Neutron Scattering study of Sr$_2$Cu$_3$O$_4$Cl$_2$

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We report a neutron scattering study on the tetragonal compound Sr$_2$Cu$_3$O$_4$Cl$_2$, which has two-dimensional (2D) interpenetrating Cu$_I$ and Cu$_{II}$ subsystems, each forming a $S = 1/2$ square lattice quantum Heisenberg antiferromagnet (SLQHA). The mean-field ground state is degenerate, since the inter-subsystem interactions are geometrically frustrated. Magnetic neutron scattering experiments show that quantum fluctuations lift the degeneracy and cause a 2D Ising ordering of the Cu$_{II}$ subsystem. Due to quantum fluctuations a dramatic increase of the Cu$_I$ out-of-plane spin-wave gap is also observed. The temperature dependence and the dispersion of the spin-wave energy are quantitatively explained by spin-wave calculations which include quantum fluctuations explicitly. The values for the nearest-neighbor superexchange interactions between the Cu$_I$ and Cu$_{II}$ ions and between the Cu$_{II}$ ions are determined experimentally to be $J_{I-II} = -10(2)$meV and $J_{II} = 10.5(5)$meV, respectively. Due to its small exchange interaction, $J_{II}$, the 2D dispersion of the Cu$_{II}$ SLQHA can be measured over the whole Brillouin zone with thermal neutrons, and a novel dispersion at the zone boundary, predicted by theory, is confirmed. The instantaneous magnetic correlation length of the Cu$_{II}$ SLQHA is obtained up to a very high temperature, $T/J_{II} \approx 0.75$. This result is compared with several theoretical predictions as well as recent experiments on the $S = 1/2$ SLQHA.

I. INTRODUCTION

Quantum magnetism has been studied for many decades since the advent of quantum mechanics. Most of the early theoretical work is based on semi-classical methods such as spin-wave theory. Quite remarkably, spin-wave theory has been successful in describing many physical properties of a variety of magnetic systems. Despite the fact that it is essentially a $1/(zS)$ expansion, where $z$ is the coordination number, and thus one would expect it to be less accurate for a small spin quantum number $S$, spin-wave theory has been a very powerful tool in investigating quantum magnetism, and the “semi-classical” description of quantum magnets has been sufficient to understand most experimental results. In a seminal paper, Haldane pointed out the special significance of the spin quantum number in one-dimensional (1D) quantum Heisenberg antiferromagnet (QHA). In his now famous conjecture, he mapped the 1D QHA onto the quantum nonlinear $\sigma$ model (QNL$\sigma$M), and noted the
fundamental difference in the ground states for half-odd-integer $S$ and integer $S$. Specifically, the 1D QHA with half-odd-integer $S$ has a quasi-long-range ordered ground state with a gapless excitation spectrum, while that with integer $S$ has a quantum disordered ground state with a large energy gap in the excitation spectrum. Subsequent developments of quantum field theory, numerical simulations and experiments have confirmed Haldane’s conjecture.

In contrast, quantum effects in the two-dimensional (2D) QHA are typically less dramatic. In fact, the qualitative behavior of the 2D QHA is similar to that of the classical one. Quantum fluctuations usually manifest themselves through uniform renormalization of physical quantities, such as the staggered magnetization or the spin-wave velocity. However, in certain magnetic systems, where the primary exchange couplings are highly frustrated, the effects of quantum fluctuation can be revealed *qualitatively* in the low-energy spin dynamics. As an example, isostructural compounds Sr$_2$Cu$_3$O$_4$Cl$_2$ and Ba$_2$Cu$_3$O$_4$Cl$_2$, the so-called 2342 materials, offer a dramatic and clear demonstration of such quantum effects as “order from disorder.”

In this paper, we describe our detailed neutron scattering study of the frustrated 2D $S = 1/2$ antiferromagnet Sr$_2$Cu$_3$O$_4$Cl$_2$, including experimental evidence for quantum fluctuation induced order. Some of the results reported here were briefly presented in a recent letter.

The discovery of high temperature superconductivity in 1986 has triggered much work on the magnetism in lamellar copper oxides. These materials contain CuO$_2$ planes whose 2D spin fluctuations can be modeled by the $S = 1/2$ square lattice (SL) QHA. Through a combination of experimental, numerical, and theoretical efforts, a quantitative understanding of the $S = 1/2$ SLQHA has emerged. Notably, neutron scattering measurements of the instantaneous spin-spin correlation length of the model compound Sr$_2$CuO$_2$Cl$_2$ are found to be in quantitative agreement with quantum Monte Carlo results and both in turn are well-described by analytic theory for the QNLoM. Angle resolved photoemission spectroscopy (ARPES) on this insulating system has also provided important information on the behavior of a single hole in a paramagnetic background, hence testing the applicability of the $t – J$ model.

The structure of Sr$_2$Cu$_3$O$_4$Cl$_2$, shown in Fig. 1(a), is similar to that of Sr$_2$CuO$_2$Cl$_2$. As shown in Fig. 1(b), the CuO$_2$ layers are replaced by Cu$_3$O$_2$ layers, which contain an additional Cu$_{II}^{2+}$ ion at the center of every second plaquette of the original Cu$_1$O$_2$ square lattice. The configuration in the neighboring plane is obtained by translating the whole plane by $(\frac{a}{2}, \frac{b}{2})$. The in-plane isotropic interaction $J_{I-\frac{I}{2}}$ between Cu$_I$ and Cu$_{II}$ subsystems is frustrated such that they form interpenetrating $S = 1/2$ SLQHA’s with respective exchange interactions $J'_I$ and $J_{II}$.

Due to the complete frustration of the isotropic coupling between Cu$_I$ and Cu$_{II}$, 2342 exhibits many fascinating magnetic phenomena. In their magnetic susceptibility and electron paramagnetic resonance measurements on Ba$_2$Cu$_3$O$_4$Cl$_2$ powder, Noro and coworkers first observed anomalous features at $T \sim 320$K and $T \sim 40$K and attributed these to respective antiferromagnetic ordering of the Cu$_I$ and Cu$_{III}$ spins. Subsequent neutron scattering measurements by Yamada et al. showed that 2342 exhibits antiferromagnetic order of the Cu$_I$ and Cu$_{III}$ subsystems below the respective Néel temperatures $T_{N,I}$ and $T_{N,III}$. Far-infrared electron spin resonance (ESR) and submillimeter wave resonance experiments showed that there is a low energy out-of-plane excitation in the long-wavelength limit. The dispersion of a single hole in both antiferromagnetic and paramagnetic spin background was measured simultaneously in the same Cu$_3$O$_4$ plane by ARPES experiments. One of the most intriguing features in earlier studies is the weak ferromagnetic moment that appears below $T_{N,I}$. We have recently reported that anisotropic bond-dependent interactions such as pseudo-dipolar couplings can in fact explain such weak ferromagnetic moments.
We consider two specific consequences of the frustration in this paper. First, in the mean field approximation, the Cu\textsubscript{I} and Cu\textsubscript{II} subsystems are decoupled, so that in addition to the well known Cu\textsubscript{I} SLQHA, the Cu\textsubscript{II}’s form their own $S = 1/2$ SLQHA with an order of magnitude smaller superexchange, $J_{II}$. Chou et al.\cite{20} have shown that the magnetic susceptibility of the Cu\textsubscript{II} subsystem is very well described as a $S = 1/2$ SLQHA by comparing the experimental result with the results of a quantum Monte Carlo calculation. Since $J_{II} \sim 10$ meV is matched well with the energy of thermal neutrons, this is an ideal $S = 1/2$ SLQHA system for neutron scattering experiments. In Sec. [IVD], we show the spin-wave dispersion of the Cu\textsubscript{II} subsystem throughout the entire Brillouin zone, including a theoretically predicted dispersion along the zone boundary. In Sec. [V B], the correlation length data measured from the Cu\textsubscript{II} SLQHA are presented as a function of temperature and compared with various theoretical predictions as well as quantum Monte Carlo results. Because $J_{II}$ is an order of magnitude smaller than $J_{I}$, we are able to access a rather high temperature ($T/J_{II} \approx 0.75$).

