Two-Dimensional Antiferromagnetic Quantum Spin-Fluid State in La_2CuO_4

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Elastic, quasielastic, and inelastic neutron scattering measurements in La_2CuO_4 reveal novel two-dimensional antiferromagnetic behavior. At high temperatures the spins are ordered instantaneously over long distances two dimensionally but there is no measurable time-averaged staggered moment. The energy scale of the spin fluctuations is large, corresponding to an effective dispersion of $\gtrsim 0.4$ eV Å. The relevance to the high-temperature superconductivity in this class of materials is noted.

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It is broadly viewed that the magnetism may play a central role in the high-temperature superconductivity[1] in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ families of materials.[2] Further, especially in the La_2CuO_4 system, the magnetism is expected to be highly two dimensional in character by analogy to other well-studied isostructural magnetic materials such as K_2NiF_4 and K_2MnF_4.[3] Three-dimensional (3D) antiferromagnetic ordering with Néel temperatures varying between 50 and $\simeq 300$ K and moments between $0.2\mu_B$ and $0.5\mu_B$ has been observed in $La_2CuO_{4-\delta}$.[4] Both the Néel temperature and the moment seem to be sensitive to the oxygen content δ and inadvertent dopants. However, no clear evidence has emerged for the expected two-dimensional (2D) character of the magnetism. This is especially puzzling given the lamellar nature of the La_2CuO_4 structure and the highly directional bonding in the CuO_2 planes.

In this paper we report a neutron scattering study of the magnetic correlations in single-crystal La_2CuO_4. These measurements reveal novel two-dimensional antiferromagnetic behavior. Specifically, we find in a crystal with $T_N = 195$ K that at 300 K the spins are ordered two dimensionally *instantaneously* over distances exceeding 200 Å. However, there is no time-averaged staggered moment in spite of the fact that the energy scale for the correlations is remarkably large, corresponding to an effective dispersion of $\gtrsim 0.4$ eV Å. This behavior is quite unlike that seen in previously studied 2D magnets such as K_2NiF_4.[3] We label this novel 2D magnetic state a *quantum spin-fluid* (QSF) state; it is a fluid because the structure factor is entirely dynamical in character. The large energy scale for the magnetic coupling gives credence to models of the superconductivity which rest on magnetic interactions for the pairing.[2]

The experiments were carried out on the H7 triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor. Graphite monochromator, analyzer, and filters were employed. The neutron energies were typically 13.7 meV ($k = 2.57$ Å^{-1}) and 30.5 meV ($k = 3.83$ Å^{-1}). The collimators and neutron energy were varied in order to optimize individual measurements. As we shall discuss below, both double- and triple-axis configurations were used. In the double-axis configuration, the analyzer crystal is removed and all neutrons of any energy scattered in a specific direction are detected.

Before discussion of the experimental results it will prove useful to review the various correlation functions measured in magnetic neutron scattering experiments. Generally, one has

$$\frac{\partial^2\sigma}{\partial\Omega_f\,\partial E_f} \sim \sum_\alpha (1-\hat{Q}_\alpha^2) S^{\alpha\alpha}(\mathbf{Q},\omega), \tag{1}$$

where

$$S^{\alpha\alpha}(\mathbf{Q},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{\infty} e^{-i\omega t}\langle S^\alpha(-\mathbf{Q},0) S^\alpha(\mathbf{Q},t)\rangle dt, \tag{2}$$

where $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ with $\mathbf{k}_i$ and $\mathbf{k}_f$ the incoming and outgoing neutron wave vectors, respectively. In an experiment where one integrates over the energy at fixed $\mathbf{Q}$ one measures the *instantaneous* correlation function

$$S^{\alpha\alpha}(\mathbf{Q}) = \int d\omega\, S^{\alpha\alpha}(\mathbf{Q},\omega) = N^{-1}\langle S^\alpha(-\mathbf{Q},0) S^\alpha(\mathbf{Q},0)\rangle. \tag{3}$$

Alternatively, for a system with long-range order (LRO) the Bragg scattering is given by the $\omega = 0$ response in Eq. (1) with $\mathbf{Q}$ a magnetic reciprocal-lattice vector.

