of the Fermi surface. Suitable tuning of the band structure can yield agreement with the neutron observations[18-19]; however, the weak-correlation picture would not be consistent with a strong modulation of the charge and spin densities, such as the existence of a static segregation of holes into domain walls in lightly-doped La_2CuO_4, as inferred from a study of bulk susceptibility[20].

If one believes that charge and spin stripe correlations exist in the copper oxides, where might one look for corroborating evidence? It has been suggested (ref. 15 and J. Zaanen, personal communication) that partial substitution of Zn for Cu, which is known to suppress superconductivity, might also pin domain walls, leading to static correlations; however, disorder would tend to make them difficult to detect. Instead, we have chosen to investigate whether stripe order might be associated with the anomalous suppression of superconductivity at a dopant concentration near $x=\frac{1}{8}$ first observed[1] in $La_{2-x}Ba_xCuO_4$. Studies of this and related copper-oxide systems have established that the suppression phenomenon requires, in addition to the unique hole concentration[13,21,22], a distortion of the lattice from the usual low-temperature orthorhombic (LTO) to the low-temperature tetragonal (LTT) structure[13,23,24]. The LTT phase can be stabilized in $La_{2-x}Sr_xCuO_4$ by partial substitution of Nd for La[13], with the width (in x) of the suppression anomaly increasing at higher Nd concentrations[24]. The fact that the suppression occurs when the hole concentration is close to a simple fraction suggests that a commensurability effect is involved, and commensurate pinning of a striped phase could yield long-range order. Also suggestive is the observation of static magnetic correlations in $La_{1.875}Ba_{0.125}CuO_4$ by muon spin-rotation measurements[25,26].

A comparison of the LTO and LTT structures (Fig. 2) makes it clear why the latter phase might be especially favourable for pinning a horizontal stripe phase. The atomic displacements in the LTO structure form a diagonal pattern, whereas the pattern of displacements is horizontal (or vertical) in the LTT case. Thus horizontal charge stripes would tend to be pinned by the lattice potential in the LTT, but not in the LTO, phase.

Our recent neutron scattering study confirms this conjecture. A piece (~0.1 cm^3) of a $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ single crystal (the transport properties of which were reported previously[14]) was studied by neutron diffraction using triple-axis spectrometers at the High Flux Beam Reactor located at Brookhaven National Laboratory. The crystal was initially mounted in a cryostat with the [001] axis vertical, so that the $(hk0)$ zone of reciprocal space could be probed (Fig. 3*a*). In a scan along $(\frac{1}{2}, \frac{1}{2}+q, 0)$ at a temperature of 11 K (Fig. 3*b*), peaks are clearly observed at $|q|=\varepsilon=0.12$. (The neutron wavelength had to be tuned to minimize multiple scattering at $q=0$, a small remnant of which is visible in the figure.) These peaks are very close to the commensurate positions ($\varepsilon=\frac{1}{8}$) that we expect for magnetic reflections if the Cu spins order in the horizontal stripe pattern shown in Fig. 1*b*. Also, ε is consistent with the values observed in the inelastic magnetic scattering studies[2-4] of $La_{2-x}Sr_xCuO_4$. Third-harmonic peaks are not and should not be detectable in the present experiment (because of the signal-to-noise level), so we cannot distinguish between relatively sharp domain walls and broader density-wave modulations.

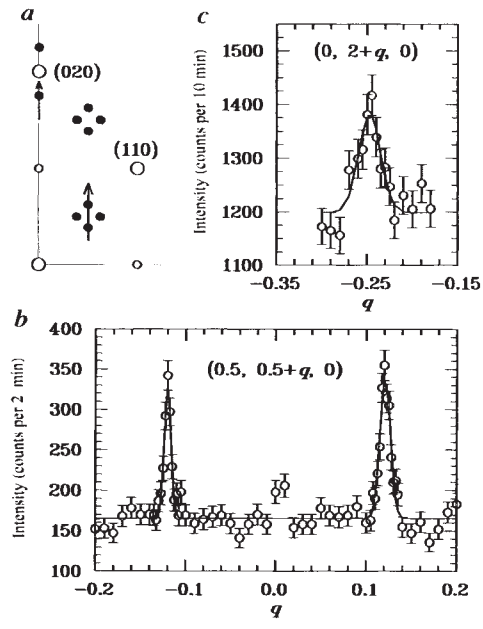

FIG. 3 Scans of superlattice peaks consistent with the proposed spin and charge stripes, in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ at 11 K. *a*, Diagram of the $(hk0)$ zone of reciprocal space. Open circles indicate locations of Bragg peaks for the LTT structure; solid circles denote spin- and charge-ordering superlattice peaks. Arrows indicate the regions scanned. *b*, Scan along $(\frac{1}{2}, \frac{1}{2}+q, 0)$ through the $(\frac{1}{2}, \frac{1}{2}\pm\varepsilon, 0)$ peaks measured with a neutron energy of 13.9 meV. The small peak width indicates that the in-plane correlation length is greater than 150 Å. *c*, Scan along $(0, 2+q, 0)$ through the $(0, 2-2\varepsilon, 0)$ peak using 14.7-meV neutrons. The lines in *b* and *c* are the result of least-squares fits to gaussian peak shapes plus a flat background.

