High-Resolution Study of Spin Excitations in the Singlet Ground State of $SrCu_2(BO_3)_2$

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High-resolution, inelastic neutron scattering measurements on $SrCu_2(BO_3)_2$, a realization of the Shastry-Sutherland model for two-dimensional Heisenberg antiferromagnets, 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 $\mathbf{Q}$ 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 interest recently [1]. Several of these, such as $CuGeO_3$ [2], MEM-$(TCNQ)_2$ [3], and NaV_2O_5 [4], 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 nonmagnetic ground state with a characteristic energy gap is observed. A related state is observed in the $s = 1$ antiferromagnetic chain compounds, such as $CsNiCl_3$ [5] and NENP [6], where a nonmagnetic 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 [7,8] as a realization of the Shastry-Sutherland model [9] of interacting dimers in two dimensions. This material crystallizes [10] into the tetragonal space group $I\bar{4}2m$ 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

$$\mathcal{H} = J\sum_{nn}\mathbf{S}_i \cdot \mathbf{S}_j + J'\sum_{nnn}\mathbf{S}_i \cdot \mathbf{S}_j. \tag{1}$$

It is known that both interactions, J and J', are antiferromagnetic and similar in strength, such that the system is not far from the critical value of $x = J'/J$ for the quantum phase transition to a four sublattice Néel 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 $x = 0.68$ [7], very close to the critical value $x_c = 0.69$ [11], 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 [13], the collective singlet ground state becomes unstable when the lowest energy *two triplet bound state* goes soft. An authoritative theoretical review of the spin model for $SrCu_2(BO_3)_2$ has recently been published [14].

Much interest has focused on magnetization plateaus which appear beyond 20 T in $SrCu_2(BO_3)_2$ [15]. Strong magnetic fields generate triplets, within a background of singlets, that can undergo Bose-Einstein condensation (BEC) at densities determined by the applied magnetic field, which takes on the role of a chemical potential. Related BEC phenomena are known to occur at lower magnetic fields in $TlCuCl_3$ [16].

Earlier, relatively low resolution inelastic neutron scattering measurements [17–19] have revealed 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 [18,19] have 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, can account for both the dispersion of these excitations and the removal of the threefold 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 [20], performed on samples from the same crystal growth as that used in the present study, and through ESR measurements [21,22].

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 high energy resolution to resolve the three $n = 1$ triplet excitations in $SrCu_2(BO_3)_2$, and high **Q** resolution to discern different **Q** dependencies among the n-triplet excitations, where $n = 1, 2, 3$.

The present single crystal of $SrCu_2(^{11}BO_3)_2$ was grown from a self-flux by floating zone image furnace techniques in an O_2 atmosphere. It is cylindrical in shape, with approximate dimensions of 0.6 cm in diameter by 10 cm long. Small pieces of the crystal were used for bulk characterization, and the characteristic falloff of the dc susceptibility near 10 K, as well as well-defined plateaus in magnetization versus applied magnetic field at high field, was observed [20]. Neutron diffraction measurements, enabled by the use of a ^{11}B isotope, revealed a high quality single crystal throughout the volume of the sample with a mosaic spread of less than 0.2 deg.

The crystal was mounted in a pumped ^4He cryostat with the long cylindrical axis vertical, placing the $(H, 0, L)$ plane of the crystal coincident with the horizontal 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.

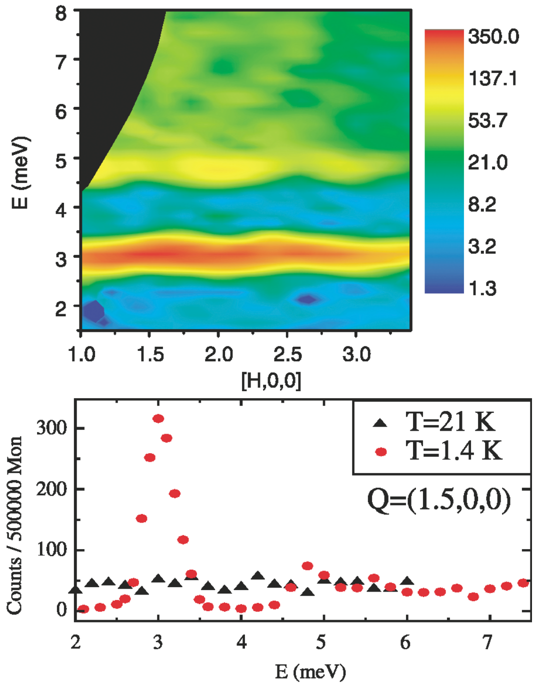

FIG. 1 (color). Top panel: A map of the measured dynamic structure factor for $SrCu_2(BO_3)_2$ at $T = 1.4$ K along the $(H, 0, 0)$ direction is shown. The intensity scale is logarithmic. The map is made up of constant-**Q** scans of the form shown in the bottom panel, where $\mathbf{Q} = (1.5, 0, 0)$ and the normalized intensity in counts/monitor is displayed.

