In-Gap Spin Excitations and Finite Triplet Lifetimes in the Dilute Singlet Ground State System SrCu$_{2-x}$Mg$_x$(BO$_3$)$_2$

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High resolution neutron scattering measurements on a single crystal of SrCu$_{2-x}$Mg$_x$(BO$_3$)$_2$ with $x \sim 0.05$ reveal the presence of new spin excitations within the gap of this quasi-two dimensional, singlet ground state system. Application of a magnetic field induces Zeeman-split states associated with $S=1/2$ unpaired spins which are antiferromagnetically correlated with the bulk singlet. Substantial broadening of both the one and two-triplet excitations in the doped single crystal is observed, as compared with pure SrCu$_2$(BO$_3$)$_2$. Theoretical calculations using a variational algorithm and a single quenched magnetic vacancy on an infinite lattice are shown to qualitatively account for these effects.

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Quasi-two dimensional quantum magnets which display collective singlet or spin gap behavior are very topical due to the novelty of their ground states and their relation to high temperature superconductivity in the copper oxides. There are relatively few such materials, and crystal growth difficulties have further limited their study in single crystal form. SrCu$_2$(BO$_3$)$_2$ is established as a realization of the two dimensional Shastry Sutherland model for interacting $S=1/2$ dimers. It is comprised of well separated layers of Cu$^{2+}$, $S=1/2$ orthogonal dimers arranged on a square lattice. The material crystallizes into the tetragonal space group I42 with room temperature lattice parameters of $a=8.995$ Å, $c=6.649$ Å.

SrCu$_2$(BO$_3$)$_2$ has been well studied by an array of experimental techniques, which show it to possess a non-magnetic ground state. In particular earlier neutron$^{6,7,8,9}$ and ESR spectroscopy$^{10,11}$ have established the leading terms in its microscopic Hamiltonian:

$$\mathcal{H} = J \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{nn} \mathbf{S}_i \cdot \mathbf{S}_j + g \mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i \ (1)$$

where $J$ is the exchange interaction within the dimers and $J'$ is the exchange interaction between $S=1/2$ spins on neighboring dimers. Subleading Dzyaloshinskii-Moriya interactions weakly split the three triplet modes even in zero applied magnetic field.$^{7,8,9,12}$

Both the exchange interactions are antiferromagnetic and their ratio $x=J/J'$ has been estimated between 0.68 and 0.60, with more recent refinements being smaller. Theoretically, such a quantum magnet is known to possess a singlet ground state so long as the ratio, $x$, of inter to intra-dimer antiferromagnetic exchange is sufficiently small.$^{13}$ All of these estimates place SrCu$_2$(BO$_3$)$_2$ on the low side of the critical value of $x$ at which a quantum phase transition occurs between a four sublattice Neel state and a collective singlet state.

In finite magnetic field, much interest has focused on a finite magnetization which develops at fields beyond $\sim 20$ T, wherein the lowest energy of the three triplet states has been driven to zero energy.$^{14,15,16}$ The magnetic field acts as a chemical potential for the triplet density within the quasi-two-dimensional planes. Magnetization plateaus ensue at higher fields, corresponding to Bose condensation of the triplets at certain densities.

While pure SrCu$_2$(BO$_3$)$_2$ has been well studied, there is little information on this quantum magnet in the presence of dopants, and no reports on doped single crystals. This problem is very interesting by analogy with the remarkable properties of doped quasi-two dimensional Mott insulators and high temperature superconductivity.$^{17}$ SrCu$_2$(BO$_3$)$_2$ is itself a Mott insulator and the theory of doped Mott insulators on the Shastry-Sutherland lattice shows the possibility of several different superconducting phases as a function of doping.$^{18,19,20}$ Several doping studies of SrCu$_2$(BO$_3$)$_2$ have been reported on polycrystalline samples wherein Al, La, Na, and Y substitute at the Sr site and Mg substitutes at the Cu site.$^{21}$

In this Letter we report high resolution time-of-flight neutron scattering measurements on large single crystals of SrCu$_{2-x}$Mg$_x$(BO$_3$)$_2$ and SrCu$_2$(BO$_3$)$_2$. These measurements show that doping of the magnetic Cu$^{2+}$ site with non-magnetic, isoelectronic Mg$^{2+}$ at the 2.5% level introduces new magnetic excitations into the singlet energy gap, and gives a finite lifetime to all three single triplet excitations, while also substantially broadening the two triplet bound state.

