Inelastic scattering studies of the geometrically frustrated spin-singlet compound Ba_2YMoO_6

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Introduction

We have conducted neutron scattering studies of powder samples of the geometrically frustrated double perovskite material Ba_2YMoO_6 using the SEQUOIA time-of-flight spectrometer at Oak Ridge National Laboratory, and the C5 triple-axis spectrometer at the Canadian Neutron Beam Centre [1]. We have observed the existence of a nonmagnetic spin-singlet ground state below $T \sim 125$ K, with a triplet excitation near 28 meV, and also observe diffuse in-gap scattering. This behavior is reminiscent (albeit at different energy and temperature scales) of that seen in the orthogonal-dimer square-lattice system $SrCu_2(BO_3)_2$, of which the present system may be a 3-D analogue, with the tetrahedrally coordinated Mo^{5+} moments forming orthogonal pairs of dimers in the ground state.

Geometrically frustrated materials [2] have been a topic of great interest to the condensed matter physics community in recent years. Whereas materials possessing magnetic moments typically develop static long-range magnetic order at sufficiently low temperatures, the crystal structure of geometrically frustrated materials prevents various magnetic interactions from simultaneously being satisfied, leading to a huge degeneracy of competing ground states. This may suppress magnetic order to significantly lower temperatures and, in some cases, preclude an ordered state altogether. In this Report we present an inelastic neutron scattering study of the geometrically frustrated compound Ba_2YMoO_6, confirming the lack of an ordered ground state, and revealing a spin-triplet excitation of a spin-singlet ground state reminiscent of the singlet ground state observed in the orthogonal-dimer system $SrCu_2(BO_3)_2$. Geometric frustration manifests itself in a wide variety of materials characterized by diverse interactions and lattice symmetries. For example, if neighbouring moments correlate antiferromagnetically, such that their interaction energy is minimized by antiparallel arrangement of neighboring moments, crystalline architectures based on triangles (in two dimensions) or tetrahedra (in three dimensions) naturally lead to frustration since all interactions cannot be simultaneously satisfied (Fig. 1a). Such systems

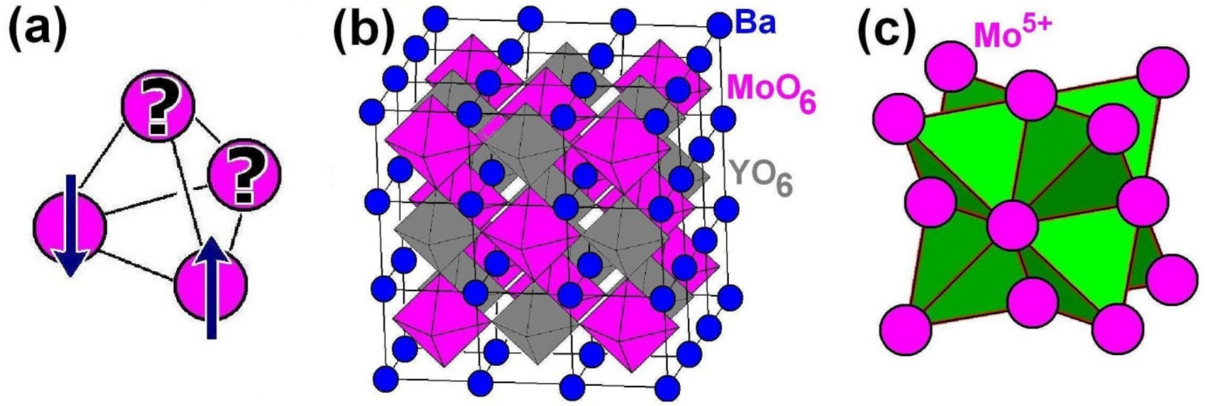

Fig. 1 (a) Frustration of antiferromagnetically correlated moments on a tetrahedron. (b) Face-centred cubic (FCC) unit cell of Ba_2YMoO_6; a ~ 8.38 Å. (c) Tetrahedrally coordinated sublattice of Mo^{5+} moments.