Second, because of the frustration, we can observe the direct effect of quantum fluctuations. When a system can be separated into two Heisenberg antiferromagnetic sublattices, so that the molecular field of the spins on each sublattice vanishes on the spins of the other, then within mean field theory the ground state has a degeneracy with respect to the relative orientation of the sublattices, and the excitation spectrum contains two distinct sets of zero energy (Goldstone) modes, reflecting the fact that these subsystems can be rotated independently without cost in energy. This degeneracy is removed by fluctuations. Shender\cite{15} showed that quantum spin-wave interactions prefer collinearity of the spins on the two sublattices. This has the following experimental consequences in Sr\textsubscript{2}Cu\textsubscript{3}O\textsubscript{4}Cl\textsubscript{2}: The symmetry of the critical fluctuations of the Cu\textsubscript{II} system is lowered to Ising due to the fluctuation-driven collinearity, and the spin-wave mode corresponding to the relative rotation of sublattice moments develops a gap. Indeed, such a gap was considered in the garnet Fe\textsubscript{2}Ca\textsubscript{3}(GeO\textsubscript{4})\textsubscript{3}. However, since a similar gap could also arise from crystalline magnetic anisotropy, the final identification was rather complex.\cite{20,22,23,24,25}

Our inelastic neutron data in Sec. [IV] show a dramatic increase of the Cu\textsubscript{I} “out-of-plane” gap below $T_{N,II}$ (see Fig. [3]), which clearly reflects a coupling between the Cu\textsubscript{I} and Cu\textsubscript{II} spins. However, within mean field theory this coupling due to frustrated interactions must vanish by symmetry. Accordingly, we conclude that the enhanced gap for $T < T_{N,II}$ is due to quantum fluctuations. Heuristically, the lowering of the symmetry on the Cu\textsubscript{II} site due to the ordering of the Cu\textsubscript{I}’s is sensed through the quantum fluctuations. This identification is corroborated by detailed theoretical calculations, which use parameters determined independently, albeit less accurately, by the susceptibility measurements.\cite{20,22,23,24,25}

There have been numerous studies on this peculiar order from disorder effect on various systems. Villain et al.\cite{20} studied a generalized frustrated Ising model in two dimensions and found that the system does not have long range order at $T = 0$, but is ferromagnetically ordered at low but non-zero temperature; thermal fluctuations are necessary to stabilize the ordered state; thus they termed this phenomenon order from disorder. Shender\cite{15} showed that quantum fluctuations can also cause order from disorder phenomena in frustrated magnetic systems. In addition to thermal or quantum disorder, substitutional disorder also causes ordering in such frustrated magnetic systems. Henley\cite{20} studied order from substitutional disorder in a planar antiferromagnet on a square-lattice with a strong second nearest neighbor exchange and discovered that anti-collinear order is stabilized by substitutional disorder, in contrast with the collinear ground state due to thermal or quantum disorder. Chandra et al.\cite{20} investigated the Heisenberg model on such a lattice using analogies between quantum antiferromagnetism and superfluidity. The Heisenberg antiferromagnet on the layered body centered tetragonal structure, where the inter-planar coupling is fully frustrated, has been also studied extensively, mainly due to its similarity to the structure of high temperature superconductors.\cite{20,22,23,24,25}
tum and energy transfer by \( Q \) and \( \omega \), which are given by \( Q \equiv k_i - k_f \) and \( \omega \equiv E_i - E_f \), respectively. We use units in which \( \hbar = k_B = 1 \) and the scattering vector \( Q = (\frac{2\pi}{a}H, \frac{2\pi}{b}K, \frac{2\pi}{c}L) \). Throughout this paper, we use \( q \) to denote physically relevant momentum transfer; that is, the momentum transfer with respect to the reciprocal lattice vector \( G \): \( q \equiv Q - G \).

The partial differential cross section for spin only scattering of unpolarized neutrons is given by:

\[
\frac{d^2\sigma}{d\Omega dE_f} \sim \frac{k_f}{k_i} f^2(Q) \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(Q, \omega),
\]

where \( \hat{Q} \equiv Q/Q \), and \( f(Q) \) is the magnetic form factor, which is the Fourier transform of the spin-density distribution around the magnetic ion, and hence depends on \( Q \).

An important feature of magnetic scattering is the directional dependence through the geometric factor \( (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) \), which picks out the components of the magnetization perpendicular to the momentum transfer \( Q \). The quantity \( S^{\alpha\beta}(Q, \omega) \), known as the dynamic structure factor, is the Fourier transform in both space and time of the spin-spin correlation function. The latter is the thermal average over the correlations between the component along the \( \alpha \)-axis of a spin at the origin at time zero and the component along the \( \beta \)-axis of a spin at site \( r \) at time \( t \):

\[
S^{\alpha\beta}(Q, \omega) = \frac{1}{2\pi} \sum_r \int_{-\infty}^{\infty} dt \, e^{i(Q \cdot r - \omega t)} \langle S^\alpha(0, 0) S^\beta(r, t) \rangle.
\]

The static structure factor is obtained from the Fourier transformation of the equal-time correlation function, and measures the instantaneous correlations between the spins:

\[
S^{\alpha\beta}(Q) = \int_{-\infty}^{\infty} d\omega S^{\alpha\beta}(Q, \omega).
\]

In principle, one can obtain the static structure factor by directly measuring the entire dynamical spectrum \( S(Q, \omega) \) and doing the energy integration at each \( Q \). However, in most systems this is impossible within a reasonable time scale. Fortunately, in 2D magnetic systems such as the lamellar copper oxides, the energy integration is effectively done by detecting neutrons without energy discrimination in a special scattering geometry. One then can determine the instantaneous correlation function in one scan.

### B Elastic scattering cross section

For elastic neutron scattering from collinearly ordered magnetic moments, the scattered intensity can be obtained from Eq. (1):

\[
I(Q) \sim f(Q)^2 (1 - (\hat{Q} \cdot \hat{e})^2) |F_M(Q)|^2,
\]

where \( \hat{e} \) the direction of the staggered magnetization. There are three factors contributing to the intensity of magnetic Bragg peaks: the geometric factor \( 1 - (\hat{Q} \cdot \hat{e})^2 \), the magnetic structure factor \( F_M(Q) \), and the magnetic form factor \( f(Q) \).

We also need to consider magnetic domains due to the tetragonal symmetry of the crystal. Consider the two types of structure shown in Fig. 2, where only Cu spins are shown. In a realistic single crystal in zero magnetic field, these two types of magnetic domain can be equally populated. These two domains give rise to different magnetic reciprocal lattice vectors. As shown in Fig. 2, different domains give different CuII magnetic Bragg reflections, which will prove useful in elucidating the spin structure of the CuII magnetic lattice. The CuII magnetic peaks, on the other hand, only occur on top of allowed nuclear Bragg reflections, and do not occur in the \((H K 0)\) zone.

### C Inelastic scattering cross section

In conventional spin-wave theory for a two-sublattice antiferromagnet, one obtains two eigenmodes. If the spins are ordered in the \( z \)-direction, the two modes have eigenvectors in the direction of \( x \) and \( y \). For a Heisenberg model, these two modes are gapless Goldstone modes due to the continuous symmetry. However, in the presence of an uniaxial anisotropy, this continuous symmetry is broken, and both modes obtain energy gaps; this energy gap corresponds to the energy cost in rotating the spins away from the \( z \)-direction. For an XY anisotropy, only one mode has an energy gap, corresponding to the energy cost in rotating spins out of the \( xy \)-plane. The other mode is a zero-energy mode at \( q = 0 \), since the continuous symmetry is preserved in the \( xy \)-plane. Since the polarization of the eigenvector of the gapped mode is perpendicular to the \( xy \)-plane, we call this mode an out-of-plane mode, while the gapless mode is called an in-plane mode.

The direction of the eigenvectors plays an important role...
role in the neutron scattering cross section. By considering geometric factors for both domains in Fig. 3 one can show that the inelastic cross section from spin-waves reduces to

\[
\frac{d^2\sigma}{d\Omega dE_f} \sim f^2 (Q) \frac{k_f}{k_i} \left[ \frac{\left(1 + \cos^2 \phi \right)}{2} S^\parallel (Q, \omega) + \sin^2 \phi S^\perp (Q, \omega) \right]
\]

where \(\phi\) is the angle subtended by \(Q\) and \([0 0 1]\), and \(S^\parallel\) and \(S^\perp\) denote the dynamic structure factor of the in-plane and out-of-plane spin-wave modes, respectively. The out-of-plane component of the dynamic structure factor, \(S^\perp (Q, \omega)\), is well approximated by

\[
S^\perp (Q, \omega) = \frac{1}{\omega} \left[ \frac{1 + n(\omega_\perp)}{\Gamma^2 + (\omega_\perp - \omega)^2} + \frac{n(\omega_\perp)}{\Gamma^2 + (\omega_\perp + \omega)^2} \right],
\]

where \(n(\omega_\perp) = 1/(e^{\omega_\perp/T} - 1)\) is the Bose population factor, \(\Gamma^{-1}\) is a small magnon lifetime, and \(\omega_\perp\) is the out-of-plane gap. A similar relation holds for the in-plane component \(S^\parallel (Q, \omega)\) with \(\omega\parallel\) replacing \(\omega_\perp\).

### D Experimental details

We have carried out both inelastic and elastic neutron scattering experiments with the triple-axis spectrometers at the High Flux Beam Reactor (HFBR), Brookhaven National Laboratory, and at the National Institute of Standards and Technology, Center for Neutron Research (NCNR). Our measurements were done mostly on thermal beamlines at these facilities, except for the data shown in Fig. 13 which were obtained using cold neutrons. Large (dimension 2 \(\times\) 2 \(\times\) 0.5 cm\(^3\)) single crystals of \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\), grown by slow cooling of a melt containing a \(\text{CuO}\) flux, are used in the experiment. The crystals remain tetragonal (space group \(I_4/\text{mmm}\)) for 15\(K < T < 550\)K with lattice constants \(a = 5.457\)\(\AA\) and \(c = 12.52\)\(\AA\) at \(T < 50\)K.

The (002) reflection of pyrolytic graphite (PG) was used as both monochromator and analyzer. A PG filter was placed either before or after the sample to eliminate higher order contamination. Various experimental configurations with different sets of collimations and neutron energy were used. A typical setup used in the inelastic experiments was a fixed final neutron energy of \(E_f = 14.7\) meV and collimations of 40°−40°−Sample−40°−80°. The sample was sealed in an aluminum can filled with helium exchange gas, and mounted in a closed-cycle helium refrigerator. The temperature was controlled within ±0.2K in the range 10\(K < T < 400\)K.

