Spin Correlations in the Paramagnetic Phase and Ring Exchange in La_2CuO_4

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Spin correlations in the paramagnetic phase of La_2CuO_4 have been studied using polarized neutron scattering, with two important results. First, the temperature dependence of the characteristic energy scale of the fluctuations and the amplitude of the neutron structure factor are shown to be in quantitative agreement with the predictions of the quantum nonlinear sigma model. Second, a comparison of a high-temperature series expansion of the equal-time spin correlations with the diffuse neutron intensity provides definitive experimental evidence for ring exchange.

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Heisenberg was the first to realize that strong effective spin interactions arise from the principle of the indistinguishability of the particles [1]. Dirac generalized this concept, in the context of group theory, to include higher-order interactions [2]. Multiparticle exchange dominates the physics of the quantum solid ^{3}He [3] but, surprisingly, is generally not taken into account for electronic magnetic materials. The most powerful technique for exploring exchange interactions is the study of excitations from the ordered phase using inelastic neutron scattering. However, ambiguities in the interpretation of magnon dispersion curves sometimes mean that higher-order terms remain hidden. By employing the independent approach of studying the instantaneous spin correlations in the paramagnetic phase, we obtain complementary information that enables a better understanding of the exchange mechanism. In this Letter we describe studies of the diffuse magnetic scattering from La_2CuO_4 which provide compelling, quantitative evidence for the existence of four-particle cyclic exchange.

La_2CuO_4 is of great intrinsic interest both as the parent compound of a canonical high-temperature superconductor and as a very good realization of a two-dimensional quantum Heisenberg antiferromagnet (2DQHAF). Magnetic Raman experiments [4], infrared absorption studies [5,6], and inelastic neutron scattering measurements [7] show definitively the inadequacy of the nearest-neighbor Heisenberg model and suggest the possibility that four-particle exchange may be significant.

In an important series of experiments to study the diffuse magnetic scattering from La_2CuO_4 using unpolarized neutrons [8], the temperature dependence of the magnetic correlation length was found to agree with the predictions of the quantum nonlinear sigma model (QNLσM) [9]. However, the observed amplitude shows dramatic deviations from the predictions of this theory [8]. The QNLσM is the simplest possible effective action for a 2DQHAF that is compatible with the long-wavelength spin waves and that does not assume a spontaneously broken symmetry. Moreover, its predictions should hold even in the presence of four-spin exchange, as discussed below. Here we study the dynamical spin correlations above the Néel temperature using polarized neutrons, and find complete agreement of the observed 2D critical fluctuations with the predictions of the QNLσM.

Dirac's approach provides the most transparent theoretical framework to examine higher-order exchange interactions [2]. His analysis leads to an effective spin Hamiltonian

$$\mathcal{H}_{\text{eff}} = -\sum_{\lambda}(-1)^{p_\lambda} J_\lambda \mathcal{P}^{\sigma}_{\lambda}, \tag{1}$$

where λ runs over all possible permutations of spin $\mathcal{P}^{\sigma}_{\lambda}$ within the symmetric group, J_λ is the exchange energy associated with a given permutation, and p_λ its parity. Any permutation can be expressed in terms of cyclic exchange processes. Thouless was the first to point out that cyclic permutations of an even number of spins lead to antiferromagnetic (AF) exchange, whereas when an odd number of spins are permuted the resulting interaction is ferromagnetic (FM) [10]. Only the values of the exchange parameters J_λ depend on the choice of model; the form of interaction between spins is quite general.

In La_2CuO_4, retaining the most important exchange processes involved in a plaquette, the general effective spin Hamiltonian is given by:

$$\mathcal{H}_{\text{eff}} = J_2^{(1)} \sum_{\langle ij \rangle}^{(1)} \mathcal{P}^{\sigma}_{ij} + J_2^{(2)} \sum_{\langle ij \rangle}^{(2)} \mathcal{P}^{\sigma}_{ij} + J_2^{(3)} \sum_{\langle ij \rangle}^{(3)} \mathcal{P}^{\sigma}_{ij} - J_3 \sum_{\langle ijk \rangle} [\mathcal{P}^{\sigma}_{ijk} + (\mathcal{P}^{\sigma}_{ijk})^{-1}] + J_4 \sum_{\langle ijkl \rangle} [\mathcal{P}^{\sigma}_{ijkl} + (\mathcal{P}^{\sigma}_{ijkl})^{-1}]; \tag{2}$$