These experiments were carried out with a large single crystal of La_2CuO_4 of $\simeq 0.5$ cm^3 in volume grown at

NTT by means of a copper-oxide flux technique. In this crystal, the room-temperature, orthorhombic lattice constants are $a=5.350$ Å, $b=13.134$ Å, and $c=5.390$ Å. We confirmed that the soft-phonon modes discovered previously[5] in a crystal grown at Massachusetts Institute of Technology occur identically in the NTT crystal. The neutron diffraction in La_2CuO_4 is complicated by the fact that in a single crystal, domains with $\mathbf{a}^*$ and $\mathbf{c}^*$ in the same direction occur with equal probability. Thus, as illustrated at the top of Fig. 1, the two reciprocal lattices are superimposed in a diffraction experiment.

The crystals were oriented with $\mathbf{a}^*$ (or $\mathbf{c}^*$) perpendicular to the scattering plane. We first studied the 3D antiferromagnetic ordering; these experiments utilized a triple-axis spectrometer set for $\omega=0$. 3D Bragg scattering appears at $\simeq 200$ K at the (100) position [see Fig. 1(a)] but not the (001) position, consistent with previous conclusions[4] that the spin direction is (001) [cf. the $(1-Q_a^2)$ factor in Eq. (1)]. The Bragg intensity versus temperature is shown at the bottom of Fig. 2. The Néel temperature is 195 ± 5 K with some rounding so that a Bragg tail extends above 200 K. From the intensity at low temperatures we deduce that the 3D ordered moment is $(0.35\pm0.05)\mu_B$. This phase transition has two notable features which contrast sharply with the behavior in systems such as[3] K_2NiF_4 and K_2MnF_4: (a) The Bragg intensity temperature variation is characteristically 3D suggesting that the phase transition is driven by 3D effects; (b) using the triple-axis configuration with $\omega=0$ we could locate neither 3D critical scattering nor any significant 2D diffuse scattering.

Because of the unique nature of the 2D $S=\frac{1}{2}$ Heisenberg antiferromagnet we conjectured that the fluctuations could have anomalous dynamical character. Thus, in an attempt to locate the anticipated 2D fluctuations, we changed to a two-axis configuration so that only the outgoing neutron direction but not energy was fixed. In a conventional magnetic system where the energy scale for the critical fluctuations is small, such an experiment yields the *instantaneous* correlation function. 2D correlations should manifest themselves as rods of scattering perpendicular to the CuO_2 planes along $(1,\zeta,0)$ and $(0,\zeta,1)$.[3] The quasielastic scattering cross section along $(1,\zeta,0)$ is shown in Fig. 1(b). The scan shows a prominent peak at (1,0.59,0). No corresponding peak occurs at $(1,-0.59,0)$ so that this effect does not have the symmetry of the reciprocal lattice and hence cannot be intrinsic to $LaCu_2O_4$. In fact, this phenomenon was discovered previously in two-axis experiments in K_2NiF_4 although there the effect was much less dramatic.[3] As illustrated in Fig. 1(a), for $k=2.57$ Å^{-1} from simple geometry one finds that $\mathbf{k}_f$ is exactly along $\mathbf{b}^*$ at the (1,0.59,0) rod position for $\omega=0$. Thus in a two-axis experiment the energy integration is accomplished via the momentum component perpendicular to the planes. Hence, for this position along the rod one measures the 2D correlation function $\langle S^a(-\mathbf{Q}_{2D},0)S^a(\mathbf{Q}_{2D},0)\rangle$ cor-

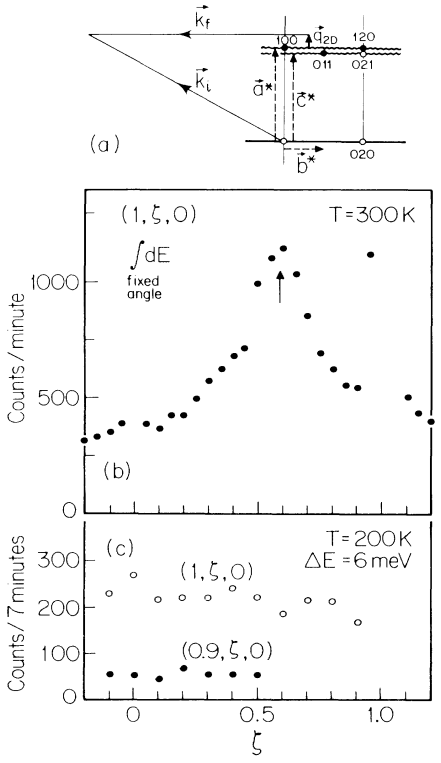

FIG. 1. (a) Reciprocal-lattice and scattering diagram for orthorhombic La_2CuO_4 with $\mathbf{a}^*$ and $\mathbf{c}^*$ domains superimposed. The wiggly lines are the 2D magnetic ridges. The open (filled) circles are points where 3D nuclear (magnetic) scattering is observed. (b) Scan along the top of the $(1,\zeta,0)$ ridge at $T=300$ K. The neutron wave vector is 2.57 Å^{-1}. The arrow gives the position at which $\mathbf{k}_f \| \mathbf{b}^*$. (c) Scans along $\mathbf{b}^*$ at a fixed energy transfer of 6 meV.

