High Resolution Study of Spin Excitations in the Shastry-Sutherland Singlet Ground State of SrCu$_2$(BO$_3$)$_2$

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High resolution, inelastic neutron scattering measurements on SrCu$_2$(BO$_3$)$_2$ reveal the dispersion of the three single triplet excitations continuously across the (H,0) direction within its tetragonal basal plane. These measurements also show distinct $Q$ dependencies for the single and multiple triplet excitations, and that these excitations are largely dispersionless perpendicular to this plane. The temperature dependence of the intensities of these excitations is well described as the complement of the dc-susceptibility of SrCu$_2$(BO$_3$)$_2$.

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Quantum magnets which display collective singlet ground states have been of much recent interest. Several of these, such as CuGeO$_3$, MEM-(TCNQ)$_2$, and NaV$_2$O$_3$ result from spin-Peierls phenomena in low dimensions where the lattice combines with $s=1/2$ spin degrees of freedom to break translational symmetry below some characteristic phase transition temperature, and a non-magnetic ground state with a characteristic energy gap is observed. A related state is observed in the $s=1$ antiferromagnetic chain compounds, such as CsNiCl$_3$ and NENP, where a non-magnetic ground state with an energy gap, the Haldane gap, forms in the absence of translational symmetry breaking.

SrCu$_2$(BO$_3$)$_2$ has been proposed as a realization of the Shastry-Sutherland model of interacting dimers in two dimensions. This material crystallizes into the tetragonal space group $I42m$ with lattice parameters $a=8.995$ Å, $c=6.649$ Å. Magnetically, it can be thought of in terms of well isolated basal planes populated by antiferromagnetically coupled $s=1/2$ moments on the Cu$^{2+}$ sites. These are arranged in dimers at right angles to each other and forming a square lattice. The microscopic Hamiltonian appropriate to this system is based on:

$$\mathcal{H} = J \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{n,m} \mathbf{S}_i \cdot \mathbf{S}_j$$  \hspace{1cm} (1)$$

It is known that both interactions, $J$ and $J'$, are antiferromagnetic and similar in strength, such that the system is not far removed from the critical value of $x=J'/J$ known to be appropriate to the quantum phase transition which separates a 4 sublattice Neel state from a collective singlet ground state.

The estimated values of $J$ and $J'$ have evolved over time as both theory and experiment have improved. Early estimates of $J$ and $x$ were $J=8.6$ meV and $x=0.68$, very close to the critical value $x_c=0.60$, where the single triplet excitation goes soft. More recently Miyahara and Ueda$^{12}$ found $J=7.3$ meV and $x=0.635$ from fits to the magnetic susceptibility. Somewhat smaller values were obtained by Knetter et al$^{13}$ who compared theoretical and experimental ratios of the energy of the lowest $S=1$ two triplet bound state to the single triplet gap, to obtain $J=6.16$ meV and $x=0.603$. Note that within this theory, the collective singlet ground state becomes unstable when the lowest energy two triplet bound state goes soft.

Earlier, relatively low resolution inelastic neutron scattering measurements$^{14,15,16}$ have directly identified three bands of excitations corresponding to single ($n=1$) triplet excitations, as well as to two ($n=2$), and to three ($n=3$) triplet excitations. These measurements directly show the appearance of the energy gap in the spectrum of excitations with decreasing temperature, as well as the dispersion of these excitations in an applied magnetic field.

The more recent of these studies$^{15,16}$ has been able to investigate subleading terms in the spin Hamiltonian. Terms such as the Dzyaloshinski-Moriya (DM) interaction, which is allowed by symmetry between spins on neighboring dimers, and anisotropic exchange, can be responsible for both dispersion of these excitations, and the removal of the three-fold degeneracy which would otherwise characterize the $n=1$ triplet excitation spectrum in SrCu$_2$(BO$_3$)$_2$. The presence of such small terms in the spin Hamiltonian has also been investigated through high field specific heat measurements$^{17}$, performed on samples from the same crystal growth as that used in the present study, and through ESR measurements$^{19,20}$.

In this letter, we report new high resolution inelastic neutron scattering measurements, which probe both the energy and $Q$ dependencies of these previously identified bands of excitations with new precision. Measurements were performed on two different high resolution cold neutron instruments, allowing both sufficiently high energy resolution to resolve the three $n=1$ triplet excitations in SrCu$_2$(BO$_3$)$_2$, and sufficiently high $Q$ resolution to discern different $Q$-dependencies of the $n$-triplet excitation...
tions, where \( n = 1, 2, 3 \).