### III. ANTIFERROMAGNETIC ORDERING OF COPPER SPINS

Since the 2D SLQHA does not have long-range order at \(T > 0\), such order must arise from spin anisotropy terms or inter-plane coupling. For \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\), as the Néel temperature is approached from above, successive crossovers from 2D Heisenberg to 2D XY to three-dimensional (3D) XY behavior are expected to take place, albeit with a 3D critical regime that is extremely narrow. For \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\), on the other hand, the inter-plane coupling between \(\text{Cu}_I\) spins, \(J_{1,3D}\), is larger than the XY anisotropy. Upon lowering the temperature in the paramagnetic phase, we then expect a crossover from 2D Heisenberg behavior, characterized by a spin-spin correlation length \(\xi_0(T)\) that increases exponentially in \(T^{-1}\), to 3D Heisenberg behavior at a temperature given by the relation \(\xi_0^2 J_{1,3D}/J_1 \sim 1\), where \(J_{1,3D}\) is the interplane coupling between \(\text{Cu}_I\) spins. In other words, we expect 3D effects to become important for \(\xi_0/a \sim 30\). The correlation length of the SLQHA is known to be about 40 lattice constants at \(T/J \simeq 0.26\). For \(J_1 \simeq 130\) meV, this corresponds to a temperature of \(~390\)K, which agrees with \(T_{N,1}\).

Unlike for the \(\text{Cu}_I\) subsystem, the isotropic inter-plane \(\text{Cu}_I\lbrack\text{Cu}_I\rbrack\) coupling is frustrated, similar to that of \(\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2\). Therefore, \(T_{N,1}\) is expected to be determined mostly by spin anisotropies, originating from both in-plane quantum fluctuations and from inter-plane dipolar and pseudodipolar interactions. For \(T < T_{N,1}\), the ordered \(\text{Cu}_I\) spins fluctuate mainly in the directions...
transverse to their staggered moment $M_{s,I}$. $J_{I-I}$ then generates fluctuations in the Cu$II$ spins along the same direction, causing an effective reduction in the corresponding transverse exchange components of $J_{I-II}$. This yields an effective biquadratic term $-\delta (S_I \cdot S_{II})^2$, where $\delta \propto J_{I-II}^2/(J_I + J_{II})$. This implies an effective Ising-like anisotropy $J_{I-II}^2 \propto \delta S_L^2$, which favors ordering of the Cu$II$ spins collinearly with $S_I$, consistent with our measured structure, Fig. 1(a). Indeed, $T_{N,II} \sim 40K$ agrees with $\xi(T_{N,II})^2 \propto 1$, where $\xi \sim 0.01$ is independently deduced from our spin–wave gaps, as discussed in Sec. V.D. We next show experimentally that the ordering direction of Cu$I$ spins is indeed parallel to that of the Cu$I$ subsystem, and that this ordering is a 2D Ising transition.

A Magnetic structure

The Cu$I$ spin ordering direction shown in Fig. 1 has been determined in previous magnetization measurements. This ordering is similar to that in a bilayer cuprate YBa$_2$Cu$_3$O$_6$. Unlike other “214” type materials, the Cu$I$ spins of “2342” have unique nearest neighbors in the c-direction, just like YBa$_2$Cu$_3$O$_6$. For such a structure, the observed ordering direction along the Cu–O–Cu bonds has been attributed to the quantum fluctuations.

Next, let us consider Cu$II$ magnetic diffraction peaks in the $(H \ K \ 0)$ zone. In Table 1, we summarize our results. The neutron energy was fixed at 14.7 meV, and collimations of $20'–40'–S–40'–80'$ were used. One can fit the peak intensities with Eq. (4) with $\hat{e}$ as a free parameter. The fit gives the spin direction shown in Fig. 2, namely, $\hat{e}$ along the [1 1 0] direction for domain A, and along the [1 1 0] direction for domain B. In order to determine how the copper oxide layers are stacked, we show in Fig. 3 the peak intensity for each magnetic Bragg peak in the $(H \ H \ L)$ zone. From the domain structure and the stacking scheme in Fig. 3, one can show that magnetic Bragg peaks occur at even $L$ due to domain A, together with magnetic Bragg peaks at odd $L$ due to domain B. Since our momentum transfer, $\mathbf{Q}$, is along the $(H \ H \ L)$ direction, $\mathbf{Q}$ is always perpendicular to the spin ordering direction, $\hat{e}$, in domain A. However, in domain B, this is not true, and $\hat{e} \cdot \mathbf{Q} = \sin \phi$. Therefore, the geometric factor only matters for the peaks from domain B. As shown in Fig. 3, only the odd-$L$ data exhibit the expected geometric factor dependence. In fact, the agreement is excellent between odd-$L$ data (triangles) and the calculation ($\times$). It should be noted that the stacking scheme of the Cu$II$ spins is identical to that of Sr$_2$CuO$_2$Cl$_2$.

In their study on YBa$_2$Cu$_3$O$_6$, Shimoto et al. reported an anisotropic Cu magnetic form factor, which depends not only on the magnitude of $\mathbf{Q}$, but also on the direction of $\mathbf{Q}$. Specifically, the magnetic form factor was found to drop more rapidly with increasing $Q$, if $\mathbf{Q}$ is perpendicular to the $L$-direction. The small deviation between the even-$L$ data (open circles) and the solid line at large $Q$ is probably due to this anisotropy in the magnetic form factor, since most of our large-$Q$ data has a relatively small $L$-component.

The magnetic Bragg peak intensity, for the Cu$I$ data is plotted for even-$L$ (open circle) and odd-$L$ (closed triangle). The solid line is a plot of magnetic form factor of free Cu$^{2+}$ ions. The symbol $\times$ represents the magnetic form factor squared multiplied by the geometric factor in Eq. (4). Clearly, even-$L$ data show the same $Q$-dependence as the magnetic form factor, while odd-$L$ data do not. The agreement between odd-$L$ data and the calculated results are very good.

B Order parameters

The antiferromagnetic Bragg intensity is proportional to the square of the staggered magnetization, $M_s$, which is the order parameter of the Néel ordered phase. We measured the temperature dependence of the $(1 \ 0 \ 1)$ peak, using neutrons with energy 13.4 meV and collimations of $20'–40'–S–40'–80'$. The temperature dependence of the magnetic Bragg intensity at the $(1 \ 0 \ 1)$ reciprocal lattice position is shown in Fig. 4(a). Since nuclear Bragg scattering is only weakly temperature dependent, we subtract the high-temperature $(1 \ 0 \ 1)$ nuclear intensity from the observed intensity. We also studied the temperature dependence of the $(3 \ 0 \ 1)$ peak, which shows the same temperature dependence as the $(1 \ 0 \ 1)$ peak.

We fit the $T > 300K$ data to the form $I \sim (T_N - T)^2\beta$, where
FIG. 5: (a) Filled circles are the integrated intensity of the 3D magnetic Bragg peak at (1 0 1). Open circles are the intensity on the 2D rod of Cu at (1 0 0.55). The peak intensity of (1/2 1/2 0) peak is plotted as filled circles. Open circles are the intensity on the 2D rod of Cu at (1 0 0.55). (b) Cu at (1/2 1/2 0). Solid lines are fits to the intensity of the 2D magnetic rod as a function of temperature. The solid line is the result of fitting data for $T > 30K$ with $T_{N,II} = 39.6(4)K$ and $\beta_I = 0.13(1)$. This strongly suggests that the ordering of the CuII spins is in the 2D Ising universality class. As discussed in Sec. IV, evidence from spin dynamics experiments is necessary to clarify this point.

Another way to probe the 3D magnetic ordering is to plot the intensity of the 2D magnetic rod as a function of temperature. Quasi-2D materials, such as K$_2$NiF$_4$, La$_2$CuO$_4$ [13] and Sr$_2$CuO$_2$Cl$_2$ [14] show strong 2D dynamic fluctuations above the 3D ordering temperature $T_N$; this is exhibited as rods of scattering perpendicular to the 2D plane, whose locations are shown in Fig. 3. One can observe this by accepting all energies of neutrons at the detector in the two-axis configuration. At $T_N$, the 2D inelastic scattering intensity begins to decrease rapidly, as the spectral weight is shifted from 2D inelastic scattering to 3D Bragg scattering. Therefore, this measurement shows the 2D nature of the system, as well as the 3D transition temperature, complementing the order parameter measurement. In Fig. 3(a) and (b), we show these 2D rod intensities at (1 0 0.55) and (0.5 0.5 0.25) for the CuI and CuII sublattices, respectively. Indeed, we see rapid decreases of both the CuI and the CuII 2D rod intensities as the system is cooled through their respective 3D Néel transitions. The non-zero intensity below the Néel temperature is due to the contributions from phonons.
TABLE II: Parameters used in the spin Hamiltonian [Eq. (8)]. These values are determined from our neutron scattering experiment. Superexchange energies are in units of meV and $\alpha$ is dimensionless.

| meaning | value |
|---------|-------|
| $J_{II}$ Cu$_I$–Cu$_I$ superexchange (in-plane) | 130(5) |
| $J_{I-II}$ Cu$_II$–Cu$_I$ superexchange | 10.5(5) |
| $J_{I-II}$ Cu$_I$–Cu$_II$ superexchange | -10(2) |
| $J_{I,3D}$ Cu$_I$–Cu$_II$ superexchange (out-of-plane) | 0.14(2) |
| $\alpha_I$ XY-anisotropy in $J_I$ ($T=200K$) | 5.2(9) $\times 10^{-4}$ |
| $\alpha_{II}$ XY-anisotropy in $J_{II}$ ($T=10K$) | 1(5) $\times 10^{-4}$ |