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 deg. Using 5.1 meV incident neutrons, the energy resolution was 0.09 meV. The SPINS triple axis spectrometer was operated using seven pyrolytic graphite analyzer blades accepting 7 deg 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 ~0.5 meV.

A program of constant-**Q** measurements across the $(H, 0, L)$ plane of $SrCu_2(BO_3)_2$ at 1.4 K was carried out covering energies from 1 to 8 meV. A compendium of such scans with intervals of $\Delta H = 0.2$ is shown in the color contour map in Fig. 1 (top panel), which displays data within the $\hbar\omega$, H plane at $L = 0$. Representative scans making up this map are shown in Fig. 1 (bottom panel). One clearly identifies both the $n = 1$ triplet excitation near $\hbar\omega = 3.0$ meV and the $n = 2$ triplet excitation, whose spectral weight is maximum near $\hbar\omega \sim 4.9$ 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.* [17], within the $(H, K, 0)$ plane of $SrCu_2(BO_3)_2$ 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 [17]. Also, as we discuss next, the **Q** dependence of these excitations is different from that reported by Kageyama *et al.* [17].

Figure 2 shows the results of constant energy scans performed at $\hbar\omega = 3$, 4.8, and 9 meV, corresponding to the n-triplet excitations with $n = 1, 2, 3$, respectively. These measurements show most of the weight of 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 multitriplet excitations. Knetter and Uhrig [23] have recently calculated the $n = 2$ triplet contribution to the dynamic structure factor within the $(H, K, 0)$ plane of $SrCu_2(BO_3)_2$ by perturbative techniques. They specifically show that it is peaked at $(2, 0, 0)$, consistent with the present set of inelastic scattering measurements. Furthermore, where the present

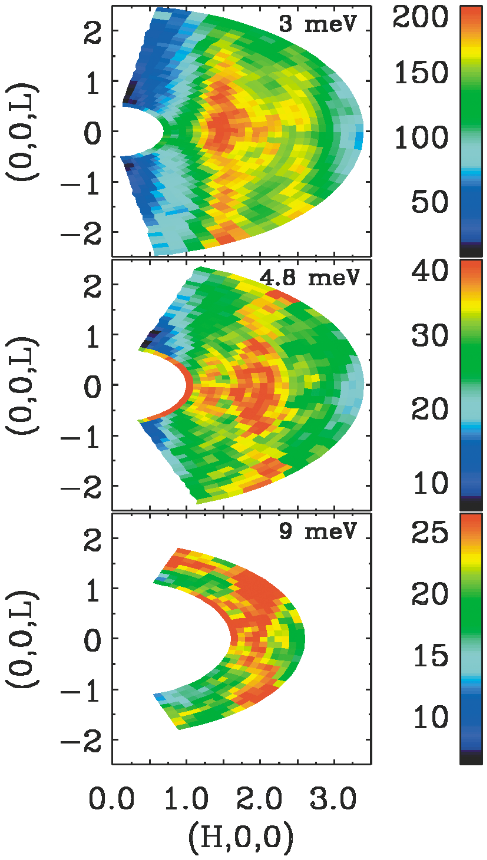

FIG. 2 (color). Constant energy scans at 3 (top panel), 4.8 (middle panel), and 9 meV (bottom panel) probing the **Q** dependence of the $n = 1, 2$, and three triplet excitations in $SrCu_2(BO_3)_2$ within the $(H, 0, L)$ plane at $T = 1.4$ K.

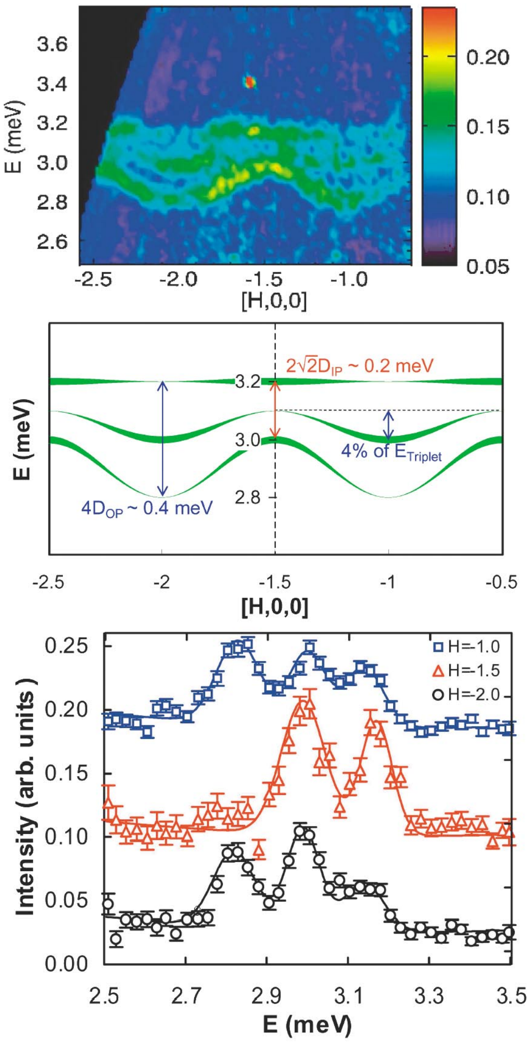

FIG. 3 (color). Top panel: Color contour map of the dynamic structure factor for the $n = 1$ triplet excitations along the $(H, 0)$ direction within the basal plane of $SrCu_2(BO_3)_2$. These measurements, taken with the DCS spectrometer at $T = 1.4$ K, integrate along L. Middle panel: A cartoon of the dispersion and form factors appropriate to the S^z and $S^{\pm}$ $n = 1$ triplet excitations, along with the relation between the measured splitting and dispersion to parameters in the Hamiltonian. Bottom panel: Cuts through the map of the top panel are shown, which approximate constant-**Q** scans and clearly resolve the three branches to the $n = 1$ triplet excitation.

