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**Abstract**
Sr$_2$Cu$_3$O$_4$Cl$_2$ has Cu$_{I}$ and Cu$_{II}$ subsystems, forming interpenetrating $S=1/2$ square lattice Heisenberg antiferromagnets. The classical ground state is degenerate, due to frustration of the intersubsystem interactions. Magnetic neutron scattering experiments show that quantum fluctuations cause a two dimensional Ising ordering of the Cu$_{II}$’s, lifting the degeneracy, and a dramatic increase of the Cu$_{I}$ out-of-plane spin-wave gap, unique for order out of disorder. The spin-wave energies are quantitatively predicted by calculations which include quantum fluctuations.

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Sr$_2$Cu$_3$O$_4$Cl$_2$ has Cu$_I$ and Cu$_{II}$ subsystems, forming interpenetrating $S = 1/2$ square lattice Heisenberg antiferromagnets. The classical ground state is degenerate, due to frustration of the intersubsystem interactions. Magnetic neutron scattering experiments show that quantum fluctuations cause a two dimensional Ising ordering of the Cu$_{II}$’s, lifting the degeneracy, and a dramatic increase of the Cu$_I$ out-of-plane spin-wave gap, unique for order out of disorder. The spin-wave energies are quantitatively predicted by calculations which include quantum fluctuations.

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The classical ground states of many magnetic systems are degenerate due to frustration. Quantum or thermal fluctuations often lift this degeneracy, yielding order due to disorder [1–4]. For example, when a system can be separated into two Heisenberg antiferromagnetic (AFM) sublattices, so that the molecular field of the spins in each sublattice vanishes on the spins of the other, then classically the sublattices order independently of each other, the ground state is degenerate, and the excitation spectrum contains two distinct sets of zero energy (Goldstone) modes, reflecting the fact that these sublattices can be rotated independently without cost in energy. As shown by Shender, quantum spin-wave (SW) interactions prefer collinearity of the spins in the two sublattices [2]. Concomitantly, this also generates a fluctuation driven gap in the SW spectrum. Indeed, such a gap was hypothesized in the garnet Fe$_2$Ca$_3$(GeO$_4$)$_3$ [5]. Since a similar gap could also arise from crystalline magnetic anisotropy, the final identification was rather complex.

In parallel to these developments, the discovery of high temperature superconductivity triggered much work on the magnetism in lamellar copper oxides. These materials contain CuO$_2$ planes, whose two-dimensional (2D) spin fluctuations can be modeled well by the $S = 1/2$ square lattice quantum Heisenberg antiferromagnet (SLQHA) [6].

The above two advances combine in the isostructural compounds Sr$_2$Cu$_3$O$_4$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$ (2342). In the present paper, we show that these materials offer a dramatic and clear demonstration of ordering due to fluctuations. As shown in Fig. 1(a), the CuO$_2$ plane is replaced in 2342 by a Cu$_I$O$_4$ one, which contains an additional Cu$_{II}$ ion at the center of every second plaquette of the original CuO$_2$ square lattice [7]. The configuration in the neighboring plane is obtained by translating the whole plane by $(\frac{b}{2}, \frac{b}{2})$. In the plane, the Cu$_I$ and Cu$_{II}$ subsystems form interpenetrating $S = 1/2$ SLQHA’s with exchange interactions $J_I$ and $J_{II}$. The isotropic interaction $J_{I,II}$ between these subsystems is frustrated; that is, its molecular field vanishes as described above, and one needs nontrivial theories to explain their ordering and SW gaps. Experimentally, 2342 exhibits AFM order of the Cu$_I$’s and Cu$_{II}$’s below the Néel temperatures $T_{N,1}$ and $T_{N,II}$, respectively [8,9]. For temperatures $T > T_{N,II}$, the Cu$_{II}$ susceptibility behaves as in a SLQHA, with $J_{II} \sim 10$ meV [10]. $J_{II} \sim 130$ meV is known from other cuprates. For $T < T_{N,II}$, the magnetization data were interpreted assuming Shender collinearity [10].