the $J_2^{(n)}$ are pair-exchange frequencies between nearest (1), next-nearest (2), and next-next-nearest neighbors (3); J_3 and J_4 represent three- and four-particle cyclic exchanges in a plaquette. In terms of spin operators

$$\mathcal{H}_{\text{eff}} = (2J_2^{(1)} - 8J_3 + 2J_4)\sum_{\langle ij\rangle}^{(1)} \mathbf{S}_i\cdot\mathbf{S}_j + (2J_2^{(2)} - 4J_3 + J_4) \times \sum_{\langle ij\rangle}^{(2)} \mathbf{S}_i\cdot\mathbf{S}_j + 2J_2^{(3)}\sum_{\langle ij\rangle}^{(3)} \mathbf{S}_i\cdot\mathbf{S}_j + 4J_4\sum_{\langle ijkl\rangle}[(\mathbf{S}_i\cdot\mathbf{S}_j) \times (\mathbf{S}_k\cdot\mathbf{S}_l) + (\mathbf{S}_j\cdot\mathbf{S}_k)(\mathbf{S}_l\cdot\mathbf{S}_i) - (\mathbf{S}_i\cdot\mathbf{S}_k)(\mathbf{S}_j\cdot\mathbf{S}_l)]. \quad (3)$$

We note that the four-particle cyclic exchange J_4 in Eq. (2) contributes both four-spin and two-spin terms to Eq. (3). On a square lattice, with the two-sublattice antiferromagnetic Néel phase, there is a remarkable (although fortuitous) exact cancellation of all contributions of the J_4 terms in linear spin-wave theory. This means that all quantities (in particular the magnon dispersion) calculated within this simple framework are the same as those corresponding to the pure Heisenberg Hamiltonian

$$H_{\text{Heis}} = \sum_{n=1}^{n=3} 2\tilde{J}_2^{(n)} \sum_{\langle ij\rangle}^{(n)} \mathbf{S}_i . \mathbf{S}_j, \quad (4)$$

with $\tilde{J}_2^{(1)} = J_2^{(1)} - 4J_3$, $\tilde{J}_2^{(2)} = J_2^{(2)} - 2J_3$, and $\tilde{J}_2^{(3)} = J_2^{(3)}$, and are completely blind to the four-particle permutation term J_4.

For simplicity, we can model the Cu-O planes in La_2CuO_4 using the half-filled one-band Hubbard model

$$H = -t\sum_{ij\sigma} c_{i\sigma}^{+} c_{j\sigma} + U\sum_i n_\uparrow n_\downarrow, \quad (5)$$

where the hopping energy t characterizes the kinetic energy, the potential energy $U \gg t$ is the penalty for double occupancy, c (c^+) are the annihilation (creation) operators, and $n = c^+ c$ is a number operator. At fourth order in a $\kappa = t/U$ expansion, the J_λ's appear as $J_2^{(1)}/U = 2\kappa^2(1 + 4\kappa^2)$, $J_2^{(2)}/U = 12\kappa^4$, $J_2^{(3)}/U = 2\kappa^4$, $J_3/U = 10\kappa^4$, and $J_4/U = 20\kappa^4$ [11,12]. More intricate expressions are obtained for a more general three-band Hubbard model [13]. The effective interaction between next-nearest neighbor pairs $\tilde{J}_2^{(2)}$ becomes negative (i.e., FM) because of the presence of the FM three-particle term J_3. The next-next-nearest-neighbor term is small and can be neglected. The magnitude of the four-particle cyclic exchange J_4 is large.

Since spin waves are insensitive to four-particle cyclic exchange, the curvature of the magnon dispersion at the zone boundary [7] is instead entirely due to the ferromagnetic effective next-nearest-neighbor exchange $\tilde{J}_2^{(2)}$. In contrast, there is no such cancellation of the four-spin term for the static susceptibility at high temperatures. We have, therefore, studied the diffuse scattering in the paramagnetic phase, and this is a new approach to the investigation of higher-order exchange. The dynamical structure factor for neutron scattering is given by

$$S(\mathbf{Q},\omega) = \frac{\omega}{1 - e^{-\omega/T}}\frac{S(0)}{1 + (q\xi)^2} \times \left[\frac{\Gamma}{(\omega - cq)^2 + \Gamma^2} + \frac{\Gamma}{(\omega + cq)^2 + \Gamma^2}\right], \quad (6)$$

where Γ is the characteristic energy. Integration over energy transfer yields information on the equal-time spin-spin correlations since

$$\int_{-\infty}^{\infty} S(\mathbf{Q},\omega)d\omega \approx \sum_i e^{i\mathbf{Q}\cdot\mathbf{R}_i}\langle S_i^z S_0^z\rangle \approx T\chi(\mathbf{Q}). \quad (7)$$

The wave-vector-dependent static susceptibility $\chi(\mathbf{Q})$ can be calculated from the exchange energies using a high-temperature series expansion.

