Quantum effects in a weakly-frustrated S=1/2 two-dimensional Heisenberg antiferromagnet in an applied magnetic field

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We have studied the two-dimensional S=1/2 square-lattice antiferromagnet Cu(pz)$_2$(ClO$_4$)$_2$ using neutron inelastic scattering and series expansion calculations. We show that the presence of antiferromagnetic next-nearest neighbor interactions enhances quantum fluctuations associated with resonating valence bonds. Intermediate magnetic fields lead to a selective tuning of resonating valence bonds and a spectacular inversion of the zone-boundary dispersion, providing novel insight into 2D antiferromagnetism in the quantum limit.

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Some of the best examples of macroscopic quantum magnets can be found in low-dimensional antiferromagnets that preserve strong quantum fluctuations to very low temperatures. Cases in point are antiferromagnetic (AF) chains that are quantum critical at zero temperature and feature deconfined spinon excitations for S=1/2 \cite{1}, but a spin liquid with gapped triplet excitations for S=1 \cite{2}. In two dimensions, quantum effects are generally reduced and the ground state of S=1/2 square-lattice antiferromagnets is long-range ordered, albeit with a reduced ordered moment and spin-waves whose energy is renormalized by quantum fluctuations \cite{3,4}. Importantly, however, short range quantum correlations are preserved in the ground state and lead to a quantum-induced dispersion at the AF zone boundary and to a weak continuum of states at high energies \cite{4,5,6,7,8,9,10,11,12}.

Competing interactions generally increase quantum fluctuations, particularly for materials close to a quantum critical point. For the 2D S=1/2 antiferromagnet, one source of competition can be next-nearest neighbor interactions that destabilize a simple nearest-neighbor antiparallel alignment and thus enhance fluctuations \cite{13,14}. Such a scenario has been extensively investigated using the $J_1 - J_2$ model, where $J_1$ and $J_2$ give the strength of the nearest and next-nearest neighbor interactions \cite{13}. The $J_1 - J_2$ model features two different types of order for $J_2/J_1 < 0.38$ and $J_2/J_1 > 0.6$, and probably a spin-liquid phase in between. The behavior of the 2D S=1/2 antiferromagnet in magnetic fields was studied theoretically for the case of nearest neighbor interactions \cite{14,15,16} as well as for $J_1 - J_2$ model \cite{17,18}. However, little is known experimentally about the magnetic field behavior of the 2D S=1/2 antiferromagnet, particularly in the presence of next-nearest neighbor interactions.

We have studied a weakly-frustrated S=1/2 AF square-lattice where next-nearest neighbor interactions are a small perturbation that allows us to study the change of the magnetic properties upon introduction of competing interactions. Our inelastic neutron scattering experiments were performed using the 2D square lattice Heisenberg antiferromagnet Cu(pz)$_2$(ClO$_4$)$_2$. Deuterated Cu(pz)$_2$(ClO$_4$)$_2$ crystallizes in the monoclinic C2/c space group \cite{20}. Each Cu$^{2+}$ ion in Cu(pz)$_2$(ClO$_4$)$_2$ carries S=1/2 and is surrounded by two pairs of identical cis pyrazine molecules, creating a two dimensional square array of copper atoms linked by pyrazine molecules in the bc plane. The two fold rotation axis (0, y, 1/2) and the mirror plane parallel to the ac plane ensures that all nearest neighbor interactions between Cu$^{2+}$ ions on the square lattice are identical. From the temperature dependence of the magnetic susceptibility, it was concluded that Cu(pz)$_2$(ClO$_4$)$_2$ represents a S=1/2 2D square lattice antiferromagnet with nearest-neighbor exchange $J = 1.53(8)$ meV and a saturation field of $\mu_0H_{\text{sat}} \sim 45$ T \cite{21,22}. Due to interplane interactions, Cu(pz)$_2$(ClO$_4$)$_2$ adopts long-range AF order below $T_N \sim 4.2$ K and the ratio between the interlayer to intralayer exchange has been estimated as $J'/J = 6.8 \cdot 10^{-4}$ \cite{20,22}.

