2G-03

Spin gaps and quantum fluctuations in a frustrated magnet

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Abstract

$\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ consists of two weakly coupled spin 1/2 Heisenberg antiferromagnetic subsystems, Cu I and Cu II. In the high temperature (HT) regime ($40\text{K} < T < 386\text{K}$) only the Cu I subsystem orders antiferromagnetically. In the low temperature (LT) regime ($T < 40\text{K}$) both subsystems are antiferromagnetically ordered, but the interactions between them are frustrated. The observed coupling between sublattices results from quantum fluctuations (QF's). This picture is confirmed by observations (mostly via inelastic neutron scattering) of the spin-wave gaps at zero wave vector. In the HT regime the in-plane gap results from QF and is observed by antiferromagnetic resonance. In the LT regime, QF's play a crucial role in determining the energies at zero wave vector of the low energy modes. This system therefore dramatically illustrates the effects of QF's.

Keywords: Frustration, Quantum fluctuations, Spin waves, Cuprates

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In seminal work, Shender [1] considered the mean field degeneracy in a two-sublattice antiferromagnet which occurs when the molecular field at one sublattice due to the second sublattice vanishes. He showed that quantum fluctuations resolve this frustration. This is not surprising since the lack of intersublattice interactions does not reflect a true, exact, symmetry of the system. This paper will describe experimental and theoretical work which illustrates this phenomenon in a most dramatic fashion.

The system we consider is the lamellar cuprate insulator, $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$, which we will refer to as "2342." Its magnetic properties are due to the Cu ions all of which are in a $3d^9$ configuration. This system is approximately described by a five-band Hubbard Hamiltonian, $\mathcal{H}$, with one hole per site, where (in a form simplified from Ref. 2)

$$\mathcal{H} = \sum_{i,\alpha,\sigma} E_\alpha c_{i,\alpha,\sigma}^\dagger c_{i,\alpha,\sigma} + \sum_{i,j,\alpha,\beta\sigma} t_{i\alpha;j\beta} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + U \sum_i n_{i,\uparrow} n_{i,\downarrow} + \lambda \sum_{\text{holes}} \mathbf{L}(h) \cdot \mathbf{s}(h) ,$$

where $c_{i,\alpha,\sigma}^\dagger$ creates a σ -spin electron in the α th 3d state on site i , $\mathbf{t} \approx 1\text{eV}$ is a hopping matrix, $U \approx 8\text{eV}$ is the on-site Coulomb interaction, and $\lambda \approx 0.1\text{eV}$ is the spin-orbit interaction. Anderson[3] showed that the effective spin Hamiltonian for this system for $\lambda = 0$ is an isotropic Heisenberg model of localized spin $1/2$'s. The magnetic structure of 2342 in the regime $T < 40\text{K}$, as determined by neutron diffraction[4], is shown in Fig. 1. The unusual feature of this material is that it consists of two very weakly coupled subsystems, which we refer to as Cu I's and Cu II's, each of which nearly independently display the behavior of a Heisenberg antiferromagnet. Although all the Cu ions are chemically equivalent, the behavior of the Cu I and Cu II subsystems are very different. The Cu I spins behave like other lamellar cuprate antiferromagnets. In particular, for temperature T in the regime, $100\text{K} < T < T_I = 386\text{K}$, the staggered magnetization of the Cu I's, N_I , follows a power law

of the form $N_I \sim (T_I - T)^\beta$, with $\beta \approx 0.28$. Similarly, for $10\text{K} < T < T_{II} = 39.6\text{K}$, the staggered magnetization of the Cu II's, N_{II} follows a power law of the form $N_{II} \sim (T_{II} - T)^{\beta'}$, with $\beta' \approx 0.13$ and $N_{II} = 0$ for $T > T_{II}$. This value of β' is easily understood as that of the two-dimensional Ising model, inasmuch as the Cu I sublattice provides an effective easy-axis anisotropy, as we will see below. For $T_{II} < T < T_I$, the Cu II sublattice displays very weak ferromagnetism induced by the Cu I staggered moment, whose study[5] enables one to fix the values of many of the exchange interactions. This near decoupling of subsystems is easily understood from the magnetic structure where one sees that within mean field theory the isotropic interactions between the Cu I and Cu II spins are exactly frustrated. We will see both experimentally and theoretically that this frustration does not reflect a true symmetry of the system and in fact is removed by quantum fluctuations.