IV. SPIN DYNAMICS

The spin Hamiltonian used in the spin-wave calculation and the data analysis is as follows:

$$\mathcal{H} = \mathcal{H}_I + \mathcal{H}_{II} + \mathcal{H}_{int}$$

(7)

$$\mathcal{H}_I = J_I \sum_{\langle i,j \rangle_I} (\mathbf{S}_i \cdot \mathbf{S}_j - \alpha_I S_i^z S_j^z) + J_{I,3D} \sum_{\langle i,j \rangle_{I,3D}} S_i \cdot S_j$$

$$\mathcal{H}_{II} = J_{II} \sum_{\langle m,n \rangle_{II}} (\mathbf{S}_m \cdot \mathbf{S}_n - \alpha_{II} S_m^z S_n^z)$$

$$\mathcal{H}_{int} = J_{I-II} \sum_{\langle i,m \rangle_{I-II}} S_i \cdot S_m,$$

where $i,j$ and $m,n$ denote Cu$_I$ sites and Cu$_II$ sites, respectively. The symbols $\langle i,j \rangle_I$ and $\langle i,j \rangle_{I,3D}$ label Cu$_I$ intra-planar and inter-planar nearest neighbors, whereas $\langle m,n \rangle_{II}$ and $\langle i,m \rangle_{I-II}$ refer to the nearest-neighbor Cu$_II$–Cu$_II$ and Cu$_I$–Cu$_II$ bonds, respectively. The reduced exchange anisotropy, $\alpha = (J - J^2)/J$, is used here, and is therefore dimensionless. We left out other smaller terms, such as the in-plane anisotropy in $J_I$ and $J_{II}$, the pseudo-dipolar interaction between Cu$_I$ and Cu$_II$, $J_{int}$, the interplanar dipolar $\text{Cu}_I$–Cu$_II$ interaction, and the four-fold anisotropy terms. It turns out that these small terms do not affect the spin dynamics on the energy scale probed by thermal neutrons, although they are essential in explaining such behavior as the spin-flop transition or ESR experiment results.

A. Spin-wave theory

Our measured spin-wave energies can be explained within the framework of $T = 0$ interacting spin-wave theory (SWT). The theory is discussed in detail in Ref. 9. Here we give only a brief summary with the salient results. Starting from the spin structure shown in Fig. 49, we express each of the six spins (four Cu$_I$’s and two Cu$_II$’s) in the unit cell by the Dyson-Maleev transformation for general spin $S$. The sums in $\mathcal{H}_I$ and $\mathcal{H}_{II}$ are then truncated at the harmonic order in the spin-wave boson operators. However, the $\mathcal{H}_{int}$ 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 spin-wave operators by contracting operator-pairs in all possible ways. This yields new quadratic terms, whose coefficients contain the parameter $\delta = 2J_{I-II} (ac)/S$, where $a$ and $c$ are boson operators associated with Cu$_I$ and Cu$_II$, respectively. This coefficient contains the factor $1/S$, thus representing quantum corrections due to spin-wave interactions. The spin-wave energies are then found as the eigenvalues of the $6 \times 6$ matrix which arises from the resulting bilinear spin-wave Hamiltonian.

Since the magnetic unit cell contains 6 Cu spins, the spin-wave spectrum has six branches. Two of these are optical modes which are practically degenerate at $\omega = 4SZcJ_I$. In this paper we will only discuss the remaining four modes. The large in-plane spin-wave velocity for the Cu$_I$ spins makes it difficult to study the dispersion other than at the 2D zone center along the $L$ direction, where the mode energies can be found analytically. The energies of these modes at $T = 0$ for wavevectors $(1 0 L)$ are (in order of increasing energy)

$$\omega_1 = S \sqrt{32J_{II}\delta x_3/(\delta + 2x_3)}$$

(8)

$$\omega_2 = S \sqrt{32J_{II}\left(Z_0^2 J_{II}\alpha_{II} + \frac{2J_{II}Z_0^2 \alpha_{II} + x_3}{4J_{II}Z_0^2 \alpha_{II} + \delta + 2x_3}\right)}$$

(9)

$$\omega_3 = S \sqrt{8J_I \left[2x_3 + \delta \left(1 - \frac{J_{I-II}}{J_I} + \frac{J_{II}}{J_I \delta + 2x_3}\right)\right]}$$

(10)

$$\omega_4 = S \sqrt{8J_I \left[4Z_0^2 J_I \alpha_{II} + 2x_3 + \delta \left(1 - \frac{J_{I-II}}{J_I} + \frac{J_{II}}{J_I \delta + 2x_3 + 4Z_0^2 J_I \alpha_{II}}\right)\right]}$$

(11)

where $Z_0 = 1 + O(1/S) \approx 0.6$ is the quantum renormalization factor for the spin-wave anisotropy gap when $S = 1/2$, and $x_3 = Z_0^2 J_{I,3D} [1 + \cos(\pi L)]$, where $Z_0 = 1 + O(1/S) \approx 0.9$. In Eqs. (8-11) we have kept only
terms up to $O(1/S)$. 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. Note also that $J_{1,3D}$ and $J_{1,3D}$ appear always with the renormalization factors $Z_g$ and $Z_{II};$ thus, we can only determine the products $Z_g^2 J_{1,3D}$.

The physics of these modes can be deduced from the structure of the mode energies. Because only $\omega_2$ and $\omega_4$ involve the XY anisotropies, $a_1$ and $a_{II}$, we see that these modes are out-of-plane modes, i.e., modes in which the spins oscillate out of the easy plane. Correspondingly, $\omega_1$ and $\omega_3$ are in-plane modes in which the spins move within the easy plane. In this connection note that the energies for $\omega_1$ and $\omega_3$ can be obtained from $\omega_2$ and $\omega_4$, respectively, by omitting all factors which involve the XY anisotropies. Likewise, modes $\omega_3$ and $\omega_4$ involve $J_I$ and are hence modes which primarily exist on the CuII sublattice (CuII modes), whereas modes $\omega_1$ and $\omega_2$ involve $J_{II}$ and are modes which primarily exist on the CuI sublattice (CuI modes). From this it follows that the modes $\omega_1$ and $\omega_2$ will have high intensity near CuII Bragg positions and low intensity near CuI Bragg positions and conversely for the modes $\omega_3$ and $\omega_4$. Finally, we should point out that $\omega_1 \to 0$ as $q \to 0$ only because we have here neglected the small pseudodipolar interactions and four-fold anisotropy which lead to in-plane anisotropy.

One should be careful in determining the absolute value of the XY-anisotropy of the exchange coupling, since the quantum renormalization factor for the spin-wave gap ($Z_g$) is different from that of the spin-wave velocity ($Z_c$). Moreover, the value of $Z_g$ is not known accurately. $Z_g$ was first discussed by Barnes et al. in their Monte Carlo study of a Heisenberg-Ising antiferromagnet. They discovered that the anisotropy gap was almost a factor of two smaller than that of the ferromagnet. We also require that $Z_c$ has been known since Oguchi’s work, and a number of high-precision calculations of $Z_c$ have become available recently. The series expansion results by Singh and by Igarashi are $Z_c = 1.176$ and $Z_c = 1.1794$, respectively. The series expansion results by Singh and Gelfand are $Z_c = 1.176$ and $Z_c = 1.1794$, respectively. We use the Monte Carlo result of Beard et al., $Z_c = 1.174$.

As pointed out by Barnes et al., the factor $Z_g$ can be physically understood by considering the effect of fluctuations. Spin wave theory assumes a classical Néel ground state with a perfectly ordered moment, and the resulting dispersion relation is for the spin-waves propagating in such a background. Clearly, both quantum fluctuations and thermal fluctuations substantially reduce the ground-state alignment; long wavelength spin-waves thus see a “softened” antiferromagnetic background, and we see the renormalization of the gap, which is proportional to the staggered magnetization that is reduced from its classical value due to fluctuations. The effect of thermal fluctuations is well known from the studies of K$_2$NiF$_4$ and Sr$_2$CuO$_2$Cl$_2$, where the gap energy follows the temperature dependence of the order parameter. Analogously, quantum fluctuations also reduce the gap energy from the classical value even at zero temperature. In the $S = 1/2$ SLQHA, the zero temperature ordered moment is reduced by $\sim 40\%$. We use the renormalization $Z_g \sim 0.6$ from this fact.

2 Temperature dependence of the Mode Energies

As we shall see, fitting the experimentally determined mode energies to the expressions of Eqs. (12) suggests that the temperature dependence of $\delta$ is the same as that of $M_{II,II}$. Combining the zero temperature results with the random phase approximation results for $\delta = 0$ we propose to describe the mode energies at nonzero temperature (but for $x_3 = 0$) by

$$\omega_1^2 = 32J_II S_{II} \left( Z_g^2 J_{II} \alpha_{II} S_{II} + \frac{\delta_0 S^2_{II}}{S_I} \right)$$

$$\omega_2^2 = 8J_II S_{II}^2 \left( 1 - \frac{J_{II}}{J_I} \right)$$

$$\omega_3^2 = 8J_II S_I \left( 4Z_g^2 J_I \alpha_{I} S_I + \frac{\delta_0 S^2_{II}}{S_I} \right)$$

$$\omega_4^2 = 8J_II S_I \left[ 4Z_g^2 J_I \alpha_{I} S_I + \frac{\delta_0 S^2_{II}}{S_I} \left( 1 - \frac{J_{II}}{J_I} \right) \right],$$

where $S_I = S(1 - T/T_{N,I})^\beta_I, S_{II} = S(1 - T/T_{N,II})^\beta_{II}$, and $\delta_0$ is the value of $\delta$ for $T = 0$.