A 2 g single crystal of La_2CuO_4 from the array used to study the spin waves in the ordered phase [7] was mounted inside furnaces, and the diffuse magnetic scattering was measured in the temperature range 300–500 K using the polarized neutron spectrometers D7 and IN20 at the Institut Laue-Langevin. *XYZ* polarization analysis was employed to separate the magnetic signal from the coherent structural and spin-incoherent backgrounds [14]. The scattering intensity measured in the $(h, 0, l)$ plane at room temperature using the multidetector on D7 is presented in Fig. 1(a) for the nuclear scattering showing the structural Bragg reflections and Fig. 2(b) for the purely magnetic signal showing the appearance of a rod of intensity perpendicular to the cuprate planes. The integrated intensity along the $\mathbf{Q}^{3D} = (1, 0, l)$ rod for La_2CuO_4 was measured as a function of temperature with the incident wave vector fixed, $k_i = 2.08$ Å^{-1}, and the final wave vector parallel to the normal to the cuprate planes in a similar manner to Ref. [8] so that the cuprate square-lattice wave vector remained fixed at $\mathbf{Q}^{2D} = (\frac{1}{2}, \frac{1}{2})$ for all energy transfers. For a quantitative temperature dependence of the intensity integrated over energy transfer, it is essential to determine how the spectral line shape varies with temperature. Energy scans were performed with $\mathbf{Q}$ fixed using the triple-axis spectrometer IN20, and typical spectra are presented in Fig. 2(a).

In the QNLσM, the correlation length ξ is given by [9]

$$\xi(T) = C_\xi\left[\frac{\hbar v_s}{\rho_s}\right]\exp\left[\frac{2\pi\rho_s}{k_B T}\right], \quad (8)$$

and the energy width Γ is related to ξ by

$$\Gamma = C_\Gamma v_s\left[\frac{T}{2\pi\rho_s}\right]^{1/2}\frac{1}{\xi}, \quad (9)$$

where v_s is the spin-wave velocity, ρ_s is the spin stiffness, and C_ξ and C_Γ are undetermined constants of order one. Figure 2(b) compares the temperature dependence of ξ deduced from Eq. (9) using the values of Γ determined in energy scans. There is excellent agreement between the dynamical predictions of the QNLσM and the correlation lengths measured using unpolarized neutrons by Birgeneau *et al.* [8]. The intensities measured in fixed-$\mathbf{Q}$ energy scans on IN20 integrated over energy transfer were converted to the amplitude $S(0)$ in Eq. (6) using the known correlation lengths [8]. The intensities measured on D7 without energy analysis were corrected using the spectral line shapes extrapolated from Fig. 2(b), the instrumental energy window, the Cu^{2+} magnetic form factor, and the correlation lengths, and the amplitudes from both experiments are combined in Fig. 3. The leading term in the expression for the ratio of the amplitude to the correlation length squared in the QNLσM is [9]

$$\frac{S(0)}{\xi^2} \approx \left(\frac{k_B T}{2\pi\rho_s}\right)^2. \qquad (10)$$

Figure 3(a) shows that when data collected on D7 are corrected with a full knowledge of the spectral line shape, they follow the same curve as those collected at fixed **Q** on IN20. Furthermore, the temperature dependence of intensities obtained using polarized neutrons is now in agreement with the predictions of the QNLσM. The insensitivity of linear spin-wave theory to four-particle terms means that the expansion of four-spin exchange operators in terms of gradients of the Néel vector does not add any new terms to the QNLσM. It is, therefore, gratifying that the clean measurements of the diffuse magnetic signal using polarized neutrons agree now with the predictions of the QNLσM for the renormalized-classical phase.