The result of Anderson[3] was generalized by Moriya[6] to include spin-orbit interactions, in which case the effective spin Hamiltonian becomes an anisotropic Heisenberg model. In the present case the effective Hamiltonian for a single Cu-O-Cu bond in a locally tetragonal environment is of the form[2]

$$J_{\parallel} S_{i,\parallel} S_{j,\parallel} + J_{\perp} S_{i,\perp} S_{j,\perp} + J_z S_{i,z} S_{j,z} , \quad (1)$$

where the direction $\parallel$ is parallel to the i - j bond, $\perp$ is in the CuO plane but perpendicular to this bond, and z is perpendicular to the CuO plane. It is crucial to note that in general these three directions have different exchange coupling. Experiment indicates that in most cuprates the average J , denoted J_{av} , is about 130 meV (i. e. $J_{\text{av}}/k_B = 1500\text{K}$). From the work of Refs. 2 and 7 and from experiments discussed below, one concludes that the anisotropy in $\mathbf{J}$, e. g. $J_{\perp} - J_{\parallel}$ or $J_z - \frac{1}{2}(J_{\perp} + J_{\parallel})$, is of order 0.05 meV.

The main aim of this paper is to understand simply the spin-wave energies in 2342 as observed by inelastic neutron scattering (INS) [8, 4] and by antiferromagnetic resonance (AFMR) [9], with special emphasis on zero wave vector. (One may easily treat wave vectors perpendicular to the CuO plane[8].) For this discussion it is useful to keep track of the size of the magnetic unit cell in the different temperature regimes. Disregarding the three dimensional structure, the planar unit cell of 2342 is that shown in the upper panel of Fig. 2 for the two regimes, the high-temperature (HT) regime when only the Cu I's are ordered, and the low-temperature (LT) regime when both the Cu I's and the Cu II's are ordered. This doubling of the size of the unit cell when the Cu II's order is reflected by the corresponding halving of the Brillouin zone, as shown in the lower panel of Fig. 2. In the HT regime one has two Cu I's per magnetic unit cell and so, neglecting anisotropy, one has the two-fold degenerate spectrum shown in the upper panel of Fig. 3. At LT, as shown in the bottom panel of Fig. 3, this spectrum is "folded over" because of the halving of the Brillouin zone (see Fig. 2) and also low energy Cu II modes develop. Although a detailed analysis of the spin-wave spectrum, including the various anisotropies and quantum fluctuations, is rather complicated,[10] most of the results in this paper can be understood in terms of the well-known formula for the zero wave vector energy of an anisotropic Heisenberg model, namely,

$$\omega^2 = 2H_E H_A , \quad (2)$$

providing one identifies properly (perhaps with the benefit of hindsight) the exchange field H_E and the anisotropy field H_A . Here ω , H_A , and H_E are defined to be in energy units.

Usually, the anisotropy field comes from a single ion term in the Hamiltonian of the form $-K S_{iz}^2$ which describes anisotropy with respect to an easy axis along the z -direction. In the

present case, since we deal with $S = 1/2$, such a term is a c-number and so the anisotropy field arises from anisotropic exchange as in Eq. (1) above. Indeed, in Ref. 2 it is shown that there is an anisotropy field for tipping the spins out of the easy plane, given by

$$H_A^{\text{out}} = 2(J_{\parallel} + J_{\perp})S - 4J_z S > 0 .$$

Next consider the anisotropy within the easy plane, for which purpose one calculates the ground state energy as a function of the angle, θ_N , which the staggered magnetization makes with the (1,0,0) direction within the easy plane. In the absence of quantum fluctuations, this energy does not depend on θ_N , because of the average over bonds in the two perpendicular directions within the easy plane. This invariance with respect to θ_N obviously does not reflect a true symmetry of the system and is therefore an artifact of mean field theory. The in-plane anisotropy can be obtained either by using anharmonic spin-waves,[11] or more simply, by calculating how the quantum zero-point energy per spin, E_Q , depends on θ_N . Here $E_Q = (2N)^{-1} \sum_{\mathbf{q},\tau} \hbar\omega(\mathbf{q},\tau)$, where $\omega(\mathbf{q},\tau)$ is the frequency of the τ th mode at wave vector $\mathbf{q}$ and N is the total number of spins. The result, given in Ref. 2 is that per Cu I spin $E_Q = E_Q(\theta_N = 0) - \frac{1}{8}H_A^{\text{in}}S \cos(4\theta_N)$, with