The neutron experiments were performed using the cold-neutron triple-axis spectrometers PANDA at FRM 2 at Garching and IN14 at ILL at Grenoble, and an array of deuterated Cu(pz)$_2$(ClO$_4$)$_2$ single crystals with a total mass up to 2g co-aligned with a mosaic of 0.5°. The sample was aligned with its reciprocal (0, k, l) plane in the horizontal scattering plane. A cryomag-
net allowed the application of vertical magnetic fields up to 14.9T. The magnetic field was thus nearly perpendicular to the square-lattice plane. To probe the ground state as a function of magnetic field, we used a dilution refrigerator, reaching temperatures of the order of 50-100mK in each of the two experiments. The measurements were performed using a fixed final energy $E_f = 4.66$ meV and $E_f = 2.98$ meV for the PANDA and IN14 experiments, respectively, obtained via the (002) Bragg reflection from a pyrolytic graphite (PG) monochromator, a focused analyzer and a cooled Be filter before the analyzer. The chemical unit cell contains four Cu$^{2+}$ atoms, thus nearest-neighbor AF order does not break translational invariance, and $Q = (0,1,0)$ and $Q = (0,0,1)$ correspond to the AF point $(\pi,\pi)$. Consequently, $Q = (0,m \pm 1/2,n \pm 1/2)$, where $m$ and $n$ are integers, correspond to $(\pi,0)$, while $Q = (0,m \pm 1/2,n)$ corresponds to $(\pi/2,\pi/2)$.

A color plot of the normalized neutron scattering spectra at the zone boundary is shown in Fig. 1 for zero field and $H \sim J$. The normalized scattering intensity $I(Q,\omega)$ at $T = 80$ mK, showing the dispersion from $(\pi,0)$ to $(\pi/2,\pi/2)$ at zero field and $\mu_0 H = 14.9$ T under otherwise identical conditions. Both panels present smoothed data obtained by performing six constant $Q$-scans from $(\pi/2,\pi/2)$ to $(\pi,\pi)$ with a 0.05 meV energy step.

![Color plot of the normalized neutron scattering spectra at the zone boundary.](image)

**FIG. 1:** Color plot of the normalized neutron scattering spectra at zero field and $H \sim J$. The normalized scattering intensity $I(Q,\omega)$ at $T = 80$ mK, showing the dispersion from $(\pi,0)$ to $(\pi/2,\pi/2)$ at zero field and $\mu_0 H = 14.9$ T under otherwise identical conditions. Both panels present smoothed data obtained by performing six constant $Q$-scans from $(\pi/2,\pi/2)$ to $(\pi,\pi)$ with a 0.05 meV energy step.

We developed series expansion calculations for the $J_1 - J_2$ model in a magnetic field [23, 26, 27]. Since the magnetic field causes the spins to become non-collinear, this requires the technically difficult multi-block method to be used [27]. Our series expansion calculations for the $J_1 - J_2$ model [23, 26, 27] show that the addition of $J_2$ leads to an enhancement of the zone boundary dispersion. Fig. 2 shows the calculated single-magnon energies for different relative strengths $J_2/J_1$ between nearest to next-nearest neighbor interactions. For Cu(pz)$_2$(ClO$_4$)$_2$ we thus attribute the increased zone-boundary dispersion to a small AF next-nearest neighbor interaction of the order of $J_2 \sim 0.02 - 0.05J$.

According to spin wave theory, the energy at $(\pi/2,\pi/2)$ is equal to $E((\pi/2,\pi/2)) = 2(J_1 - J_2)$ at all fields. Next-nearest neighbor interactions thus lead to a smaller zone-boundary energy, and thus to a smaller effective nearest-neighbour exchange $J$. Using $J = J_1 - J_2$ and $J = 1.53(8)$ meV determined from susceptibility measurements [21, 22], the field-induced change of $E((\pi/2,\pi/2))$ is obtained from the field dependence of the renormalization factor $Z_c = E((\pi/2,\pi/2))/2J$, yielding $Z_c = 1.19(2)$ at zero field in excellent agreement the predicted value of $Z_c = 1.18$ [3].

![Series expansion calculations of the zone-boundary dispersion.](image)

**FIG. 2:** Series expansion calculations of the zone-boundary dispersion. Theoretical magnon dispersion for different values of the next-nearest neighbor exchange interaction $J_2$ in zero magnetic field (left panel) and in a $\mu_0 H = 14.9$ T magnetic field (right panel). The value of the nearest neighbor interaction $J$ has been normalized to fit the experimental data. The normalization constants are shown in the legend.
square-lattice antiferromagnet. The extended continuum in \( \text{Cu}(\text{pz})_2(\text{ClO}_4)_2 \) is also in contrast to well-defined excitations observed in \( \text{La}_2\text{CuO}_4 \) near \((\pi, 0)\), suggesting that ring exchange has the opposite effect on the continuum to next-nearest neighbor interactions. Further, Fig. 1 also provides evidence of an energy gap around \((\pi/2, \pi/2)\) that separates a main mode and a much weaker continuum above 4.2 meV, as predicted by Ho et al. \[\text{[7]}\].