results in Fig. 1 and theory overlap, for the $n = 2$ triplet in the $(H, 0, 0)$ direction, the agreement between the two is excellent.

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 such 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 excitations in the $(H, 0)$ direction within the tetragonal basal plane. This is what is shown in Fig. 3, where the top panel shows a color contour map of the inelastic scattering. The bottom panel shows 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 triplet excitation. Earlier work [18–22] suggests that the dispersion of these branches arises, in the first instance, from the DM interaction. The energies of the top and bottom modes at $Q = (-2, 0)$ and $(-1, 0)$ are in excellent agreement with the ESR results of Nojiri *et al.* [22] who find states at 2.81 meV (679 ± 2 GHz) and 3.16 meV (764 ± 2 GHz) for $Q = 0$. This splitting arises from the out-of-plane DM interaction, D_{OP}. To lowest order in J'/J, i.e., ignoring quantum fluctuations, this splitting has the value $4D_{OP}$. Of course, quantum fluctuations renormalize the entire spectrum and, in particular, its bandwidth. Cepas *et al.* [18] have estimated this renormalization to reduce the bandwidth by about a factor of 2.

The gap between the $S^z = \pm 1$ modes at $Q = (-1.5, 0)$ has been attributed [19] to the in-plane DM interaction, D_{IP}, which arises from the buckling of the planes. This splitting, which has the theoretical value of $2\sqrt{2}D_{IP}$, is observed to be about 0.18 meV. It is not presently known how quantum fluctuations renormalize the value of this

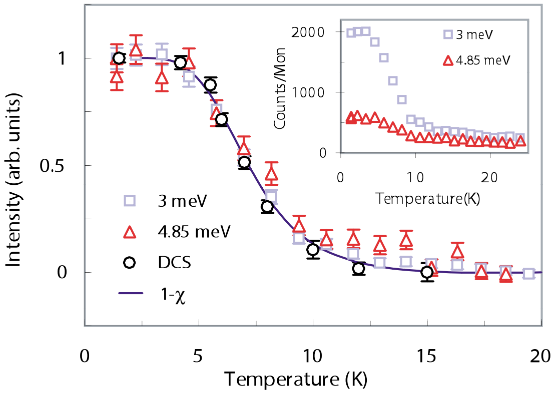

FIG. 4 (color). The temperature dependence of inelastic intensity at (1.5, 0, 0) and $\hbar\omega = 3$ meV, as well as at (2, 0, 0) and $\hbar\omega = 4.85$ meV, is shown. The inset shows the raw intensity data, while the main figure shows the normalized intensity assuming zero at 25 K. This is compared to the complement of the measured dc susceptibility ($1 - \chi$), which clearly describes well the observed temperature dependence.

gap. However, if the renormalization were similar for in and out-of-plane DM interactions, then $D_{\rm IP}$ would be about $0.7D_{\rm OP}$, which is surprisingly large in light of the small magnitude of the buckling of the layers.

The $S^z = 0$ mode, which is sketched along with higher and lower energy $S^{\pm}$ modes in the cartoon in the middle panel of Fig. 3, is predicted to have a zero form factor at $Q = (-1.5, 0)$ [18] and is expected to be centered between the top and bottom $S^{\pm}$ bands, whose form factors are maximal near $(-1.5, 0)$. The bandwidth of the $S^z = 0$ mode is extremely small, roughly 0.1 meV. It is known to be least affected by anisotropic interactions; hence it is most directly comparable to calculations of the $n = 1$ triplet excitation based on Eq. (1). This bandwidth, which scales as x^6, is similar to the bandwidth found by Weihong *et al.* [11] for $x = 0.6$. It 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 at $\mathbf{Q} = (1.5, 0, 0)$ and $(2, 0, 0)$ and energy transfers of $\hbar\omega = 3$ and 4.85 meV, sample the $n = 1$ and $n = 2$ triplet excitations, respectively, and are shown in Fig. 4. 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 wave vectors 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 is identical, which may not have been concluded from earlier measurements [17]. The temperature dependence of the inelastic scattering can be very well described as the complement of the dc susceptibility. That is, the temperature dependence to the inelastic scattering follows that of the dc susceptibility [20]. The complement of χ, referred to as $1 - \chi$ in Fig. 4, is given by $\chi(T = 20\ \mathrm{K}) - \chi(T)$. This quantity is scaled to compare 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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