$$H_A^{\text{in}} = 16C_2(J_{\parallel} - J_{\perp})^2/J_{\text{av}} \equiv H_A^I , \quad (3)$$

where $C_2 = 0.01$ is a lattice sum. The fact that $H_A^{\text{in}}/H_A^{\text{out}}$ is of order $1/S$ indicates that the in-plane anisotropy is a quantum effect. Also since H_A^{in} is quadratic in $(J_{\parallel} - J_{\perp})$ it is expected to be much smaller than H_A^{out} .

In the HT regime, the anisotropies H_A^{out} and H_A^{in} (together with the well-known value of $H_E = 4J_{\text{av}}S \approx 260$ meV), determine the two spin-wave gaps via Eq. (2). The out-of-plane

gap of energy ~ 5 meV has been observed in several lamellar cuprates and is qualitatively explained by the Hubbard model calculation [2, 7] of the exchange anisotropy. The smaller in-plane gap was first obtained by AFMR result. (The order of magnitude of this gap was correctly predicted in Ref. 2.)

Figure 4 shows the temperature dependence of the spin-wave gaps at zero wave vector as determined from INS.[8, 4] Throughout both temperature regimes the temperature dependence of the modes can be understood semiphenomenologically (as is done in Refs. 2 and 4 by replacing S by $\langle S \rangle$). The coupling between the Cu I and Cu II subsystems is clearly evident from the dramatic increase in the mode energies just as the Cu II sublattice begins to order. This coupling can not be understood without fluctuations because the interaction is completely frustrated within mean field or linear spin-wave theory.

We now discuss how the two modes at HT evolve into four modes at LT. We first address the coupling between subsystems due to the frustrated interaction between them. To interpret the result of Ref. 1, we compare the situations shown in the three panels of Fig. 5. Configurations A and A' are related via a mirror reflection through the dashed line. Since condensed matter interactions (unlike the weak interactions) are inversion invariant, these two situations must have exactly the same energy and can not be distinguished. Now we compare configuration B to the others. Write $\mathbf{S}_i = \langle \mathbf{S}_i \rangle + \delta \mathbf{S}_i$, where $\langle \rangle$ indicates a thermal average. Then the interaction between spins i and j on different sublattices is

$$\mathcal{H}_{ij} = \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_j \rangle + \langle \mathbf{S}_i \rangle \cdot \delta \mathbf{S}_j + \delta \mathbf{S}_i \cdot \langle \mathbf{S}_j \rangle + \delta \mathbf{S}_i \cdot \delta \mathbf{S}_j .$$

At low temperatures longitudinal fluctuations can be neglected, so that $\delta \mathbf{S}_i \perp \langle \mathbf{S}_i \rangle$. Now note that in situation A both transverse components of spins i and j can couple, whereas in

situation B only one transverse component of spin i couples to a transverse component of spin j . Hence the energy gained by fluctuations in situation A is twice as favorable as that in situation B. But since situations A and A' are indistinguishable, the effective interaction due to fluctuations must be, not an exchange interaction, but rather a biquadratic exchange interaction of the form $\mathcal{H}_{ij} = -j_{\text{eff}} S^{-2} (\mathbf{S}_i \cdot \mathbf{S}_j)^2$, where, in the zero-temperature limit

$$j_{\text{eff}} = C J_{I-II}^2 / (J_{\text{av}} S) .$$

Here C is a constant which is evaluated numerically,[10] so that there are no free parameters in the identification of this effective interaction. (Since pairs of spins 1/2 do not support real biquadratic interactions, j_{eff} arises solely from fluctuations.)

A detailed spin-wave analysis shows that in the LT regime the four low energy modes at zero wave vector can be approximately categorized as a) in-plane modes in which the spins oscillate mainly within the easy plane and b) out-of-plane modes in which the spins oscillate mainly out of the easy plane. This identification can be inferred from the dependence of the mode energies on H_A^{out} and H_A^{in} . This can also be confirmed by observing or calculating the dependence of the INS cross-section on the scattering vector. (I. e. one compares scattering at two or more scattering vectors which differ by reciprocal lattice vectors.) Also each mode can further be characterized as having amplitude mainly on the Cu I sublattices or mainly on the Cu II sublattices. The so-called Cu I modes involve mainly Cu I coupling constants with small corrections from Cu II coupling constants and similarly for Cu II modes. So we refer to modes as "I,out," "II,in," etc. This classification provides a qualitative understanding of what kind of spin oscillation each mode corresponds to.