include the widely-studied Kagome and triangular lattice systems in 2D, and pyrochlores and spinels in 3D, though many others exist. While in some of these materials a compromise ordered state with a more complex arrangement of moments, such as a spin glass, spin ice, or helimagnetism, eventually prevails, in others static magnetic order is suppressed to the lowest available temperatures. In the latter, the normally dominant terms in the Hamiltonian are cancelled by exquisite balancing, so subtle interactions which are normally difficult or impossible to detect contribute significantly to the overall behavior, leading to rich phase diagrams featuring exotic physics and large changes in properties caused by small external changes. Due to this high sensitivity to external parameters, and to the accessibility of subtle underlying physics and exotic ground states, such materials are of intense interest to both basic and applied researchers.

Ba_2YMoO_6 crystallizes into a double perovskite structure, in which the B-site cations Y^{3+} and Mo^{5+}, each octahedrally coordinated by O^{2-} anions, are arranged with NaCl-like "rock-salt" ordering (Fig. 1b). While the Y^{3+} ions have no unpaired electrons and thus zero magnetic moment, the Mo^{5+} ions have a single electron in the 4*d* subshell, giving them an overall spin-½ moment. It can be seen that, after eliding all non-magnetic ions, the magnetic Mo^{5+} ions comprise a face-centred cubic (FCC) sublattice. This sublattice, shown in Fig. 1c, can equivalently be considered to form a network of edge-sharing tetrahedra, giving rise to geometric frustration of the Mo^{5+} moments. While other geometrically frustrated lattices, including the aforementioned pyrochlore, Kagome and triangular lattices have been extensively studied, and despite the commonality of FCC structures in nature, there have been comparatively few studies of such geometrically frustrated FCC systems.

Neutron diffraction, magnetic susceptibility and muon spin relaxation experiments [3] have determined that neither long-range nor short-range static magnetic order exist in Ba_2YMoO_6 down to $T = 2$ K; coupled with a Weiss temperature of $\Theta_w = -219$ K a frustration index $f = |\Theta_w|/T_{order} > 100$ can be derived, indicating significant frustration. ^{89}Y NMR measurements from the same study indicate that Y nuclei are surrounded by two distinct environments, one corresponding to paramagnetic-like fluctuating spins, and another indicative of a spin-singlet ground state; these states appear to coexist in the sample at 2K, with the singlet state gradually disappearing above about 140K. In such a spin-singlet state, neighboring spin-½ moments form into pairs. Quantum mechanics dictates that there are four possible combinations of a pair of s=½ spins. One of these - the singlet - corresponds to an overall $s = 0$ state whose spin wavefunction is antisymmetric under exchange, and the other three - the triplet - to $s = 1$ states whose spin wavefunctions are symmetric under exchange. The singlet state has the lowest energy, and in zero magnetic field the three triplet states are at equal energies Δ above the ground state. Thus such a system is described as having a singlet ground state, with a triplet excited state lying above a spin gap Δ.

Experiment

Our present study utilizes neutron scattering to study the ground and excited states of polycrystalline Ba_2YMoO_6 as a function of temperature. While NMR measurements indirectly reveal the existence of a spin gap at low temperatures, inelastic neutron scattering is able to directly probe the spectrum of excitations from the ground state, and as a result can directly confirm the existence of the singlet state, determine the singlet-triplet energy gap Δ and possibly elucidate any associated dispersion, and investigate the existence of any other magnetic scattering.

Given substantial uncertainties about the scattering vector (Q) and energy (E) dependence of the inelastic neutron scattering signal, and expectations of a weak signal due to the s=½ moments in the sample, our experiments were performed in two stages. As the first stage, the SEQUOIA spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory was used. With its high incident flux, wide range of incident energies, and a three-story 2-dimensional array of neutron detectors, SEQUOIA is especially suited to a broad survey measurement to search for weak magnetic signals. Following this survey experiment, which demonstrated the existence of a magnetic scattering signal, the magnetic signal was probed in more depth using the C5 triple-axis spectrometer at Chalk River. With its high sensitivity, low background, extraordinary freedom of configuration, and a vertically-focusing pyrolytic graphite (PG) monochromator to increase neutron flux on the sample, C5 is ideally suited to perform parametric measurements of magnetic signals.