B $T > T_{N,II}$

At high temperatures ($T \gg T_{N,II}$), we can ignore the CuII’s and treat the CuI system as a two-sublattice anti-
position is given by
\[
\omega_\perp = 4SJ_1 \left[ 2Z^2_0 \alpha_I + Z^2_e (q_{2D} \delta)^2 \right]^{1/2} + \frac{Z^2_e J_{1,3D}}{J_1} (1 + \cos (\pi L))^{1/2}.
\]

Here, \( q_{2D} \) is the momentum transfer in the plane, \( q_{2D} = \frac{2\pi}{\sqrt{(H-1)^2 + K^2}} \), and \( a \) is the lattice constant. Note that the distance between the Cu-I-Cu nearest neighbors is \( a/\sqrt{2} \). The in-plane mode, \( \omega_\parallel = \omega_2 \), has the same dispersion relation, with \( \alpha_I \) replaced by zero, because we assume zero in-plane anisotropy.

From a measurement of the spin-wave dispersion along \([1 0 L]\), it is then possible to extract both \( \alpha_I \) and \( J_{1,3D} \), using Eq. \( (13) \). In Fig. \( 4 \) such measurements are shown. We have chosen a relatively high temperature of \( T = 200K \approx T_{N,I}/2 \) in order to take advantage of the magnon population factor \( n(\omega) \) in the cross section. The experiment was carried out in the constant-\( Q \)-mode, in which the final neutron energy was fixed at \( E_F = 14.7\text{meV} \) and the spectrometer was set to operate in the neutron energy loss configuration. A horizontal collimation sequence \( 20'–40'–S–80'–80' \) was employed, which resulted in energy resolutions (full width) between \( \sim 1.4 \) and \( \sim 1.7\text{meV} \) for energy transfers between 3 and 12\text{meV}. In this figure, \((1 0 1)\) is the zone center and \((1 0 2)\) is the zone boundary. In order to show that the gap \( 7\text{meV} \) for energy transfers between 3 and 12\text{meV}. In this figure, \((1 0 1)\) is the zone center and \((1 0 2)\) is the zone boundary. In order to show that the gap energy, indicated by the arrows, is slightly smaller than the apparent peak position, and the peaks appear to have wider widths than the resolution.

The summary plot in Fig. \( 9 \) clearly shows the change in the out-of-plane gap. In previous studies of the tetragonal SLQHA \( K_2\text{NiF}_4 \) \((S = 1/2)\) and \( \text{Sr}_2\text{CuO}_2\text{Cl}_2 \) \((S = 1/2)\), it has been found that the gap energies exhibit the same temperature dependences as the respective order parameters throughout the entire ordered phase. As discussed above in Sec. \( VA \), this is due to the softening of the anti-ferromagnetic background by thermal fluctuations. Figure \( 8 \) shows constant-\( Q \) scans at various temperatures at the Brillouin zone center \((1 0 1)\). The data can be fitted well with Eq. \( (1) \); the fitting results are shown as solid lines in the figure. Due to the steep in-plane dispersion, the fitted gap energy, indicated by the arrows, is slightly smaller than the apparent peak position, and the peaks appear to have wider widths than the resolution.

The summary plot in Fig. \( 9 \) clearly shows the change

\[
\omega_\perp = 4SJ_1 \left[ 2Z^2_0 \alpha_I + Z^2_e (q_{2D} \delta)^2 \right]^{1/2} + \frac{Z^2_e J_{1,3D}}{J_1} (1 + \cos (\pi L))^{1/2}.
\]
of the gap energy as a function of temperature. As expected, \( \omega_3 \) follows the Cu\(_{II} \) order parameter from \( T_{N,II} \approx 40 \text{K} \) up to \( T_{N,I} \). However, a large increase is observed below \( T_{N,II} \). Further new low-energy features appear below 40K. We discuss this dramatic behavior of the long-wavelength spin-waves below 40K in the next subsection.

### C \( T < T_{N,II} \)

The dramatic behavior of the low-energy, long-wavelength spin waves at \( T < T_{N,II} \) results from the effective biquadratic interaction, \( \delta \), produced by quantum fluctuations. We now discuss the effect of \( \delta \) on the spin-wave energies on the basis of Eqs. (8-11). The energy of the out-of-plane mode \( \omega_4 \) increases dramatically as the Cu\(_{II} \) spins order and \( \delta \) comes into play. For the in-plane mode the effect of \( \delta \) is even more dramatic because in the absence of in-plane anisotropy, its energy is zero for \( \delta = 0 \). The existence of the out-of-plane mode \( \omega_2 \) requires long-range order of the Cu\(_{II} \) subsystem. Here nonzero \( \delta \) causes an increase in the out-of-plane anisotropy (from \( J_{II} \alpha_{II} \) to approximately \( J_{II} \alpha_{II} + 2J_I \alpha_I \)) because the quantum fluctuations strongly couple the two subsystems. As mentioned above, the effective biquadratic exchange does not create an energy gap in the mode \( \omega_1 \).

1. The Cu\(_{II} \)-like modes

The peak in our data for \( T < 40 \text{K} \), in Fig. 8, is identified as an overlap of peaks from the \( \omega_3 \) and \( \omega_4 \) modes. These spin-wave modes could not be resolved due to both the steep in-plane dispersion of the Cu\(_{II} \)-like mode and the existence of a nearby phonon peak. However, one can obtain indirect evidence for the correctness of this description by exploiting the different polarizations of the \( \omega_3 \) and \( \omega_4 \) modes. In Fig. 10(a), we compare scans at the \((1 0 \bar{1})\) position and the \((1 0 7)\) position. The data at the \((1 0 \bar{1})\) position can be satisfactorily fitted with both a single peak and two peaks. Specifically, the dashed line in Fig. 10(a) assumes \( \delta \) is zero in Eq. (11), so that there is only one energy gap from \( \omega_4 \). The solid line assumes non-zero \( \delta \), thus producing a double peak feature: both...
ω₃ and ω₄. Using the same set of parameters obtained from fitting the (1 0 1) data, we plot the solid and dashed lines for the peak profile at (1 0 7). Evidently, an in-plane gap (ω₃) is necessary to explain the data at (1 0 7), where the contribution of the out-of-plane mode becomes very small due to the geometric factor. Therefore, we have shown that this peak below 40K results from an overlap of ω₃ and ω₄. We have, therefore, fitted all of the data assuming that there are two modes. We emphasize that for T < T_{N,II}, the non-zero energy of ω₃(q = 0) is a pure quantum effect; the close values of ω₃ and ω₄ simply reflect the fact that the effective anisotropy associated with δ is larger than the intrinsic Cu out-of-plane anisotropy αₐ [see Eqs. (10) and (11)], thus illustrating the quantitative importance of quantum fluctuations.

We have measured the dispersion along the L-direction of the ω₃ and ω₄ modes for T < T_{N,II}. Each scan is fitted with the cross section containing both ω₃ and ω₄. The fitting results are shown in Fig. 10(b) as filled and open circles for ω₃ and ω₄, respectively. The solid lines in Fig. 10(b) are drawn using Eqs. (10-11) and (13-14), with δ₀ = 0.26(4)meV determined by fitting ω₃ with fixed Jᵢ = 130meV. Note that we have assumed the temperature dependence of δ as discussed in Sec. IV A 2. Using the theoretical relation δ₀ = 0.3372(Jᵢ−II) / Jᵢ = 0.26 from Ref. 49, we obtain |Jᵢ−II| = 10(2) meV, in excellent agreement with the earlier magnetization study.

2 The Cu_{II}-like modes at (1 0 1)

The low-energy mode that appears at temperatures below 40K is attributed to ω₂. At least two experimental observations support this identification. In Fig. 11(a), we compare this mode at different L positions; the peak evident at the (1 0 1) position disappears at the (1 0 7) position, thus proving that this gap is an out-of-plane mode. Next, in order to show that this mode is Cu_{II}-like, the (1 0 1) scan is compared with the scan at the (1.02 0 1) position in Fig. 11(b). Although there is no discernible peak at (1.02 0 1), the remaining intensity

FIG. 9: Temperature dependence of the spin-wave gap at the 3D zone center (1 0 1). Open triangles, filled circles and open circles denote ω₂, ω₃, and ω₄, respectively. Solid, dashed, and dot-dashed lines represent respective spin-wave calculation, Eq. (12-14). Inset: Same data plotted in a different scale to magnify the low temperature region.

FIG. 10: (a) Constant-Q scan of the spin-wave gap at the 3D zone center at 10K. The (1 0 1) scan shows an overlap of in-plane (ω₃) and out-of-plane (ω₄) mode, while the scan at (1 0 7) is almost entirely in-plane mode, due to the geometric factor of the neutron cross section. The baseline of the (1 0 7) data is offset by 50. The solid and dashed curves are fits for two peaks and one peak, respectively. (b) Dispersion along L of Cu_{II}-like modes at T=30K.
is consistent with the calculation using the CuII spin-wave velocity (∼95meVÅ). If the CuI spin-wave velocity (∼830meVÅ) is used instead, the dashed line is obtained, which is basically at the background level. Therefore, this low-energy feature is the CuII-like out-of-plane mode: \(\omega_2\).

In Fig. 11(c), the temperature dependence of the \(\omega_2\) gap at the (1 0 1) position is shown. As expected, the \(\omega_2\) gap vanishes for \(T > 40K\). The temperature dependence of \(\omega_2\) is summarized in Fig. 8 as open triangles. The lines in Figs. 8 correspond to Eqs. (2-3-4). The agreement between the calculation and the experimental results over the entire temperature range is excellent, if one takes into account the inherent difficulty in resolving \(\omega_4\) and consequent large error bars for \(\omega_4\).