This paper reports on theory and neutron scattering experiments in Sr$_2$Cu$_3$O$_4$Cl$_2$. The inelastic neutron data show a dramatic increase of the Cu$_I$ “out-of-plane” [11]
gap below $T_{N,11}$ (see Fig. 2), which clearly reflects a coupling between the Cu$_1$ and Cu$_{11}$ spins. However, since symmetry indicates that within mean field theory this coupling due to frustrated interactions must vanish, we conclude that the enhanced gap for $T < T_{N,11}$ is due to fluctuations. This identification is particularly strong, since our data are quantitatively predicted by detailed theoretical calculations, which use parameters determined independently, albeit less accurately, by the static measurements [10]. The SW dispersion along (1 0 L), shown in Fig. 3, depends crucially on the fluctuations. Most of the in-plane dispersion is described by the linear terms or interplane couplings. Our data indicate that the enhanced gap for $T < T_{N,11}$, the ordered Cu$_1$ spins fluctuate mainly in the directions transverse to their staggered moment $M_{s,1}$. $J_{1,1}$ then generates fluctuations in the Cu$_{11}$ spins along the same directions, causing an effective reduction in the corresponding transverse exchange components of $J_{11}$ [2].

This yields an effective term $-\tilde{\delta}(M_{s,1} \cdot S_{11})^2$, where $\tilde{\delta} \approx J_{1,1}^I/(J_1 + J_{11})$. This implies an Ising-like anisotropy $J_{11}(a_{eff}^I \approx \tilde{\delta} M_{s,1}^2$, which favors ordering of the Cu$_{11}$ spins collinearly with $M_{s,1}$, consistent with our measured structure, Fig. 1(a). Indeed, $T_{N,11} \sim 40$ K agrees with $\xi_0(T_{N,11})^2 a_{eff}^I \approx 1$, where $a_{eff}^I \sim 0.01$ was deduced from our SW gaps. Heuristically, the lowering of the symmetry on the Cu$_1$ site due to the ordering of the Cu$_1$’s is sensed through the quantum fluctuations.

Since the SLQHA does not have long-range order at $T > T_{N,11}$, such order must arise from spin anisotropy terms or interplane couplings. Our data indicate that $T_{N,11} \sim 385$ K is determined by the latter, via $\xi_0(T_{N,11})^2 J_{1,3D}/J_1 \sim 1$, with $J_{1,3D} \sim 0.1$ meV. Here, $\xi_0(T)$ is given by the SLQHA correlation length [6,12]. The spin structure, shown in Fig. 1(a), has been uniquely determined from analyzing 13 different neutron diffraction peaks in the plane [13], confirming the conjecture in Ref. [10]. As in YBa$_2$Cu$_3$O$_6$ [14], the Cu$_1$ spins order along the Cu$_1$-Cu$_{11}$ bonds, as expected when the quantum fourfold anisotropy is dominant [15]. Unlike the Cu$_1$’s, the interplane Cu$_{11}$-Cu$_{11}$ coupling is frustrated, similar to that in Sr$_2$Cu$_2$O$_2$Cl$_2$ [6], and therefore $T_{N,11}$ is expected to be determined mainly by in-plane spin anisotropies. Indeed, the 2D nature of the Cu$_{11}$ subsystem has been established from both the existence of rods of 2D scattering for $T > T_{N,11}$ and the small SW dispersion along L [13]. For $T < T_{N,11}$, the ordered Cu$_1$ spins fluctuate mainly in the directions transverse to their staggered moment $M_{s,1}$. $J_{1,1}$ then generates fluctuations in the Cu$_{11}$ spins along the same directions, causing an effective reduction in the corresponding transverse exchange components of $J_{11}$ [2].

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Large ($\sim 2$ cm$^3$) single crystals of Sr$_2$Cu$_3$O$_4$Cl$_2$, grown by slow cooling of a melt containing CuO flux, are used in the experiment. The crystal remains tetragonal for $15 < T < 550$ K [10]. Our neutron scattering experiments were carried out with the triple-axis spectrometers at the High Flux Beam Reactor, Brookhaven National Laboratory, and at the National Institute of Standards and Technology Research Reactor. Collimation of 40'-40'-S-40'-80' and fixed final neutron energy of 14.7 meV were used for most of the inelastic measurements. When better resolution was required, we used a fixed initial neutron energy of 13.7 meV and tighter collimations.