Two single crystal samples, SrCu$_2$(BO$_3$)$_2$ and SrCu$_{2-x}$Mg$_x$(BO$_3$)$_2$, were grown by floating zone image furnace techniques at a rate of 0.2 mm/hour in an O$_2$
FIG. 1: (a) The two left hand panels show neutron scattering data from SrCu$_2$(BO$_3$)$_2$ at T=2K. The scattering has been integrated along L and we show data in a magnetic field of zero and 7 T. The right hand panels show the same data for SrCu$_{2−x}$Mg$_x$(BO$_3$)$_2$. The energy axis is on a logarithmic scale. The Zeeman-split S=1/2 level in this data. The one triplet excitations show significantly greater breadth in energy in SrCu$_{2−x}$Mg$_x$(BO$_3$)$_2$ as compared with SrCu$_2$(BO$_3$)$_2$. In addition, application of a H=7 T magnetic field gives rise to an inelastic peak at $g\mu_B H$=0.8 meV in H=7 T, which is centered around $[H=1.4, 0, 0]$ in Q-space, but extends in wavevector H to almost $[H=3, 0, 0]$. Both of these features are discussed at length below.

Figure 1 shows representative time-of-flight neutron scattering data, taken at T=2 K and H=0 and 7 T for SrCu$_2$(BO$_3$)$_2$ (a and c) and for SrCu$_{2−x}$Mg$_x$(BO$_3$)$_2$ (b and d). This data was integrated along L, in which direction the spin excitations show little dispersion. Note the logarithmic energy and intensity scales, chosen to draw attention to the details of the in-gap excitations seen in SrCu$_{2−x}$Mg$_x$(BO$_3$)$_2$. The splitting of the triplet excitations near 3 meV on application of the 7 T magnetic field is clear. In finite field, weak dispersion of the triplet excitations as a function of wavevector H is seen, and this has been attributed to subleading terms in the spin Hamiltonian - terms other than those in Eq. 1. There are several qualitative features evident on examination of this data. The one triplet excitations show significantly greater breadth in energy in SrCu$_{2−x}$Mg$_x$(BO$_3$)$_2$ than in SrCu$_2$(BO$_3$)$_2$. In addition, application of a H=7 T magnetic field gives rise to an inelastic peak at $g\mu_B H$=0.8 meV in H=7 T, which is centered around $[H=1.4, 0, 0]$ in Q-space, but extends in wavevector H to almost $[H=3, 0, 0]$. Both of these features are discussed at length below.

Figures 2b and 2d show the same experimental data as in Fig. 1, now integrated in wavevector along L and also in H between H=1 rlu and H=3 rlu, and plotted as a function of energy. The data in a magnetic field of 0 and 7T is shown in Figs 2b and 2d, respectively. The extra breadth in both the single triplet excitations and the two triplet bound states above it is clear. Broad inelastic peaks appear within the gap, which possess little magnetic field dependence, indicating a longitudinal nature. Sharp, field-induced inelastic scattering at $\hbar\omega \sim 0.8$ meV is also evident.
Numerical calculations have also been carried out using a new variational approach\( ^{23} \) to solve the model of a single quenched impurity on the two dimensional Shastry-Sutherland lattice. This method generates a variational space by successively applying the off-diagonal parts of the Hamiltonian, Eq. 1, on the starting approximation for the single impurity ground state, which consists of a free spin 1/2 neighboring the impurity site, embedded within a dimer background. The resulting small spin polaron structure and exponential growth of the variational space with each iteration guarantee good convergence of the spin polaron ground state, as well as for the lowest energy excited states. Full details will be given separately\( ^{24} \).

For energies below \( \sim 3 \) meV the method provides accurate and converged results for both the longitudinal, \( S^{zz}(Q,\omega) \), as well as the transverse, \( S^{yy}(Q,\omega) \) components of the dynamical spin structure factor. These are compared directly to the neutron scattering experiments in Fig. 2.

Figures 2a and 2c show the calculated \( S^{zz}(Q,\omega) + S^{yy}(Q,\omega) \), integrated over the same range of wavevectors as the experimental data, and at magnetic fields of 0 (a) and 7 T (c). The comparison between theory and experiment is qualitatively good. The numerical results confirm that quenched magnetic vacancies induce in-gap states, substantial spectral weight below the zero field gap energy of \( \sim 3 \) meV. A component of these in-gap states show little magnetic field dependence, and appear in the \( S^{zz}(Q,\omega) \), longitudinal channel. The calculation also shows the \( g\mu_B H \) transverse, \( S^{yy}(Q,\omega) \), excitation in finite magnetic field. Furthermore, the calculation\( ^{23} \) allows a determination of the spatial distribution of the spin polaron \( S=1/2 \) degree of freedom and its low lying excited states, and these can guide the interpretation of the \( Q \)-dependence of the field-induced \( g\mu_B H \) transverse spin excitation observed in the experiments.