The dispersion of \(\omega_2\) along \(L\) at \(T = 12K\) is shown in Fig. 11(d); the summary is plotted in Fig. 8(b) as open diamonds. The solid lines in Fig. 8(b) for \(\omega_1\) and \(\omega_2\) have no adjustable parameters; all the parameters have been determined independently from separate measurements. We set \(\alpha_{II} = 0\), since our least square fit of the data to Eq. 4 yields \(\alpha_{II} = 0.0001(5)\), which is indistinguishable from zero.

The \(\omega_1\) mode could not be identified as a distinct mode in our experiment, due to the presence of an acoustic phonon. Note that the (1 0 1) position is a nuclear Bragg position as well as a magnetic zone center. However, in a recent study, Katsumata et al. reported an observation of antiferromagnetic resonance modes at \(T = 1.5K\) using the ESR techniques. They showed that there are two modes: an out-of-plane mode at 422.5 GHz (∼1.75meV) in good agreement with our \(\omega_2\) value \(\omega_2(T \to 0) \approx 1.72\)meV, and an in-plane mode at 36.1 GHz (∼0.15meV), which is too small to be observed with thermal neutrons. These results are plotted as filled diamonds in Fig. 11.

Therefore, the combined inelastic neutron scattering results and spin-wave calculations in Figs. 7 and 8 clearly demonstrate the success of our model Hamiltonian in explaining the observed temperature and momentum dependences of the spin-waves.

### 3 The CuII-like modes at (1/2 1/2 0)

The discussion so far has been of the excitations observable near the reciprocal lattice vector (1 0 1), the CuI magnetic Bragg peak position. Unlike the spin-wave energy, which depends only on the reduced wave vector \(q = Q - G\), the neutron scattering intensity from spin waves depends also on the reciprocal lattice vector \(G\). The neutron scattering intensity is strong near an antiferromagnetic \(G\), or (π π) position, while it is weak near a nuclear Bragg position, (0 0). From the spin-wave calculation, we have found that the CuII-like modes have very large intensity near the CuII magnetic Bragg position, while the CuI-like modes have vanishingly small intensity. Although the CuII-like modes have large intensity near (1/2 1/2 L), as illustrated in Fig. 12(a), a rather complex dispersion relation results due to the presence of different magnetic domains (see Fig. 8). Spin-waves from domain A are shown as dashed lines, while those from domain B are shown as solid lines in the figure. Therefore, one expects to observe three or four peaks within an 1 meV range around \(\omega = 2.5\) meV from neutron scattering; this is an extremely difficult task, considering that the experimental resolution is about 0.2 – 0.3meV in this energy range with cold neutrons.

Representative scans are plotted in Fig. 12(c); the data have been taken at the SPINS spectrometer at the NCNR with collimations of 30–80°–S–80°–100°, and with the final neutron energy fixed at 5 meV. The solid line and the
The constant-Q scan reveals that there is more than one mode in the 2 to 3 meV energy range, roughly coinciding with the theoretical prediction. Note that the theoretical prediction, shown as solid and dashed lines in Fig. 12(a), is obtained with parameters determined from previous sections, and thus contains no adjustable parameters. Second, in agreement with the theoretical prediction, one of these modes is an in-plane mode and the other an out-of-plane mode. However, more experiments with higher resolution will be valuable in understanding the observed spin-wave dispersion.

D Spin-wave dispersion of Cu\textsubscript{II} in the plane

Because \(J_{\text{II}}\) is relatively small, the Cu\textsubscript{II} zone-boundary spin-wave energies are low enough to be accessed with thermal neutrons. We have measured spin-waves in the \(ab\)-plane, along the high-symmetry directions. The experiment was conducted at 10K, which is well below \(T_{N,\text{II}}\), and in the \((H K 0)\) zone; that is, \(ab\)-plane is in the scattering plane. Both constant-\(\omega\) scans and constant-Q scans were carried out. Some typical constant-\(\omega\) scans, along the \([1 1 0]\) direction, are shown in Fig. 13(a). The solid lines are obtained from a least-square fit to the cross section, convoluted with the instrumental resolution. Examples of constant-Q scans along the zone boundary are shown in Fig. 13(b).

Our zone boundary data exhibit a double-peak structure. The feature at the high energy is the spin-wave, while the low-energy feature is a phonon. We have verified the different nature of the scattering of the two features by measuring the respective peak intensities at equivalent reciprocal lattice positions with larger \(|Q|\). Such measurements at \((\frac{3}{2} 1 0), (\frac{5}{2} 1 0), (\frac{3}{2} 1 0)\), and \((\frac{3}{2} 1 0)\) are shown in Fig. 13(c): The intensity of the low-energy feature increases approximately as \(\sim |Q|^2\), characteristic of phonon scattering, while the intensity of the second feature is nearly independent of \(|Q|\).

Figure 14 summarizes our results. From the zone boundary spin-wave energy of 25meV one can deduce \(J_{\text{II}}\) rather accurately as \(J_{\text{II}} = 10.5(5)\)meV, in excellent agreement with the value deduced in Ref. 21 from the Cu\textsubscript{II} susceptibility. The gap energy at the zone center, \(\sim 3\)meV, corresponds to the modes found at \(L = 0\) in Fig. 12. Away from the 2D zone center, \(\omega_1\) and \(\omega_2\) from both domains are degenerate and can be approximated as the excitations of a simple SLQHA with the exchange interaction \(J_{\text{II}}\). The long-wavelength effects of the spin-wave interactions can be absorbed into an effective anisotropy \(\alpha_{\text{eff}}^{\text{II}}\). With \(\alpha_{\text{II}} \approx 0\), Eq. (8) can be interpreted as resulting from an effective anisotropy given by \(J_{\text{II}}\alpha_{\text{eff}}^{\text{II}} = 2J_{\text{II}}\alpha\delta/(4J_{\text{II}}\alpha + \delta) \approx 0.1\)meV, or \(\alpha_{\text{eff}}^{\text{II}} \approx 0.01\).

Simple linear SWT with \(\alpha_{\text{eff}}^{\text{II}} = 0.01\) and \(J_{\text{II}} = 10.5\)meV gives the dashed line in Fig. 14. This is a good approximation, except for the dispersion near the zone.
edge (π 0). As seen by the continuous line, our data are in much better agreement with a recent series expansion prediction by Singh and Gelfand. This theory predicts a local minimum at the zone boundary position (π 0), lower by about 7% than the value at (π 2 — π 2). A non-zero dispersion along the zone boundary may also result from a non-zero next-nearest-neighbor interaction J_II^nn, within linear SWT. The magnitude of the dispersion between (π 0) and (π 2 — π 2) is given by 2S J_II^nn. Considering that J_II is already of order 10 meV and the next-nearest-neighbor distance is large (~7.7 Å), it is unlikely that the next nearest neighbor effects contribute strongly to the observed zone–boundary energy difference of ~2 meV in Sr_2Cu_3O_4Cl_2.

Therefore, this dispersion can be regarded as a pure quantum mechanical effect for the S=1/2 nearest neighbor Heisenberg model. Canali et al. obtained similar but smaller zone boundary dispersion in their higher order SWT. They calculated the correction to Z_c up to 1/S^2 order, and found that the correction is not uniform along the zone boundary, giving ~2% dispersion. In their spin-rotation-invariant theory, Winterfeldt and Ihle also obtained a local minimum at the (π 0) position which is smaller than the energy at the (π 2 — π 2) position by almost 10%. Recent quantum Monte Carlo study by Syljuåsen and Rønnow also gives similar zone boundary dispersion of 6%, in good agreement with the series expansion result and our experimental result.

V. MAGNETIC CORRELATION LENGTH

The static structure factor provides valuable information about thermodynamic quantities such as the correlation length. As discussed in Sec. I, the necessary energy integration can be done automatically, in low-dimensional systems, via a 2-axis neutron scattering technique. In this section, we present our neutron scattering results from such 2-axis measurements, for both the Cu_I and Cu_II subsystems at temperatures higher than their respective Néel temperatures.

A. Cu_I system

The magnetism above T_{N,I} of the Cu_I system is essentially the same as that of La_2CuO_4 or Sr_2CuO_2Cl_2. The difference in the inter-plane coupling is not important at temperatures well above T_{N,I}. The only difference is the antiferromagnetic superexchange J_I, which is estimated...
to be 132(4)meV for La$_2$CuO$_4$ from the neutron scattering experiment.\cite{Greven2012} Greven et al.\cite{Greven2012} extracted 125(6)meV for Sr$_2$CuO$_2$Cl$_2$ from the two magnon Raman scattering experiment by Tokura and coworkers.\cite{Tokura1985} The Cu–O–Cu superexchange energies as well as in-plane lattice constants in these materials are compared in Table III, where the value for $J_I$ in Sr$_2$Cu$_3$O$_4$Cl$_2$ is extracted from our correlation length data.

The cross section for an energy integrating scan across the Cu$_I$ 2D fluctuations is given by

$$I(q_{2D}) \approx \int_{-\infty}^{E_i} dq S(Q, \omega)$$  \hspace{1cm} (16)

$$\approx [(\sin^2 \phi)S^T(q_{2D}) + (\sin^2 \phi + 2\cos^2 \phi)S^L(q_{2D})],$$

where $q_{2D} = \frac{2\pi}{\lambda} |H - 1|$, and $S^T$ and $S^L$ are the transverse and longitudinal components of the static fluctuation. Here $\phi$ is the angle between $Q$ and [0 0 1]. At temperatures well above $T_{N,I}$ only the Heisenberg term is relevant in the Hamiltonian. In this regime the system is effectively isotropic; that is, $S^T \approx S^L$.