The present single crystal of \( \text{SrCu}_2(\text{BO}_3)_2 \) was grown from a self-flux by floating zone image furnace techniques in an \( \text{O}_2 \) atmosphere using a four mirror furnace. It is cylindrical in shape, with approximate dimensions 0.6 cm in diameter by 10 cm long, and an \( a \)-axis was roughly aligned along the cylindrical axis. Small pieces of the crystal were used for bulk characterization, and the characteristic fall off of the dc susceptibility near 10 K, as well as well defined steps in the magnetization versus applied magnetic field at high field, were observed. Neutron diffraction measurements, enabled by the use of \( ^{11} \text{B} \) isotope, revealed a high quality single crystal throughout the volume of the sample with a mosaic spread of less than 0.2 degrees.

The crystal was mounted in a pumped \( ^4 \text{He} \) cryostat with the long cylindrical axis vertical, placing the \( (H,0,L) \) plane of the crystal coincident with the horizontal plane, and hence the scattering plane. Neutron scattering measurements were performed using the Disk Chopper Spectrometer (DCS) and the SPINS triple axis spectrometer, both located on cold neutron guides at the NIST Center for Neutron Research.

The DCS uses choppers to create pulses of monochromatic neutrons whose energy transfers on scattering are determined from their arrival times in the instrument’s 913 detectors located at scattering angles from -30 to 140 degrees. Using 5.1 meV incident neutrons and the medium resolution option, the energy resolution is 0.09 meV.

The SPINS triple axis spectrometer was operated using seven pyrolitic graphite analyser blades accepting 7 degrees in scattering angle, and neutrons of 5 meV, fixed scattered energy. A cooled Be filter was placed in the scattered beam to remove contamination of higher order neutrons, and the resulting energy resolution was \( \sim 0.5 \) meV.

A program of constant-\( Q \) measurements across the \( (H,0,L) \) plane of \( \text{SrCu}_2(\text{BO}_3)_2 \) at 1.4 K was carried out covering energies from 1 to 8 meV. A compendium of such scans with intervals of \( \Delta H \approx 0.2 \) is shown in the color contour map in Fig. 1a, which displays data within the \( h\omega, \) \( H \) plane at \( L=0 \). Representative scans making up this map are shown in Fig. 1b. One clearly identifies both the \( n=1 \) triplet excitation near \( h\omega \approx 3.0 \) meV and the \( n=2 \) triplet excitation, whose spectral weight is maximum near \( h\omega \approx 4.9 \) meV. One also sees a continuous component to the \( n=2 \) triplet excitation, which extends to the highest energies collected in this set of measurements, 8 meV.

These measurements are qualitatively similar to those first reported by Kageyama et al., within the \( (H,K,0) \) plane of \( \text{SrCu}_2(\text{BO}_3)_2 \) and with lower energy resolution; however there are important differences. For example, as can be seen in Fig. 1, we observe no substantial dispersion of the maximum of the spectral weight of the \( n=2 \) triplet excitation in contrast to a bandwidth of 1.5 meV reported in these earlier measurements. Also, as we discuss next, the \( Q \)-dependence of these excitations is different from that reported by Kageyama et al.

Figure 2 shows the results of constant energy scans performed at \( h\omega=3, 4.8 \) and 9 meV, corresponding to the \( n \)-triplet excitations with \( n=1, 2, 3 \) respectively. These measurements clearly show the \( n=1 \) excitation at 3 meV to peak up at half integer values of \( H \), that is at \( H=1.5 \) and 2.5, in maps of this scattering within the \( (H,0,L) \) plane, and at integer values of \( H=2 \) for the \( n=2 \) excitation at 4.8 meV and for the \( n=3 \) excitation at 9 meV. These results indicate distinct form factors for the \( n \)-triplet excitations, with the \( n=1 \) triplet being different from the multi-triplet excitations. Knetter and Uhrig have recently calculated the \( n=2 \) triplet contribution to the dynamic structure factor within the \( (H,K,0) \) plane of \( \text{SrCu}_2(\text{BO}_3)_2 \) by perturbative techniques. They show that it is peaked at \( (2,0,0) \), consistent with the present set of inelastic scattering measurements.