We now analyze the experimental and theoretical results summarized in Table I¹². The

quantum renormalizations (Z factors) are discussed in Refs. 8 and 10. (A more accurate analysis is given in Ref. 10.) The HT out-of-plane mode has much the same energy as in other cuprates. We set $H_E = 4J_{av}S = 260$ meV and $\omega_{out}^I = 5.5$ meV to determine H_A^{out} . Fitting the formula given in Table I we get $H_A^{out} = 0.16$ meV, compared to the Hubbard model predictions[2, 7] (for a CuO square lattice) $H_A^{out} = 0.06$ meV. Similarly, we determine H_A^{in} from ω_{in}^I as $H_A^{in} = 8.3 \times 10^{-6}$ meV. This leads to $|J_{\parallel} - J_{\perp}| = 0.082$ meV, again twice as large as that (0.041 meV) given by the theory of Ref. 7. It is very satisfactory that a Hubbard model gives the exchange anisotropies within an order of magnitude.

Turning to the LT regime, we first consider the QF energy which gives rise to the effective biquadratic coupling constant j_{eff} . This is calculated[10] to be $j_{eff} = 0.065$ meV. Fitting ω_{out}^I with $H_A^{out} = 0.16$ meV, leads to $j_{eff} = 0.083$ meV. Using ω_{in}^I to determine j_{eff} gives $j_{eff} = 0.080$ meV. Thus the experimental values confirm the calculation of j_{eff} . Next we consider ω_{out}^{II} . Here the parameters are already determined: $H_E^{II} = 4J_{II-II}S = 21$ meV.[5, 8] and (from above) $j_{eff} = 0.08$ meV and $H_A^{out} = 0.16$ meV. These values give $\omega_{out}^{II} = 1.88$ meV. Even better agreement between theory and experiment (1.747 meV) would be had by allowing for a negative contribution to H_A^{in} from the Cu II's being aligned along their hard in-plane direction. Now we consider the lowest energy mode, whose energy ω_{in}^{II} is determined by the in-plane anisotropy H_A^{in} . This anisotropy has contributions from a) quantum fluctuations, as in Eq. (3) (dominantly from the Cu I's), b) the anisotropic interaction J_{pd} , and c) H_A^{inter} from dipolar interplanar interactions between Cu II's. As discussed in Ref. 9, this latter contribution dominates at low temperature and explains the previously unidentified temperature dependence found in the statics.[5] The pseudo-dipolar interaction, J_{pd} is of

the right size ($|J_{pd}| = 0.027$ meV) to be attributed to dipolar interactions. But since the sign of J_{pd} is not known, this interpretation is not certain. In the present notation these contributions may be written as

$$H_A^{\text{in}} = 2H_A^I + 8Z_\zeta S J_{pd}^2 / J_{II-II} + H_A^{\text{inter}} , \quad (4)$$

where the renormalization factor $Z_\zeta = 0.18$ [5] and $2H_A$ replaces H_A because the size of the magnetic unit cell is doubled at low temperature. Assuming that H_A^{inter} has no contributions from pseudo-dipolar exchange anisotropy[13], we have all the parameters needed to evaluate the energy of this mode ($H_A^I = 8 \times 10^{-6}$ meV, from above) and we find the three terms in the above equation for H_A^{in} to be respectively (in units of 10^{-6} meV): 16, 5, and 390. The last term is absent when the Cu II's are disordered and explains the previous mysterious dramatic increase (by an order of magnitude) observed[5] in the value of k ($k = 16H_A^{\text{in}}$) at low temperature. We thus predict $\omega_{\text{in}}^{II} = \sqrt{2H_E^{II} H_A^{\text{in}}} = 0.13$ meV which compares favorably to the experimental value of 0.15 meV.