The neutron scattering data shown in Fig. 15(a) were obtained with the incoming neutron energy fixed at $E_i = 36.4$ meV and a collimation sequence of 10’–13’–S–10’. Higher order neutrons were filtered by both PG and sapphire filters. The data were fitted to a simple 2D Lorentzian convoluted with the instrumental resolution:

$$S(q_{2D}) = \frac{S_{0}\kappa^{-2}}{q_{2D}^2 + \kappa^2},$$  \hspace{1cm} (17)

where the width of the Lorentzian $\kappa = \xi^{-1}$ is equal to the inverse correlation length.

The fitting results for the inverse correlation length, $\kappa$, are shown in Fig. 15(a) as open diamonds. We have also used $E_i = 13.7$meV neutrons to improve the resolution at lower temperatures; these results are shown as open circles in the same plot. We also plot the quantum Monte Carlo data from several studies.\cite{Greven2012, Tokura1985} The solid line is the renormalized classical (RC) expression of the QNLM:\cite{Greven2012, Tokura1985}

$$\xi = \frac{e}{8\pi} \frac{v}{a} \frac{\rho_s}{2\pi}\exp \left( \frac{2\pi\rho_s}{T} \left[ 1 - 0.5 \frac{T}{2\pi\rho_s} + O \left( \frac{T}{2\pi\rho_s} \right)^2 \right] \right),$$  \hspace{1cm} (18)

where $\rho_s$ is the spin stiffness constant and $v$ is the spin-wave velocity. For the $S = 1/2$ SLQHA, a recent Monte Carlo study by Beard et al.\cite{Beard2012} obtains $\rho_s/J = 0.1800(5)$ and $v/Ja = 1.657(2)$, and we have used these values substituted into Eq. (18) to obtain the solid line in Fig. 15(a). Although our data have large error bars, the general agreement between our experimental results and both theoretical results is quite good. We extract the value of $J_I$ by comparing our data with quantum Monte Carlo results: $J_I = 130(5)$ meV. The experimental data deviate from the 2D Heisenberg prediction as the temperature approaches $T_{N,I}$ from above, since the system crosses over to 3D Heisenberg behavior due to the inter-plane coupling $J_{IAD}$. We also show the fitting results for the Lorentzian amplitude $S_0\kappa^{-2} = S_0/\xi^2$ in Fig. 15(b). For the QNLM, this quantity is predicted to behave as $\sim T^2$ at low temperatures, while various neutron scattering studies\cite{Greven2012, Tokura1985} reveal the empirical behavior $S_0/\xi^2 \sim$constant. Our data are compared with these two scaling behaviors in Fig. 15(b). The solid line is $\sim T^2$, while the dashed line is a constant; these lines are rescaled to fit the data. One should, however, note that the low temperature data (below 400K) probably do not show true 2D Heisenberg behavior but a crossover to 3D Heisenberg behavior, and they should be excluded in the comparison. Within experimental error bars, both lines 

| $J_I$ (meV) | $S_{0}$ | $\rho_s$ | $v/Ja$ |
|------------|--------|---------|--------|
| 130(5)     |        |         |        |

and $v/Ja = 1.657(2)$, and we have used these values substituted into Eq. (18) to obtain the solid line in Fig. 15(a). Although our data have large error bars, the general agreement between our experimental results and both theoretical results is quite good. We extract the value of $J_I$ by comparing our data with quantum Monte Carlo results: $J_I = 130(5)$ meV. The experimental data deviate from the 2D Heisenberg prediction as the temperature approaches $T_{N,I}$ from above, since the system crosses over to 3D Heisenberg behavior due to the inter-plane coupling $J_{IAD}$. We also show the fitting results for the Lorentzian amplitude $S_0\kappa^{-2} = S_0/\xi^2$ in Fig. 15(b). For the QNLM, this quantity is predicted to behave as $\sim T^2$ at low temperatures, while various neutron scattering studies\cite{Greven2012, Tokura1985} reveal the empirical behavior $S_0/\xi^2 \sim$constant. Our data are compared with these two scaling behaviors in Fig. 15(b). The solid line is $\sim T^2$, while the dashed line is a constant; these lines are rescaled to fit the data. One should, however, note that the low temperature data (below 400K) probably do not show true 2D Heisenberg behavior but a crossover to 3D Heisenberg behavior, and they should be excluded in the comparison. Within experimental error bars, both lines 

![Figure 15](image-url)
describe our data equally well.

**B CuII system**

The CuII two-axis cross section is given by

\[ I(q_{2D}) = \int_{-\infty}^{-E_i} d\omega S(Q, \omega) \]

\[ \sim [(2 + \sin^2(\phi))S^T(q_{2D}) + (1 + \cos^2(\phi))S^L(q_{2D})], \]

where \( q_{2D} = \frac{2\pi}{a} \sqrt{(H - \frac{1}{2})^2 + (K - \frac{1}{2})^2} \), and \( S^T \) and \( S^L \) are the transverse and longitudinal components of the static fluctuations. \( S^L \) diverges at the Ising ordering temperature \( T_{N,II} \). The particular geometric factors result from the fact that the CuII easy-axis lies within the copper oxide layers and that there exist two types of domains that are equally probable. This gives an almost 3 to 1 ratio of transverse to longitudinal components when \( L \) is small, making it difficult to observe longitudinal fluctuations. In K\(_2\)NiF\(_4\), where the easy-axis is perpendicular to the NiF\(_2\) plane, this ratio is close to 1:1, enabling one to observe readily the longitudinal (Ising) component of the static structure factor.

Our experiment was carried out with \( E_i = 14.7 \text{ meV} \) and with collimations 20'–40'–S–40'. Representative scans are shown in Fig. 15(b). At higher temperatures, we used \( E_i = 30.5 \text{ meV} \) in order to ensure that the energy integration is done properly, since the characteristic energy scale becomes large at these temperatures. We could not distinguish the longitudinal component from the transverse component; therefore, the solid lines in Fig. 15(b) are results of fits to a single 2D Lorentzian, Eq. (17), convoluted with the experimental resolution. The so-obtained correlation lengths versus temperature are plotted in Fig. 17(a). Also shown are Monte Carlo results for the \( S = 1/2 \) nearest-neighbor SLQHA. At temperatures well above \( T_{N,II} \) the spin system is effectively isotropic, and the correlation length agrees very well with
the numerical result. However, even at lower temperatures the agreement is quite good, since the transverse term in the cross section is 3 times larger than the longitudinal term. In addition, Ising criticality has a very small critical temperature range. As the temperature is lowered, the crossover from the 2D Heisenberg to the 2D Ising symmetry presumably occurs very close to the transition temperature, \( T_{N,II} \), and hence isotropic behavior is observed for \( T \gtrsim T_{N,II} \). We also show the static structure factor peak amplitude \( S_0 \) in Fig. 17(b) along with the Monte Carlo results from Ref. 66. Similar to the inverse correlation length data, the agreement is quite good for all \( T \gtrsim T_{N,II} \).

At temperatures below \( T_{N,II} \), the inverse correlation length shows a saturation around 0.025\( \text{Å}^{-1} \). In their study of the 2D antiferromagnets, Birgeneau et al. showed that the transverse susceptibility dominates below the Néel temperature and it can be described via spin wave theory. In the presence of an Ising anisotropy, \( \alpha \), a typical spin wave dispersion is given as \( \omega_q \propto \sqrt{8J^2Z_\alpha^2 + v^2q^2/2} \) and the spin wave intensity is proportional to \( 1/\omega_q \), where \( v \) is the spin wave velocity, \( 2S\sqrt{Z_c}Ja \). For \( \omega/T \ll 1 \), the population factor is reduced to \( \omega_q^{-3} \). Thus the neutron scattering intensity of the wave vector dependent susceptibility is

\[
I \sim \omega_q^{-2} \sim \frac{1}{Z_c^2J^2a^2q^2 + 8J^2Z_\alpha^2} \sim \frac{1}{q^2 + \kappa_\perp^2}, \tag{20}
\]

which is a Lorentzian with a finite width, \( \kappa_\perp = \frac{v}{2a\sqrt{2}Z_c} \). By substituting \( \kappa_\perp \approx 0.01 \) for the \( \alpha \), we obtain \( \kappa_\perp \approx 0.026\text{Å}^{-1} \). This value, indicated as a solid line in the figure, agrees remarkably well with the experimental results.

In Fig. 18 the correlation length data for \( T > 43 \text{K} \) are plotted as a function of inverse temperature on a semi-log scale. Also plotted are the correlation length data of Sr\(_2\)CuO\(_2\)Cl\(_2\) taken from Ref. 7. These neutron scattering data are compared with various theoretical predictions. The RC expression for the correlation length is plotted as a dot-dashed line. Quantum Monte Carlo results and high temperature series expansion results are shown as solid and dotted lines, respectively. In a recent theoretical study, Cuccoli et al. treated quantum fluctuations in a self-consistent Gaussian approximation, separately from the classical contribution. This purely-quantum self-consistent harmonic approximation (PQSCHA) result is plotted as a dashed line in Fig. 18. The combined experimental data span almost two orders of magnitude in correlation length and show quantitative agreement with the Monte Carlo results without any adjustable parameters. At high temperatures, \( \xi/a \lesssim 10 \), both the series expansion and the PQSCHA, which corresponds to classical scaling, agree with the experimental data within error bars. The surprisingly good agreement between the neutron scattering data and the renormalized classical prediction even up to a very high temperature turns out to be a fortuitous one. Beard et al. pointed out that the renormalized classical scaling sets in only at large correlation lengths so that the temperature range probed by the neutron scattering experiment \( (T \gtrsim 0.2J) \) is not low enough to see this asymptotic scaling behavior. However, the deviation is smaller than the experimental errors, making it difficult to discern any discrepancies from the neutron scattering experiment.