It is also clear from Fig. 2 that the \( Q \)-dependence of all the excitations show little \( L \) dependence, consistent with well isolated two dimensional basal planes. Given that the scattering displays very little \( L \)-dependence, the DCS measurements can be integrated along \( L \), resulting in a good quality determination of the dispersion of the \( n=1 \) triplet excitation in contrast to a bandwidth of 1.5 meV reported in these earlier measurements. Also, as we discuss next, the \( Q \)-dependence of these excitations...
FIG. 2: Constant energy scans at 3 meV (top panel), 4.8 meV (middle panel) and 9 meV (bottom panel) probing the Q-dependence of the n=1, 2, and 3 triplet excitations in SrCu$_2$(BO$_3$)$_2$ within the (H,0,L) plane at T=1.4 K.

neutrons. The bottom three panels show cuts through this map, which approximate constant-Q scans at (-1,0), (-1.5,0) and (-2,0), from top to bottom, respectively.

These inelastic measurements clearly resolve three branches of excitations, corresponding to $S_z^z=0, \pm 1$ transitions from the ground state, the lower two of which are nearly degenerate at (-1.5,0). These measurements have the advantage that they track the dispersion of the single singlet-triplet excitations continuously in Q along (H,0). This color contour map is also consistent with the mapping of the Q-dependence of the integral of the singlet-triplet scattering, shown in Fig. 1a, which shows this scattering to peak in intensity near (-1.5,0).

Although the high resolution n=1 triplet dispersion curves shown in Fig. 3 have not been previously reported, a substantial amount of information is known about these spectra from ESR measurements. In particular Nojiri et al. used ESR to measure the q=0 n=1 triplet excitations finding states at 2.81 meV (679 ± 2 GHz) and 3.16 meV (764 ± 2 GHz), in excellent agreement with the lowest and highest n=1 triplet excitations at Q=(-1,0) and (-2,0) shown in Fig. 3. The splitting between these two excitations has been shown to be $4D_1$, where D is the inter-dimer DM interaction. In fact the dispersion relation shown in Fig. 3 bears similarities to the calculation shown in Fig. 2c of Cepas et al., except for the small gap, ~ 0.2 meV, we observe between the $S_z^z=0$ transition and the upper of the $S_z^z=\pm 1$ branches at Q=(-1.5,0). This gap must result from some other anisotropic interaction, such as the recently proposed perpendicular intra-dimer DM interaction.

We note that the bandwidth of the middle, $S_z^z=0$ mode in Fig. 3 is extremely small, roughly 0.05 meV. This mode is the least affected by anisotropic interactions, and hence it is the mode most directly comparable to calculations of the n=1 triplet excitation based on Eq(1). This bandwidth, which scales like $x^6$, is similar to the bandwidth found by Weihong et al. for x=0.6, which is about 4% of the n=1 triplet gap energy.

We have also measured the temperature dependence of both the n=1 and n=2 triplet excitations with the SPINS triple axis spectrometer, and that of the n=1 triplet excitations with DCS. The SPINS measurements...
FIG. 4: The temperature dependence of inelastic intensity at (1.5,0,0) and $\hbar\omega = 3$ meV, as well as at (2,0,0) and $\hbar\omega = 4.8$ meV are shown. The inset shows the raw intensity data, while the main figure shows the normalized intensity assuming zero at 25 K. This is compared to the complement of the measured dc susceptibility (1-$\chi$), which clearly describes well the observed temperature dependence.

The DCS measurements integrate the inelastic scattering in data sets of the form shown in the top panel of Fig. 3. The DCS measurements integrate between 2.7 and 3.3 meV and across all wavevectors from $H = -2.25$ to $H = -0.75$ along $(H,0)$ within the basal plane.

Figure 4 shows that the temperature dependence of the $n=1$ and $n=2$ triplet excitations are identical, which may not have been concluded from earlier measurements. We do however confirm the very rapid dropoff of this inelastic intensity with increasing temperature. Such a strong temperature dependence is not characteristic of a system undergoing a phase transition, and indeed there is no evidence of a broken symmetry associated with the appearance of the collective singlet ground state. Rather the temperature dependence of the inelastic scattering can be very well described as the complement of the dc susceptibility. That is that the temperature dependence to the inelastic scattering follows that of the dc susceptibility. This has been measured and modelled using finite temperature Lanczos method. The complement of $\chi$, referred to as $1-\chi$ in Fig. 4, is given by $\chi(T=20 \text{ K}) - \chi(T)$. This quantity is scaled to compare to the temperature dependence of the inelastic scattering, and one can see that this provides an excellent description of the temperature dependence of the inelastic scattering.

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