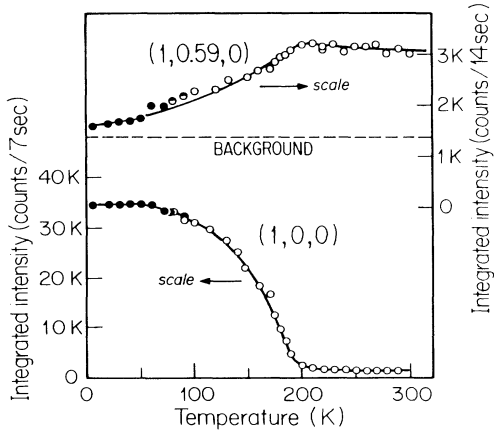

FIG. 2. Integrated intensities of the (100) 3D antiferromagnetic Bragg peak and the (1,0.59,0) 2D QSF ridge. The open and filled circles represent separate experiments which were normalized in the overlap region.

rectly. As we shall see below, the inelasticity involved in the 2D spin correlations is so large that for positions along the rod far from (1,0.59,0), the in-plane wave vector $\mathbf{Q}_{2D}$ is varied significantly in the process of integrating over the energy, thence smearing the peak and lowering the measured intensity.

We show at the top of Fig. 3 two- and three-axis scans through the 3D magnetic Bragg position (1,0,0) at 200 K. The 3D Bragg peak is still present at 200 K because of the rounding of the transition. For both the energy-integrating (two-axis) and $\omega=0$ (three-axis) measurements a sharp resolution-limited Bragg peak is observed at (1,0,0). The difference in intensity of the two-axis and three-axis scans evident in Fig. 3 is due to the 70% reflectivity of the graphite analyzer in the latter mode. Quite different behavior occurs for the scans across the 2D rod. For the two-axis scan a flat-top peak with very sharp edges is observed. This peak is actually the superposition of $(1,\zeta,0)$ and $(0,\zeta,1)$ rods of scattering [cf. Fig. 1(a)] which are slightly separated in Q as a result of orthorhombic distortion. In this case, however, barely any signal occurs in the three-axis scan. Thus the response function comes overwhelmingly from fluctuations which are at energies greater than the three-axis energy window of $\simeq 1$ meV. This is consistent with the dramatic variation of the intensity in the two-axis scan along the rod [Fig. 1(b)] as discussed above. In order to verify the 2D nature of the scattering, a scan along the rod was performed by use of a triple-axis spectrometer set for an energy transfer of 6 meV; the results are shown in Fig. 1(c). Significant scattering occurs at $(1,\zeta,0)$ whereas for $(0.9,\zeta,0)$ the intensity is at the background level. As expected, the scattering for $E=6$ meV at $(1,\zeta,0)$ is, except for trivial geometrical factors, independent of ζ, thence confirming that these dynamic spin fluctuations are purely two dimensional in character.

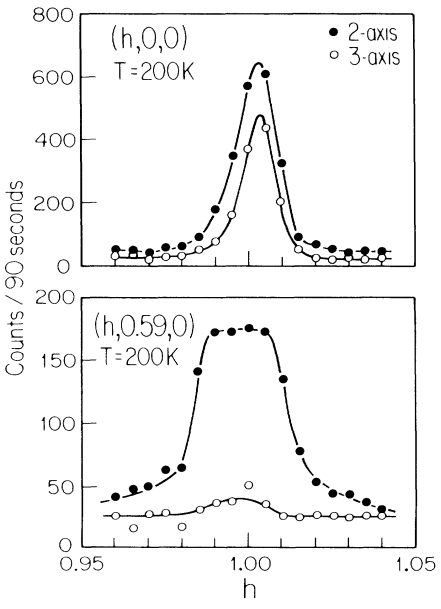

FIG. 3. Two-axis and three-axis scans across the 3D (100) magnetic peak (upper) and 2D QSF ridge (lower). The incoming wave vector was 2.57 Å^{-1} and the collimators 40′-10′-10′.