The $T$ dependences of $M_{s,1}$ and $M_{s,11}$ [proportional to the square root of the AFM Bragg intensities at the (1 0 1) and the ($\frac{1}{2} \frac{1}{2} 0$) reciprocal positions, respectively] are shown in Fig. 2(a). Since nuclear Bragg scattering is only weakly $T$ dependent, we subtract the high-temperature (1 0 1) nuclear intensity from the observed intensity. The solid lines in Fig. 2(a) represent $M_{s,1} \sim (T_N - T)^{\beta}$. The parameters given there were fitted for

![FIG. 2. (a) Temperature dependence of the Cu$_1$ out-of-plane gap energy and of the staggered magnetizations $M_{s,1}$ of Cu$_1$ and Cu$_{11}$. $M_{s,1}$ is normalized to the extrapolated zero temperature value $M_{s,1,0}$. The solid lines are the results of fits to the form $\sim(T_N - T)^{\beta}$. (b) The gap energy in a different temperature scale. The solid and dashed lines are interpolations for $\omega_t$ and $\omega_3$; see text.](image1)

![FIG. 3. (a) Magnon dispersion along the L direction at the 2D zone center for $T = 200$ K (solid circles). (b) Same for $T = 10$ K. The solid lines show Eq. (2).](image2)
T > 200 K (CuI) and T > 25 K (CuII). \( \beta_{11} = 0.13(1) \) clearly demonstrates the 2D Ising criticality of the CuII ordering. \( T_{N,1} = 385(2) \) K and \( T_{N,11} = 40.0(2) \) K agree with those from our previous magnetization study [10], while \( \beta_1 = 0.27(2) \) is consistent with that of Sr$_2$CuO$_2$Cl$_2$ and La$_2$CuO$_4$ [6].

Our measured SW energies are all explained within a \( T = 0 \) interacting SW theory. We start from the “minimal” Hamiltonian

\[
\mathcal{H} = \sum_{(i,j),\mu} J^{\mu}_{ij} S^\mu_i S^\mu_j + J_{1,3D} \sum S_i \cdot S_j + \sum_{(m,n),\mu} J^{\mu}_{11,m,n} S^\mu_m S^\mu_n + J_{1,11} \sum_{(m,n),\mu} S^\mu_m \cdot S^\mu_n,
\]

where \( i,j \) and \( m,n \) denote CuI sites and CuII sites, respectively, and where we assume that \( J^{\mu}_{ij} = J^{\mu}_{j,i} = J^{\mu}_{A} \) and \( J^{\mu}_{ij} = J^{\mu}_{j,i}(1 - \alpha A) \) for \( A = 1, 11 \) and \( \mu = a, b, c \). We also assume that \( J_1 \gg J_{1,11} \). The effects of other (smaller) terms, such as the various in-plane anisotropies [10,15], will be presented elsewhere [16]. \((i,j)\) and \((i,j)_{1,3D}\) label CuI intra- and interplanar nearest neighbors (NN’s), whereas \((m,n)_{11}\) and \((i,m)_{1,11}\) refer to the NN CuII-CuII and CuI-CuII bonds, respectively. Starting from the spin structure shown in Fig. 1(a), we express each of the six spins in the unit cell by the Holstein-Primakoff transformation for general spin \( S \). The first three sums in \( \mathcal{H} \) are then truncated at the harmonic order in the SW boson operators. However, the \( J_{1,11} \) term vanishes at the zone center, and therefore has effects only if one expands it to quartic order. We then approximate each product of four SW operators by contracting operator pairs in all possible ways. This yields new quadratic terms, whose coefficients contain the parameter \( \delta = 2J_{1,11}(ae)/S \approx \delta_0 \), where \( a \) and \( e \) are boson operators associated with CuI and CuII, respectively. This coefficient contains the factor \( 1/S \), thus representing quantum corrections due to SW interactions. The SW energies are then found as the eigenvalues of the \( 6 \times 6 \) matrix which arises from the resulting bilinear SW Hamiltonian [16].