Figure 3 shows the \( Q \) dependence of the scattering around \( g\mu_B H=0.8 \) meV in an applied magnetic field of 7 T in both SrCu\(_2\)(BO\(_3\))\(_2\) (a) and SrCu\(_{2-x}\)Mg\(_x\)(BO\(_3\))\(_2\) (b). This scattering is integrated in wavevector over \( L \), and in energy between 0.6 meV < \( h\omega < 1 \) meV and is shown in a magnetic field of both 0 and 7T. Figure 3a shows the absence of a magnetic field induced signal in SrCu\(_2\)(BO\(_3\))\(_2\) within this energy range. Figure 3b shows a clear field induced signal in SrCu\(_{2-x}\)Mg\(_x\)(BO\(_3\))\(_2\) which peaks at \( [H\sim 1.4, 0, 0] \), but extends out to almost \( [H\sim 3.0, 0, 0] \). This field induced scattering is attributed to Zeeman split \( S=1/2 \) states associated with the \( S=1/2 \) moment in a dimer whose partner site is occupied by a quenched, nonmagnetic Mg\(_{2+}\) ion. This field induced inelastic scattering is very similar to that associated with end states in Haldane spin chains, such as occur in Y\(_2\)Ba\(_2\)Ni\(_1-x\)Mg\(_x\)O\(_4\).\( ^{24} \) In this case, quenched, nonmagnetic Mg\(_{2+}\) ions produce finite \( S=1 \) magnetic chains. Spin 1/2 degrees of freedom arise at the end of finite chains of \( S=1 \) magnetic moments, as one of the two effective \( S=1/2 \) degrees of freedom making up the \( S=1 \) moments lacks a partner with which to form a singlet. Such excitations occur at an energy of \( g\mu_B H \) in finite field, and display a wavevector dependence which indicates antiferromagnetic correlations into the collective singlet of the chain segment.

The wavevector dependence of the magnetic field-induced spin excitation at 0.8 meV can be attributed to the structure of the spin polaron\( ^{25} \), whose ground state possesses strong antiferromagnetic correlations with neighboring dimers, transverse to the dimer containing the impurity site. To first non-trivial order in \( J'/J \), we obtain an analytical expression for the square of the matrix element for this transition:

\[
I^\pm \propto \left| \left( a_1^2 - a_2^2/2 \right) e^{i\eta(H\mp K)} + 2\sqrt{2} a_1 a_2 \times \sin(\eta(H \mp K)) \sin(\pi(H \mp K)) - 2\sqrt{2} a_2 a_3 \times \cos(\eta(H \mp K)) \cos(\pi(H \mp K)) \right|^2
\]

where \( a_1 \), \( a_2 \), and \( a_3 \) are the weights of the polaron variational wavefunction computed for \( J'/J = 0.6 \), \( \eta = 0.72 \) accounts for microscopic distances in SrCu\(_2\)(BO\(_3\))\(_2\). The \( \pm \) sign in Eq. 2 distinguishes between the two nonequivalent impurity positions within the unit cell. Random doping therefore implies \( I \propto I^+ + I^- \), which we show, multiplied by the square of the magnetic form factor for Cu\(_{2+}\), in Fig. 3b along with measurements on \( Q \)-dependence of this scattering in SrCu\(_{2-x}\)Mg\(_x\)(BO\(_3\))\(_2\). While the agreement between the calculation and experiment is not perfect, the calculation captures the general
oscillators (DHO): was fit to the sum of three identical damped harmonic functions 

The extracted lifetimes show little or no systematic variation with wavevector $H$, but a finite one-triplet lifetime is observed in SrCu$_2$Mg$_x$(BO$_3$)$_2$ at all temperatures, in contrast to SrCu$_2$(BO$_3$)$_2$, where the low temperature one-triplet lifetimes are very long, compared with the resolution of the spectrometer. In both SrCu$_2$Mg$_x$(BO$_3$)$_2$ and SrCu$_2$(BO$_3$)$_2$, the thermal destruction of the collective singlet ground state near $\sim 10$ K is characterized by a rapid decrease in the one triplet lifetime ($1/\Gamma$) on warming, with little or no softening of the one triplet excitation energies.

As mentioned previously, the theoretical results for $S^zz$($Q$, $\omega$) + $S^yy$($Q$, $\omega$) are not well converged for energies of $\sim 3$ meV and greater. Nonetheless, the additional broad spectral weight around the calculated one and two triplet energies seen in Fig 2a) and c) is consistent with finite triplet lifetimes in the presence of a single quenched magnetic vacancy.

To conclude, new inelastic neutron scattering measurements on SrCu$_{2-x}$Mg$_x$(BO$_3$)$_2$ with $x \sim 0.05$ show relatively broad and field-independent in-gap spin excitations as well as a magnetic field-induced excitation identified as a Zeeman-split, spin polaron state. The non-magnetic quenched vacancies also give rise to finite and measurable lifetimes in the one and two triplet excitations.

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