Fig. 3 shows that magnetic fields strongly affect the quantum fluctuations at the zone boundary: The energy of the excitation at \((\pi/2, \pi/2)\) decreases much faster with field than that at \((\pi, 0)\). The zone-boundary dispersion at \(\mu_0 H = 14.9 \text{ T} \) is inverted from that at zero field. Our series expansion calculations show that, with the application of a magnetic field, the inversion of the zone boundary dispersion only occurs for sufficiently small \(J_2/J_1\). A five percent \(J_2/J_1\) no longer shows the reversal of the dispersion that is seen in experiments. This implies that even a relatively small next-nearest neighbor interactions are effective in enhancing the continuum of excitations, consistent with our estimate that \(J_2/J_1 = 0.02\). The quantum renormalization factor \(Z_c\) decreases rapidly from \(Z_c = 1.19(2)\) at zero field and approaches \(Z_c = 0.99(2)\) at \(\mu_0 H = 14.9 \text{ T}\), also consistent with our calculations.

It is known that the wave-vector dependence of the magnetic excitations at the zone boundary is a result of resonating valence bond quantum fluctuations between nearest-neighbor spins that reduce the energy of resonant excitations near \((\pi, 0)\) below what is expected from renormalized spin-wave theory \[\text{[6, 8]}\]. The field-induced reversal of the zone-boundary dispersion reveals that magnetic fields of the order of \(H \sim J\) strongly couple to these local quantum fluctuations. This dispersion, that is not expected from spin-wave theory, demonstrates the presence of local quantum fluctuations in the 2D \(S=1/2\) square-lattice antiferromagnet even for fields of the order of \(H \sim J\). The quantum origin of the dispersion reversal is also confirmed by our series expansion calculations.

The observed dispersion suggests that the energy of the resonance at \((\pi, 0)\) is raised by 4.5(7)% above that of renormalized spin-wave theory, providing direct evidence of field-tuned resonating valence bond fluctuations.

The excitation spectrum at \(\mu_0 H = 12 \text{ T}\) features two well defined magnetic modes of excitations (Fig. 3). The spectrum consists of a Goldstone mode, that indicates unbroken rotational spin symmetry in the plane perpendicular to the magnetic field, and a gapped mode. The field dependence of the mass of gapped mode at the AF zone center, shown in Fig. 4, is linear, which is consistent with the theoretical arguments discussed in \[\text{[28]}\]. However the finite gap at zero field, obtained by the linear fit to the experimental data, implies the existence of a small anisotropy in the system and requires additional investigations. We also analyzed the spectral weight of the gapped excitation at \((\pi, \pi)\). Our calculations completely describe the observed field dependence of the peak inten-
FIG. 5: Field dependence of the zone-center excitation. Energy scans performed at (\(\pi, \pi\)) at \(\mu_0 H = 2\) T, \(\mu_0 H = 6\) T, \(\mu_0 H = 10\) T (a) and the gap energy at the AF point plotted as the function of field (b). The data was measured at \(T = 80\) mK. The solid lines in (a) are the fits of a Gaussian function convoluted with the resolution function. The filled circles in (b) represent the experimental data. The solid line in (b) is the linear fit of the gap energy. Black circles in inset (c) show the measured intensities as function of magnetic field and the curve is the scattering intensity calculated using linear spin-wave theory.

The energies merely experience a small renormalization. Magnetic fields of the order of \(H \sim J\) lead to a qualitative change of the quantum fluctuations that suppress the continuum of excitations and renormalize the spin-wave velocity, but without suppressing the zone-boundary dispersion that arises from non-trivial quantum fluctuations. In fact, in contrast to spin-wave theory, we find that the zone-boundary dispersion is inverted compared to zero field, providing direct evidence of a field-induced change of resonating valence bond fluctuations.

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After submission of our manuscript, we became aware of A. Luscher and A. Laeuchli [21] who also find theoretically that the zone boundary dispersion inverts as a function of field.

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