There are two other recent neutron scattering studies on the magnetic correlation length of the \( S = 1/2 \) SLQHA. Birgeneau et al. extended previous work on La\(_2\)CuO\(_4\) to higher temperature and showed that the data are well-described by the Monte Carlo, the PQSCHA, and series expansion results within the experimental uncertainties. They also showed that there is no evidence for a crossover from renormalized classical to quantum critical behavior, at least from the correlation length data. Ronnow et al. also have carried out a study of the correlation length in the monoclinic planar antiferromagnet copper formate tetra-deuterate
CFTD). They obtained essentially similar results to those shown here for the CuII system, agreeing with the Monte Carlo data up to a very high temperature \( T \approx 1.25J \). They were able to extend their measurement to such a high temperature by employing a special technique involving filtering out the elastic part of the signal, thus reducing the incoherent background. However, the analysis depends sensitively on the theoretical model, especially on the scaling of the characteristic energy scale \( \Gamma_{\eta=0} \), which still needs further investigation. Besides, its low-symmetry crystal structure and relatively large Dzialoshinsky-Moriya interaction make CFTD a less ideal system than Sr\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) (CuII). In fact, the combined Sr\(_2\)Cu\(_2\)O\(_2\)Cl\(_2\)-Sr\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) (CuII) system forms an ideal model: \( S = 1/2 \) SLQHA over a large temperature range \( 0.2 \lesssim T/J \lesssim 0.75 \).

In Fig. 19, the Lorentzian amplitude of the structure factor, \( S_0(\xi/a)^{-2} \), is plotted as a function of \( T/J \). Our data and the La\(_2\)CuO\(_4\) data of Birgeneau et al. are scaled to match the Monte Carlo results, which are plotted in absolute units without any free parameter. The RC prediction is also plotted as a solid line: 

\[
\frac{S_0}{\xi^2} = A_2 \pi M_2^2 \left( \frac{r}{2\pi \rho} \right)^2,
\]

with \( A_{S=1/2} = 3.2 \) from the series expansion study. The first thing to note in our data is the disappearance of the divergence at \( T_{N,II} \), which implies that the divergence in \( S_0 \) is absorbed by the \( \xi^2 \) term, or equivalently \( \eta = 0 \), as predicted for the 2D Heisenberg model. On the other hand, the critical exponent \( \eta \) for the 2D Ising model is exactly known to be \( \eta = 1/4 \); thus \( S_0(\xi^{-2} / \xi^2 - 1) \) should show a weak divergence of \( \xi^{-1/4} = (T_N - T)^{-1/4} \), which is not observed. This is not surprising, since the finite Q-resolution prevents us from observing even the strong divergence of \( \xi \) in the first place.

What is surprising, however, is the discrepancy observed at high temperatures between the two experimental sets of data. Unlike La\(_2\)CuO\(_4\), which shows constant \( S_0(\xi^{-2}) \) over the observed temperature range, the CuII system shows some temperature dependence. Specifically, \( S_0(\xi^{-2}) \) follows the Monte Carlo data closely for \( T \gtrsim 0.4J \) and deviates significantly from the RC prediction at high temperatures. \( S_0(\xi^{-2}) \) for Sr\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\) also shows behavior similar to that of La\(_2\)CuO\(_4\). Considering that CFTD has less ideal properties of these systems, SrCu\(_2\)O\(_4\)Cl\(_2\), quantum effects may be important in understanding the low temperature properties of these systems.

The second nearest neighbor interaction in the copper oxide plane of the high temperature superconductors has the same superexchange path as the CuII–CuII interaction; namely, the Cu–O–O–Cu path. Of course, the CuII–CuII interaction has additional contributions from

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**VI. DISCUSSION**

From our study, we have been able to determine two very important superexchange interactions: one is the "edge-sharing" CuI–O–CuII exchange interaction, and the other is the CuII–CuII interaction, which corresponds to the second nearest neighbor interaction in the CuI square lattice. First, we estimate the isotropic CuI–CuII interaction as \( J_{I-II} \approx -10\text{meV} \). This edge sharing superexchange interaction is crucial in understanding spin ladder materials, SrCu\(_2\)O\(_3\) and Sr\(_{14}\)Cu\(_{24}\)O\(_{41}\), as well as other 1D spin systems, such as SrCuO\(_2\) (\( S = 1/2 \) zigzag chain) and CaCu\(_2\)O\(_3\) (buckled ladder). It has been assumed that the edge sharing interactions, which happen to be frustrated in all these materials, are small, and that they therefore can be ignored in data analysis. However, as we have seen in Sr\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\), quantum effects may be important in understanding the low temperature properties of these systems.

The second nearest neighbor interaction in the copper oxide plane of the high temperature superconductors has the same superexchange path as the CuII–CuII interaction; namely, the Cu–O–O–Cu path. Of course, the CuII–CuII interaction has additional contributions from...
the path Cu–O–Cu–O–Cu; however, one would expect this contribution to be small in magnitude; it should also be ferromagnetic. Thus, we can assume that the second nearest neighbor coupling in the copper oxide plane must be close to the $J_{II}$ value: $\sim 10$ meV. This value is used to fit the ARPES data in the framework of the $t-t'-t''-J$ model by Kim et al., which shows good agreement.

One expects interesting physics to arise from doping this system with either charge carriers or non-magnetic impurities. One difficulty of studying doped Sr$_2$Cu$_3$O$_4$Cl$_2$ is that it is extremely difficult to dope this system with any impurities. Many attempts to dope this system with impurities such as Zn, Mg, K, Y, etc. have failed. In fact, there are only two successfully doped copper oxy-hallides: Sr$_2$CuO$_2$F$_{2+4}$ by Al-Mamouri et al. and (Ca,Na)$_2$CuO$_2$Cl$_2$ by Hiroi et al. Both compounds are superconducting and are synthesized at high-pressure.

In his study of a frustrated vector antiferromagnet, the next nearest neighbor coupling is much greater than the nearest neighbor coupling, Henley has shown that the disorder introduced by dilution favors anti-collinear ordering. Since quantum fluctuations prefer a collinearly ordered ground state, these two types of disorder compete with each other and produce a rich phase diagram as a function of temperature and dilution. However, diluted Sr$_2$Cu$_3$O$_4$Cl$_2$ is a little different in that the relevant coupling ratio $(J_{III}/J_{II})$ is not small, so that the simple perturbation expansion used by Henley is no longer applicable. Nevertheless we expect a dramatic change in the ground state of diluted Sr$_2$Cu$_3$O$_4$Cl$_2$: for example, a helical order, a spin glass, or even a disordered ground state might occur as a result of dilution.

VII. CONCLUSIONS

We have presented results from our neutron scattering experiments on Sr$_2$Cu$_3$O$_4$Cl$_2$, and discussed its magnetic properties as well as the novel quantum phenomena associated with order from disorder. In what follows, we briefly summarize our main results.

1. Our elastic neutron diffraction data confirm the magnetic structure obtained from a previous analysis of static properties in a magnetic field.

2. We show that Sr$_2$Cu$_3$O$_4$Cl$_2$ is a unique system having two independent phase transitions. By analyzing the intensities of the magnetic Bragg reflections we obtain the critical exponents for the parameter order for the Cu$_I$ transition at $T_{N, I} = 386(2)$ K $\beta_I = 0.28(3)$ and for the Cu$_{II}$ transition at $T_{N, II} = 39.0(4)$ K $\beta_{II} = 0.13(1)$. The Cu$_I$ transition is thought to be that of a 3D XY model, whereas the Cu$_{II}$ transition is identified as a 2D Ising transition.

3. The dramatic variation in the mode energies as the Cu$_{II}$ subsystem orders is very clear evidence of quantum fluctuations because on the mean field level the interaction between these subsystems is frustrated. Some modes (i.e. $\omega_3$) would have zero energy in the absence of quantum fluctuations. Other modes (i.e. $\omega_2$ and $\omega_4$) show remarkable effects of quantum fluctuations. In all cases, these dramatic shifts are in quantitative agreement with theoretical calculations.

4. Our measurement of the spin-wave dispersion allows precise determination of several exchange interactions, including the interplanar Cu$_I$-Cu$_I$ interaction ($J_{I, 3D} = 0.14(2)$ meV), the in-plane Cu$_I$-Cu$_{II}$ interaction ($J_{II} = 10.5(5)$ meV), and the in-plane Cu$_I$-Cu$_{III}$ interaction ($|J_{I-I}| = 10(2)$ meV).

5. We have made precise tests of spin-wave interactions at the zone boundary which support recent theoretical calculations. This test is particularly convincing for this spin 1/2 system, where these effects are too large to be attributed to further-than-nearest neighbor interactions.

6. The instantaneous spin-spin correlation length, $\xi$, of $S = 1/2$ SLQHA over a wide temperature range has also been obtained from our neutron scattering experiments. Our measured values of $\xi$ are in good agreement with recent calculations based on the quantum nonlinear $\sigma$ model and on quantum Monte Carlo simulations.

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