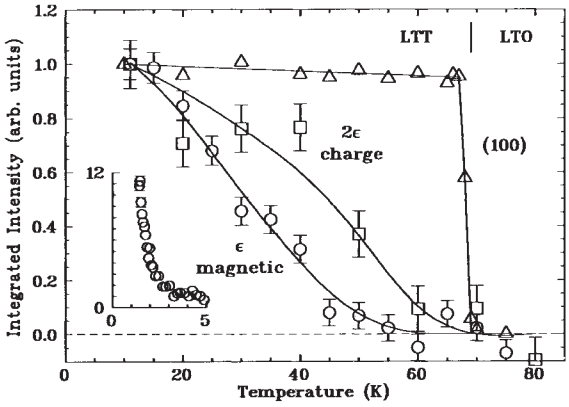

FIG. 4 Temperature dependence of superlattice peak intensities, normalized at 11 K, measured in $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$. Results shown for the magnetic $(\frac{1}{2}, \frac{1}{2}-\varepsilon, 0)$ (circles), charge-related $(0, 2-2\varepsilon, 0)$ (squares) and (1, 0, 0) (triangles). The (1, 0, 0) peak is allowed in LTT but not LTO. The lines are guides to the eye. Inset, temperature dependence of the magnetic peak intensity below 5 K.

The search for nuclear superlattice peaks associated with the hole stripes required further thought. We had initially expected, by analogy with the nickel oxides, that the characteristic wave vectors would be $(\pm 2\varepsilon, 0, 1)$, with $\varepsilon = \frac{1}{8}$; however, a search of such positions gave a negative result. Examination of Fig. 2 reveals why. If the stripes are truly pinned by the atomic displacement pattern within a layer, then they must rotate by 90° from one layer to the next to follow the LTT distortion pattern. Because of the degeneracy in positioning the spin and charge stripes within a plane, and a weak interaction between neighbouring orthogonal stripe layers, we should not expect the stripe pattern to exhibit strong correlations along the c axis. As a result, the scattering from the stripes should be essentially two-dimensional in character, with the modulation wave vectors $(\pm 2\varepsilon, 0, l)$ for the vertical stripe layers and $(0, \pm 2\varepsilon, l)$ for the horizontal stripe layers. After working through these arguments, we were able to locate the $(0, 2-2\varepsilon, 0)$ peak shown in Fig. 3*c*. The intensity of the observed peak is $\sim 10^{-6}$ times that of the strong (020) nuclear reflection.

These results led us to reinvestigate the magnetic scattering. In the process, we discovered a strong increase in the magnetic peak intensity below 3 K (Fig. 4 inset) due to ordering of the Nd moments and the development of very weak correlations between next-nearest-neighbour layers (nearest-neighbour layers remain uncorrelated), as determined from an analysis of the intensity variation of the magnetic scattering as a function of the momentum transfer perpendicular to the planes. The data and analysis will be presented elsewhere.

The temperature dependences of the magnetic (ε) and charge (2ε) peaks are plotted in Fig. 4. Although the magnetic peaks decrease faster than the charge peaks, both types of order disappear at or before the LTT–LTO structural transition at 70 K is reached. The disappearance of the static order either at or before reaching the LTT–LTO transition is consistent with our picture, as the LTT structure favours, but is not induced by, the stripe order. The difference in the temperature dependences of the static spin and charge order parameters is similar to that observed[11] in $La_{1.8}Sr_{0.2}NiO_4$.

Although further studies are needed to verify our interpretation of the second-harmonic peaks, both the similarities to and differences from the nickel oxides make a strong case for the existence of static spin and charge stripe order in our copper-oxide crystal. Accepting this point, it is then reasonable to assume that dynamical stripe correlations exist in the LTO phase. Pinning of the stripes in the LTT phase is associated with an increase in resistivity[14] and the suppression of superconductivity.