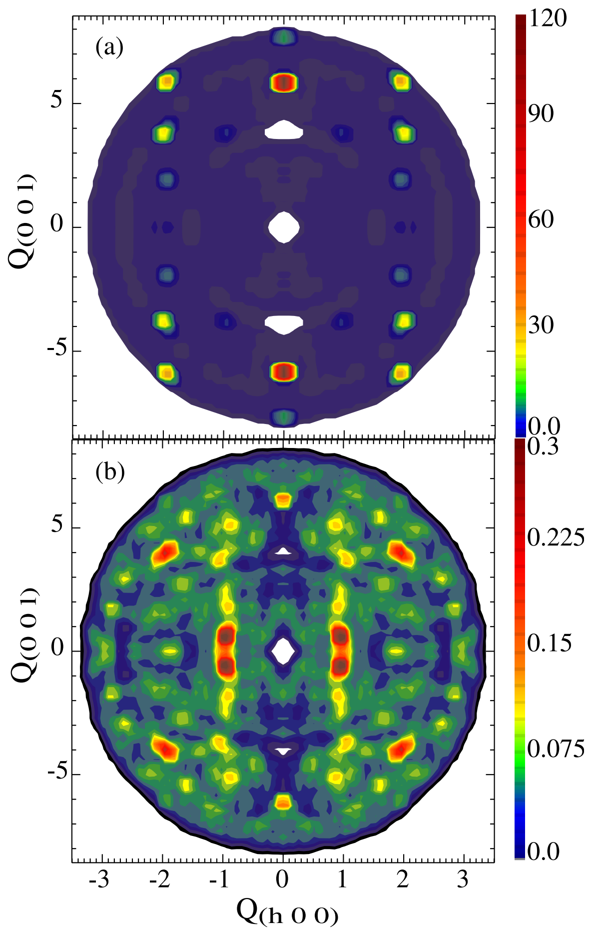

FIG. 1 (color online). Neutron scattering intensity in the $(h, 0, l)$ plane of La_2CuO_4 at room temperature, i.e., just above the Néel temperature, measured using the multidetector on D7. Three-directional polarization analysis allows separation into (a) coherent structural scattering and (b) purely magnetic scattering, with removal of the incoherent background. A rod of magnetic scattering is developing along the $[1, 0, l]$ direction showing the crossover to 2D correlations.

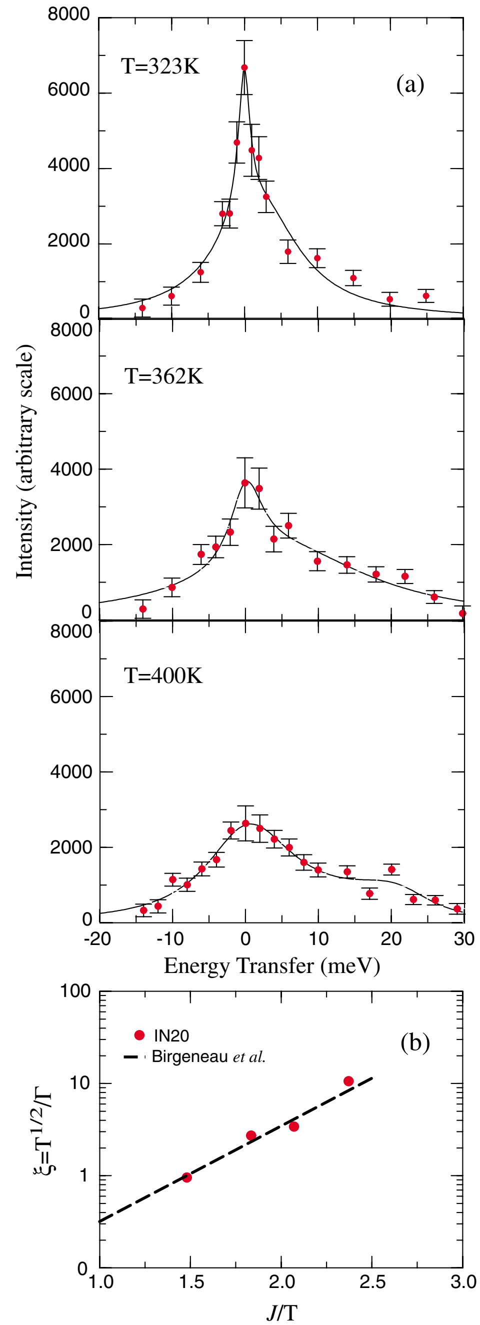

FIG. 2 (color online). (a) Scans of energy transfer at fixed wave-vector transfer at several temperatures on IN20, and in (b) the characteristic energies are compared with the correlation lengths from Ref. [8] using the QNLσM [9].