The resulting \( T = 0 \) magnon modes can be found analytically along the \( L \) direction at the 2D zone center [(1 0 0) reciprocal lattice points, \( q_c = 2\pi L/c \)]. In addition to the two optical modes, which are practically degenerate at \( \omega = 4SZJ_1 \), the low-energy modes are (in order of increasing energy)

\[
\omega_1 = S\sqrt{32J_{11}\delta x_3/(\delta + 2x_3)}, \quad (2a)
\]

\[
\omega_2 = S\sqrt{32J_{11}\left(Z_2^{J_{11}\alpha_1} + \frac{\delta(2J_1\alpha_1Z_2^2 + x_3)}{4J_1\alpha_1Z_2^2 + \delta + 2x_3}\right)}, \quad (2b)
\]

\[
\omega_3 = S\sqrt{8J_1(\delta + x_3)}, \quad (2c)
\]

\[
\omega_4 = S\sqrt{8J_1(4Z_2^2J_1\alpha_1 + \delta + 2x_3)}, \quad (2d)
\]

where \( Z_c = 1 + O(1/S) \approx 1.17 \) [17] and \( Z_c = 1 + O(1/S) = 0.6 \) [18] are the quantum renormalization factors for the SW velocity and for the SW anisotropy gap when \( S = 1/2 \) and \( x_3 = Z_2^2J_{1,3D}[1 + \cos(\pi L)] \), where \( Z_3 = 1 + O(1/S) \approx 0.9 \) [16]. In Eq. (2) we keep only terms up to \( O(1/S) \) [which leaves some ambiguity in the ratios appearing in Eqs. (2a) and (2b)]. Since \( \delta = O(1/S) \), this term is not renormalized. Note that the dispersion of \( \omega_1 \) and \( \omega_2 \) is of order \( \delta \), and hence is purely fluctuational.

Figure 3 shows our measured dispersion along the \( L \) direction, together with fits to Eq. (2), above and beyond \( T_{N,11} \). The momentum transfer is held constant at \((0 0 L)\), and the energy transfer is varied at each \( T \). For \( T > T_{N,11} \), our theory predicts only two acoustic modes, whose energies are given by \( \omega_3 \) and \( \omega_4 \) with \( \delta = 0 \). Far below \( T_{N,1} \), these can be approximated by the low-T results in Eq. (2). Fixing \( J_1 = 130 \) meV and \( \delta = 0 \), we fit the gapless data to \( \omega_3 \), and obtain \( J_{1,3D} = 0.14(2) \) meV. Identifying the data with the gap with \( \omega_4 \), that is, with the out-of-plane CuI mode, we then fit Eq. (2d) and find \( \alpha_1 = 5.2(9) \times 10^{-4} \). This value is consistent with that \((= 1.5 \times 10^{-4})\) found in Sr$_2$CuO$_2$Cl$_2$, if the anisotropy gap is renormalized by \( Z_c \) rather than by \( Z_\epsilon \) (as incorrectly done in Ref. [6]).

Below \( T_{N,11} \), Eq. (2) predicts four different low-lying modes. However, as seen in Fig. 3(b), our experiment seems to show only two low-energy modes. We interpret the higher of these as an overlap of \( \omega_4 \) and \( \omega_5 \), which could not be resolved due to the resolution and the existence of a nearby phonon peak. We emphasize that for \( T < T_{N,11} \), \( \omega_3 > 0 \) at \( L = 1 \) is a pure quantum effect; the close values of \( \omega_3 \) and \( \omega_4 \) simply reflect the fact that the effective anisotropy associated with \( \delta \) is larger than the intrinsic CuI anisotropy \( \alpha_1 \) [see Eqs. (2c) and (2d)], thus illustrating the quantitative importance of the order due to disorder effects. The lower mode is identified as \( \omega_2 \). The experimental resolution did not permit identifying \( \omega_1 \) as a distinct mode. The solid lines in Fig. 3(b) were drawn using Eq. (2), with \( \delta = 0.3(1) \) meV, \( J_{11} = 10.5 \) meV (see below and Ref. [10]) and \( \alpha_{111} = 0.0001(5) \). We found \( \delta \) by fitting \( \omega_3 \) and \( \omega_4 \) with fixed \( J_1 \) and \( \alpha_{111} \) by then fitting \( \omega_2 \) with fixed \( J_{11} = 10.5 \) meV. The error bar allows \( \alpha_{111} = 0 \).
Given the uncertainties, the theory agrees well with the data. Our measured value of $\delta < 26$ meV, as found in our earlier magnetization study [10]. Both the $\omega_1$ and $\omega_2$ modes at $L = 1$ have been observed with microwave resonance techniques in Ba$_2$Cu$_4$O$_7$Cl$_2$ [8], but not yet in Sr$_2$Cu$_4$O$_7$Cl$_2$. The Ba$_2$Cu$_4$O$_7$Cl$_2$ results are consistent with Fig. 3(b).