In summary: experiments and theory agree quite nicely. A striking conclusion is that the quantum fluctuations which give rise to j_{eff} are overdetermined by experiment and the good fit suggests that we fully understand this phenomenon. The dipolar and pseudodipolar interactions are also well understood and qualitatively explain the anomalous temperature dependence of the effective four-fold anisotropy H_A^{in} which determines the small in-plane gaps. Our present effort is to observe and fit to theory the detailed temperature dependence of the small in-plane gaps, as well as to observe these gaps in other cuprate antiferromagnets.

ACKNOWLEDGEMENTS: The author has profited immensely from collaboration with A. Aharony, R. J. Birgeneau, O. Entin-Wohlman, M. A. Kastner, and Y.-J. Kim. I thank Y.-

J. Kim for providing me with Fig. 4. Input from other coauthors is also greatly appreciated.
Support from the US-Israel BSF is gratefully acknowledged.

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TABLE

Table I. Mode energies at HT and LT. Mode energies greater than 1 meV are from INS[8, 4]. and those less than 2meV are from AFMR.[9] Here $H_E = 4JS$ and $H_E^{II} = 4J_{II-II}S$. We included renormalizations[8, 4] to reproduce energies correctly to order $1/S$ and then set $S = 1/2$. The anisotropy renormalization $Z_A = 1 - 0.2/S \rightarrow 0.6$ is the same as found for Ising anisotropy.[12] Also $\xi = 8j_{\text{eff}}S/(Z_A^2 H_A^{\text{out}} + 4j_{\text{eff}}S)$. (This complicated structure of ω_{out}^I means that Eq. (2) has its limitations!)

	LT	HT
ω_{out}^I	$\sqrt{2H_E(Z_A^2 H_A^{\text{out}} + 4j_{\text{eff}}S)}$	$Z_A \sqrt{2H_E H_A^{\text{out}}}$
Exp	10.8 meV at 10K	5.5 meV at 50K
ω_{in}^I	$\sqrt{2H_E(4j_{\text{eff}}S)}$	$\sqrt{2H_E H_A^{\text{in}}}$
Exp	9.1 meV at 10K	0.066 meV at 70K
ω_{out}^{II}	$Z_A \sqrt{2H_E^{II} H_A^{\text{out}} \xi}$	
Exp	1.747 meV at 1.5K, 10K	
ω_{in}^{II}	$\sqrt{2H_E^{II} H_A^{\text{in}}}$	
Exp	0.149 meV at 1.5K	

FIGURE CAPTIONS

FIG. 1. Magnetic structure of 2342 for $T < 40\text{K}$. There are six spins in the magnetic unit cell. The Cu I spins occupy sublattices $\underline{a}$ $\underline{b}$ $\underline{c}$, and $\underline{d}$ and the Cu II spins occupy sublattices $\underline{e}$ and $\underline{f}$. The oxygen ions occupy sites midway between adjacent Cu I spins. Thus Cu I - O - Cu I is a 180° bond and Cu I - O - Cu II is a weaker 90° bond.

FIG. 2. Top: Planar unit cell at HT (in dashed lines) containing 2 Cu I's (At HT the Cu II's are disordered.) The planar unit cell at LT which contains 4 Cu I's and 2 (ordered) Cu II's is shown in solid lines. Bottom: A Brillouin zone at HT in dashed lines and at LT in solid lines. The filled circles are reciprocal lattice vectors at HT. The X's are additional reciprocal lattice vectors which arise from the doubling of the unit cell when the Cu II's order.

FIG. 3. Spin-wave energy versus wave vector for an isotropic antiferromagnet. Each mode is doubly degenerate. Top: Spin-wave energy (schematic) versus wave vector at HT for 2 Cu I modes. Bottom: Same at LT for 4 Cu I modes and 2 Cu II modes. The Cu I modes are folded over from the top diagram and the Cu II modes are the additional modes at low energy. The energy gaps for 2342 at zero wave vector are not indicated.

FIG. 4. Mode energies from INS.[8, 4] The break in the curves coincides with the onset of long range order in the Cu II subsystem. In both the HT and LT regimes, the lowest energy mode is not seen in this data but is observed via AFMR.[9] Both experiments observe the mode at about 1.75 meV in the LT regime. The solid curve is the temperature dependence from mean field theory.

FIG. 5. Quantum fluctuation mechanism of Shender [1]. Configurations A and A' are related by mirror symmetry and are thus indistinguishable. Collinearity is favored (see text).

FIGURES