The implications of our results go well beyond resolution of the long-standing '$\frac{1}{8}$ problem'[1,13,21–24]. The results appear to be consistent with the ideas of frustrated phase separation discussed by Emery and Kivelson[8,9,15] in which the long-range part of the Coulomb force (which is assumed to be screened in the Hubbard model) plays an important role. They have suggested that correlated fluctuations of hole-rich and hole-poor regions within CuO_2 planes might explain many of the anomalous normal-state properties of the layered copper oxides. Further theoretical work would be required to give a quantitative explanation for the observed stripe correlations, and to understand whether and how they may be related to superconductivity. Experimentally, it is of interest to study how such charge and spin modulations might be realized in other copper-oxide families. For example, the inelastic magnetic scattering in metallic $YBa_2Cu_3O_{6+x}$ is found to be commensurate rather than incommensurate; nevertheless, evidence for dynamically correlated antiferromagnetic clusters with a characteristic size has been reported in a recent neutron scattering study[27] of $YBa_2Cu_3O_{6.6}$. In any case, our evidence for spin and charge stripe correlations suggests their importance in the copper oxides and a connection with superconductivity. □

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1. Moodenbaugh, A. R., Xu, Y., Suenaga, M., Folkerts, T. J. & Shelton, R. N. *Phys. Rev.* B**38**, 4596–4600 (1988).
2. Cheong, S. W. *et al. Phys. Rev. Lett.* **67**, 1791–1794 (1991).
3. Mason, T. E., Aeppli, G. & Mook, H. A. *Phys. Rev. Lett.* **68**, 1414–1417 (1992).
4. Thurston, T. R. *et al. Phys. Rev.* B**46**, 9128–9131 (1992).
5. Schulz, H. J. *J. Phys. (Paris)* **50**, 2833–2849 (1989).
6. Zaanen, J. & Gunnarson, O. *Phys. Rev.* B**40**, 7391–7394 (1989).
7. Poilblanc, D. & Rice, T. M. *Phys. Rev.* B**39**, 9749–9752 (1989).
8. Emery, V. J. & Kivelson, S. A. *Physica* C**235–240**, 189–192 (1994).
9. Kivelson, S. A. & Emery, V. J. in *Strongly Correlated Electronic Materials: The Los Alamos Symposium 1993* (eds. Bedell, K. S. *et al.*) 619–656 (Addison-Wesley, Reading, MA, 1994).
10. Tranquada, J. M., Buttrey, D. J., Sachan, V. & Lorenzo, J. E. *Phys. Rev. Lett.* **73**, 1003–1006 (1994).
11. Sachan, V., Buttrey, D. J., Tranquada, J. M., Lorenzo, J. E. & Shirane, G. *Phys. Rev.* B**51**, 12742–12746 (1995).
12. Tranquada, J. M., Lorenzo, J. E., Buttrey, D. J. & Sachan, V. *Phys. Rev.* B (in the press).
13. Crawford, M. K. *et al. Phys. Rev.* B**44**, 7749–7752 (1991).
14. Nakamura, Y. & Uchida, S. *Phys. Rev.* B**46**, 5841–5844 (1992).
15. Emery, V. J. & Kivelson, S. A. *Physica* C**209**, 597–621 (1993).
16. Zaanen, J. & Littlewood, P. B. *Phys. Rev.* B**50**, 7222–7225 (1994).
17. Bulut, N., Hone, D., Scalapino, D. J. & Bickers, N. E. *Phys. Rev. Lett.* **64**, 2723–2726 (1990).
18. Lu, J. P., Si, Q., Kim, J. H. & Levin, K. *Phys. Rev. Lett.* **65**, 2466–2469 (1990).
19. Littlewood, P. B., Zaanen, J., Aeppli, G. & Monien, H. *Phys. Rev.* B**48**, 487–498 (1993).
20. Cho, J. H., Chou, F. C. & Johnston, D. C. *Phys. Rev. Lett.* **70**, 222–225 (1993).
21. Maeno, Y., Kakehi, N., Kato, M. & Fujita, T. *Phys. Rev.* B**44**, 7753–7756 (1991).
22. Koike, Y., Kawaguchi, T., Watanabe, N., Noji, T. & Saito, Y. *Solid St. Commun.* **79**, 155–158 (1991).
23. Axe, J. D. *et al. Phys. Rev. Lett.* **62**, 2751–2754 (1989).
24. Büchner, B. *et al. J. Low Temp. Phys.* **95**, 285–291 (1994).
25. Luke, G. M. *et al. Physica* C**185–189**, 1175–1176 (1991).
26. Kumagai, K. *et al. Physica* C**185–189**, 913–914 (1991).
27. Sternlieb, B. J., Tranquada, J. M., Shirane, G., Sato, M. & Shamoto, S. *Phys. Rev.* B**50**, 12915–12919 (1994).

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