For both experiments, approximately 6-7 grams of loose Ba_2YMoO_6 powder were inserted into an aluminum sample can, with mounting hardware shielded by Cd foil to minimize background. Identically configured but empty aluminum sample cans were also measured under the same conditions for background subtraction purposes. At SEQUOIA, data was collected at six temperatures with a fixed incident energy of 60 meV, and since the sample was a powder, data were binned as a function of $|Q|$ and E to produce detector area-corrected energy slices. At Chalk River, a fixed final wavelength $\lambda_f = 1.638$ Å was used, with boral slits positioned as closely as possible around the sample can to reduce background. PG monochromator and analyser crystals were used, along with a PG filter to reduce $\lambda/2$ contributions to the signal.

Our SEQUOIA data is shown in Figure 2. The data was treated as a sum of three terms: (1) a temperature-independent background term, (2) a thermal contribution (phonons) whose temperature dependence is well-described by the Bose occupancy factor, and (3) the magnetic signal of interest. Term (1) was eliminated by subtracting from each data set its corresponding empty-can run. Following this, our background-subtracted data sets were normalized by the appropriate Bose factor for temperature and energy to yield the imaginary part of the magnetic susceptibility $\chi''(Q,\omega)$, shown in Fig. 2a for $T = 6$ K. To account for term (2), which dominates the spectrum in Fig. 2a, and to isolate the magnetic contribution to the scattering, the Bose-corrected data at 175 K was subtracted from the lower-temperature data sets, producing at $T = 6$ K the plot in Fig. 2b.

While the overall inelastic response is dominated by phonons, the magnetic scattering is dominated by a clear signal at low $Q < 2.5$ Å^{-1} and an energy of approximately 28 meV, although diffuse magnetic scattering at low Q and intermediate energies is apparent as well. The 28 meV feature is identified with the triplet excitation from the singlet ground state, and dissipates with increasing temperature by approximately 125 K, with no sign of a phase transition, consistent with earlier results. The nature of the intermediate-energy scattering is less clear, though it is reminiscent of impurity-induced in-gap scattering as has been observed in ~2.5% Mg-doped $SrCu_2(BO_3)_2$,, for example [4].

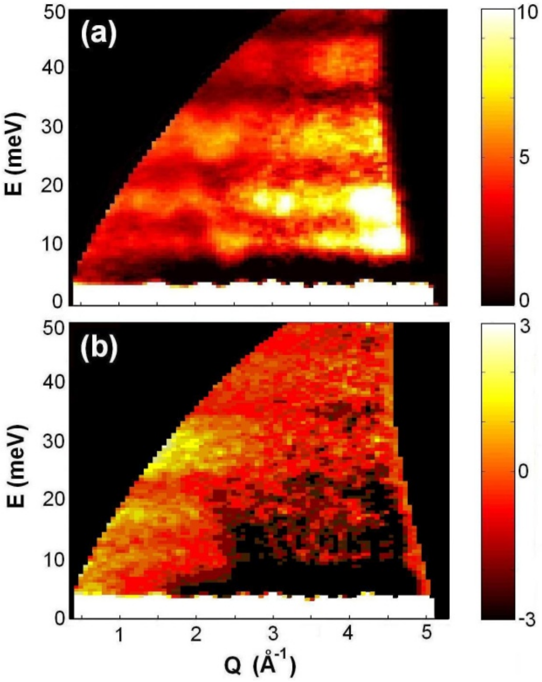

Fig. 2 SEQUOIA data. (a) Background- and Bose-corrected scattering intensity at 6K. (b) Magnetic scattering intensity produced by subtracting $\chi''(Q,\omega)$ at 175 K from that at 6 K as described in the text. The triplet excitation is seen at low Q and E ~ 29 meV; a continuum of scattering from the paramagnetic state is seen at low Q and intermediate energies.