Figure 2 shows the $T$ dependence of $\omega_4$ at the zone center, $L = 1$. In agreement with Eq. (2d), the appearance of a nonzero $\delta$ causes a unique and dramatic increase in this gap. Similar to tetragonal SLQHA’s K$_2$NiF$_4$ ($S = 1$) [19] and Sr$_2$Cu$_2$O$_7$Cl$_2$ ($S = 1/2$) [6], this out-of-plane gap roughly follows $M_{\perp 1}$ for $T > T_{c,1}$ [see Fig. 2(a)]. Below $T_{c,1}$, the measured gap represents both $\omega_3$ and $\omega_4$. The full and dashed lines in Fig. 3(b) represent Eqs. (2d) and (2c), respectively, in which we multiplied $\delta$ by $(M_{\perp 1}/M_{\perp 1,0})^2$ (as in our estimate for $a_{I1}^2$), to interpolate between 0 K and the low-$T$ value.

In addition to the above results, we also measured SW’s in the $ab$ plane, along the high-symmetry directions shown as thick lines in Fig. 1(c). Here, $(\pi \pi)$ is the $(\frac{3}{2} \frac{3}{2})$ magnetic Bragg peak position. However, because there are two types of AFM domains due to the tetragonal structure, we are actually measuring contributions from both the $(\frac{3}{2} \frac{3}{2})$ and the $(\frac{3}{2} \frac{3}{2})$ positions. Figure 4 summarizes our results at 10 K, which is well below $T_{c,1}$. Both constant energy-transfer scans and constant momentum-transfer scans were carried out. From the zone boundary SW energy of 25 meV one can deduce $J_{11}$ rather accurately as $J_{11} = 10.5(5)$ meV, in excellent agreement with the value deduced before from the Cu$_{I1}$ susceptibility [10]. The gap energy at the zone center, $-3$ meV, corresponds to the lower gap found at $L = 0$ in Fig. 3(b). It turns out that $\omega_3$ and $\omega_4$ are not observed at the $(\frac{3}{2} \frac{3}{2})$ position, due to small intensity. Away from the 2D zone center, $\omega_1$ and $\omega_2$ are degenerate and can be approximated as a simple SLQHA with the exchange $J_{11}$. With $a_{I1} = 0$, Eq. (2b) can be interpreted as resulting from an anisotropy given by $J_{11}a_{I1} = \frac{2J_1a_{I1}}{(4J_1a_{I1} + \delta)} = 0.1$ meV, or $a_{I1} = 0.01$. Using the simple (large $S$) harmonic approximation described above with this value and $J_{11} = 10.5$ meV gives the dashed line in Fig. 4. This is a good approximation, except for the dispersion near the zone edge $(\pi 0)$. As seen by the continuous line, our data are in much better agreement with recent series expansion results by Singh and Gelfand [20], calculated with the same parameters. This theory predicts a local minimum at $(\pi 0)$, lower by about 7% than the value at $(\frac{3}{2} \frac{3}{2})$. This dispersion is a pure quantum mechanical effect for the $S = 1/2$ NN Heisenberg model. A nonzero dispersion along the zone boundary may also result from a nonzero next-NN (NNN) interaction $J_{11}^{NNN}$, within linear SW theory. The magnitude of the dispersion between $(\pi 0)$ and $(\frac{3}{2} \frac{3}{2})$ is given by $2SJ_{11}^{NNN}$. Considering that $J_{11}$ is already the order of 10 meV and the NNN distance is large (~7.7 Å), it is unlikely that the NNN effects contribute strongly to the observed zone-boundary energy difference of ~2 meV in Sr$_2$Cu$_3$O$_7$Cl$_2$.

In conclusion, we have shown that quantum fluctuations in Sr$_2$Cu$_3$O$_7$Cl$_2$ lift the classical degeneracy due to the frustration and make Cu$_{I1}$ spins order with Ising criticality. We have also shown that the zero-energy modes acquire energy gaps due to the quantum fluctuations, which can be explained quantitatively by the SW calculation including the SW interaction terms.

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The term “out-of-plane” denotes the polarization of the SW eigenvector determined from neutron scattering measurements. See, e.g., Ref. [6].

[16] Details will be published elsewhere.