The integrated intensity in the two-axis scan across the rod is shown as a function of temperature at the top of Fig. 2. The rod intensity increases slightly below 300 K with decreasing temperature. However, at $T_N=195$ K the 2D scattering intensity begins to decrease. This is consistent with the heuristic notion that the 2D dynamic scattering is converted into 3D Bragg scattering at the transition to 3D LRO. It should be emphasized, however, that in La_2CuO_4 this process occurs very gradually. By contrast, in K_2NiF_4, because of the 2D Ising nature of the transition, the transfer of intensity from the rod (which in that case is nearly elastic) to the 3D Bragg peak occurs within 2% of T_N. This reflects a fundamental difference between the 3D phase transition in La_2CuO_4 and those in previously studied planar antiferromagnets. In the latter, the transitions to LRO are essentially 2D in character with the 3D ordering following parasitically. In La_2CuO_4 the 3D coupling seems to drive the transition. This immediately accounts for the extreme sensitivity of the 3D moment and Néel temperature to Sr doping and to the oxygen content[4,5] since structural disorder will strongly influence the correlations within and between the planes and any possible transition to 3D LRO.

From a quantitative analysis of profiles such as that shown at the bottom of Fig. 3 we conclude that at room temperature and below, the 2D correlation length exceeds 200 Å in both the **a** and **c** directions. However, as emphasized above, the 2D response is overwhelmingly inelastic. Thus, La_2CuO_4 at room temperature is exhibiting a QSF state; this differs markedly from previously studied $S=1$ and $S=\frac{5}{2}$ square lattice antiferromagnets in which there are conventional phase transitions with quasielastic longitudinal fluctuations to 2D LRO.[3]

In order to investigate the dynamics, we have carried out a series of scans in which the energy is fixed and the in-plane wave vector $\mathbf{Q}_{2D}$ is varied. For energy transfers up to 20 meV we see a sharp peak centered at $\mathbf{Q}_{2D}=\mathbf{a}^*$ ($\mathbf{c}^*$) with an intensity which depends weakly on ω. We are unable to resolve separately the excitations at $\mathbf{q}_{2D}=\pm|\mathbf{Q}_{2D}-\mathbf{a}^*|a^*$ because of the extreme steepness of the dispersion relation. This necessitates that the 2D excitation velocity be greater than 0.4 eV Å. We have also investigated the excitation intensity at a fixed energy of 3 meV. We find that the intensity *increases* slightly as the temperature is decreased from 300 to 200 K. However, below T_N the intensity *decreases* with decreasing temperature, and indeed below 150 K it follows accurately the Bose statistics formula $I\sim(e^{\hbar\omega/kt}-1)^{-1}+1$,

suggesting that the low-energy dynamic fluctuations we observe in the 2D QSF phase become ordinary spin waves in the 3D-ordered region below T_N. Finally, at 5 K the spin-wave gap is < 1 meV, thence necessitating that any anisotropy energy be $\lesssim 10^{-3}$ meV.

In summary, we find that at room temperature La_2CuO_4 exhibits novel 2D antiferromagnetism which differs qualitatively in character from that seen in higher-spin, more anisotropic, 2D antiferromagnets such as K_2NiF_4 and K_2MnF_4.[3] Specifically, even though there is no 2D LRO, the instantaneous 2D correlations extend over distances > 200 Å. The energy scale for the fluctuations corresponds to an effective dispersion $\gtrsim 0.4$ eV Å. Preliminary experiments on materials lightly doped with Sr^{++} and/or Li^{+}, indicate that impurities do not change the basic character of the QSF state but do severely limit the correlation length. The "paired" nature of the QSF state together with the large energy scale for the magnetic interactions suggest that these features are essential to the high-temperature superconductivity in La_2CuO_4-based materials. We expect that these features will occur in other planar or linear CuO_2 compounds such as $YBa_2Cu_3O_{7-\delta}$ so that the behavior found here should be relevant to these systems as well. Certain aspects of our experiments are adumbrated in a number of theoretical papers.[2] However, there are as yet no published quantitative predictions for the statics or dynamics of the QSF state. It should be noted that in many respects the QSF state is very much like that exhibited by the $S = \frac{1}{2}$ 1D Heisenberg antiferromagnet[6] at $T = 0$. We hope that our measurements will lead to a development of quantitative theories of superconductivity in the La_2CuO_4-type materials based on magnetic pairing mechanisms.

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