With the location of the putative magnetic signal determined, we conducted measurements at the C5 triple-axis spectrometer at Chalk River. We measured the temperature dependence of the signal in three energy bands – at 7 meV, 16.5-17 meV and 27.5-30.5 meV. As can be seen in Figure 3, the scattering in the 7 and 17 meV bands increase in intensity with increasing temperature, consistent with a phonon origin, although there is a slight low-temperature excess as compared to the expected Bose factor dependences (solid lines). However, the signal around 28 meV clearly increases in intensity with decreasing temperature below about 125 K. This behavior is identical to our earlier findings at SEQUOIA (overlaid), and with the temperature dependence of the singlet-like state observed in NMR measurements in [3].

It is interesting to compare the behavior of this system to other frustrated systems, such as the square-lattice Shastry-Sutherland system $SrCu_2(BO_3)_2$, in which neighboring pairs of moments form orthogonal pairs in perhaps a 2-dimensional analogue to the network of orthogonal dimers which may exist in Ba_2YMoO_6. Interestingly, both the energy scale of the triplet excitation, and the temperature scale at which the singlet state dissipates in $SrCu_2(BO_3)_2$ are commensurate to those in Ba_2YMoO_6, but scaled down by a factor of roughly 10. While $SrCu_2(BO_3)_2$ does not exhibit any evidence of in-gap scattering of the variety seen in the present sample, similar scattering is seen in ~2.5% Mg-doped $SrCu_2(BO_3)_2$. In the Mg-doped samples, the in-gap scattering is attributed to impurity effects, which in the present case could be due to the 3% Mo/Y-site disorder found in magic-angle spinning NMR measurements of our Ba_2YMoO_6 sample. However, it is also possible that in-gap states are intrinsic to the s=½ FCC system in the presence of spin-orbit coupling, as is expected for the $4d^1$ Mo^{5+} ion.

Together, these inelastic neutron scattering measurements provide strong evidence for a singlet or singlet-like state at low temperatures in Ba_2YMoO_6, coexisting with a paramagnetic liquid-like state present to the lowest temperatures studied, and find no evidence for a transition to a statically ordered state even at temperatures ~100 times lower than $|\Theta_w|$. This singlet or singlet-like state, with a likely singlet-triplet gap of 28 meV, gradually evaporates without a phase transition by *T* = 125K, consistent with earlier NMR results. The in-gap scattering at this time eludes a definitive explanation, although it evokes intriguing parallels with the Mg-doped specimens of the Shastry-Sutherland 2D system $SrCu_2(BO_3)_2$, to which the present system may be a 3D analogue. We hope that this work motivates sustained research in frustrated quantum magnets, particularly among less well-studied FCC systems.

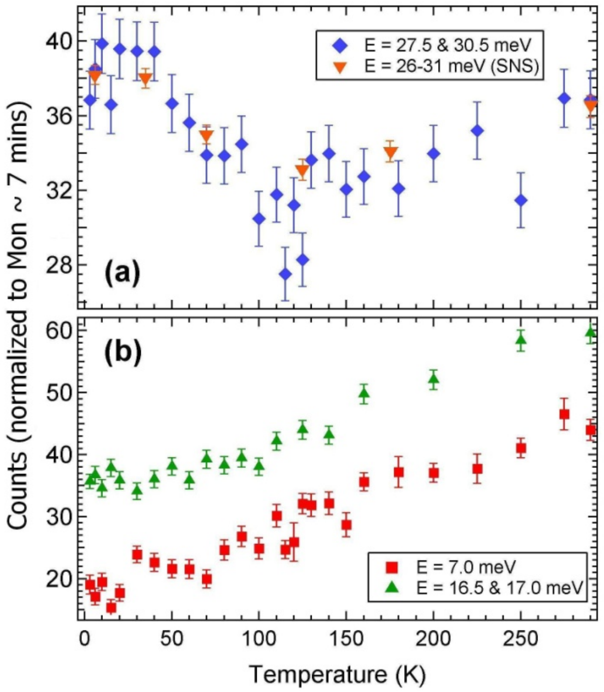

Fig. 3 CNBC data collected at the C5 spectrometer. (a) Temperature dependence of scattering intensity at 27.5 and 30.5 meV, with SEQUOIA data overlaid for comparison. (b) Temperature dependence of scattering intensity at 10 and 17 meV. The excess of low-temperature scattering in (a) is attributed to the triplet excitation.

References

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