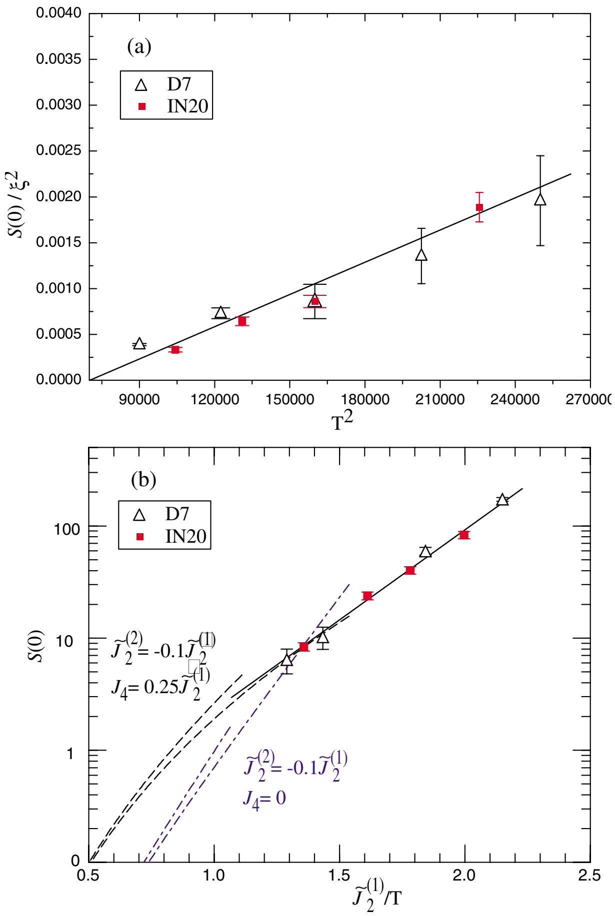

FIG. 3 (color online). The neutron scattering amplitude $S(0)$ at $\mathbf{Q} = (\frac{1}{2}, \frac{1}{2})$ of the cuprate square lattice. (a) The ratio of $S(0)$ over the square of the magnetic correlation length [8] varies linearly with temperature squared, in agreement with the QNLσM [9]. (b) The temperature dependence of $S(0)$ follows a straight (solid) line and the gradient agrees with the static susceptibility calculated in high-temperature series expansions with $J_4 = 0.25\tilde{J}_2^{(1)}$ (dashed line). The dash-dotted line shows the calculation with $J_4 = 0$. Fourth and fifth order expansions are shown, the latter extending to lower temperature.

In Fig. 3(b) we show the comparison of the measured $S(0)$ with the results of a high-temperature series expansion of the multiple-spin exchange model Eq. (2). The high-temperature series expansions were taken to fifth order and analytically continued using biased Padé approximants [15]. The values of the pair-exchange energies are those corresponding to the effective pair exchange $2\tilde{J}_2^{(1)} = 111.8$ meV and $2\tilde{J}_2^{(2)} = -11.4$ meV deduced from the magnon spectrum in the ordered phase [7]. Plotted on a semilog scale to extract the leading behavior in $1/T$, the experimental results fall on a straight line (solid line), and the gradient is in perfect agreement with the predictions of the series expansion at high temperatures with $J_4 = 0.25\tilde{J}_2^{(1)}$ (dashed line) derived from the Hubbard model. This agreement is achieved with no free parameters except an overall scale factor. The dramatic difference in slope with respect to the dash-dotted theoretical line (obtained with $J_4 = 0$) demonstrates the extreme sensitivity of the diffuse magnetic scattering to this term. These data constitute the first quantitative evidence for four-spin cyclic exchange in La_2CuO_4. We note that the ratio $J_4/\tilde{J}_2^{(1)} \approx 0.25$ is compatible with the predictions of the one-band Hubbard model, but more accurate neutron data would allow comparison with a more general three-band model [13].

The higher-order terms found to be of crucial importance in the physics of solid ^{3}He are also shown to be significant in an electronic magnetic material. It seems highly likely that ring exchange will be important in many other electronic magnetic systems, especially in those with strong hybridization paths, such as the Cu_4O_4 plaquettes. Optical experiments indicate that higher-order exchange is important in other high-temperature superconductors including $YBa_2Cu_3O_{6.2}$, $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_{8+y}$, Nd_2CuO_4, and Pr_2CuO_4 [4]. The magnitude of the four-spin cyclic exchange is comparable to the pairing energies, and it is possible that circulating electronic currents have an important role in the mechanism of superconductivity. Ring exchange is also believed to be important in related ladder compounds, such as $La_6Ca_8Cu_{24}O_{41}$ and $Sr_{14}Cu_{24}O_{41}$ [16].

In summary, four-spin cyclic exchange has been resolved in diffuse scattering experiments in the paramagnetic phase of La_2CuO_4, and the 2D critical fluctuations are correctly described by the QNLσM.

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