

Pressure Dependent Diffraction and Spectroscopy of a Dimerized Antiferromagnet

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We present pressure dependent neutron diffraction and inelastic neutron scattering measurements of the dimerized antiferromagnet $\text{Ba}_3\text{Mn}_2\text{O}_8$. The room temperature diffraction measurements reveal a linear decrease in lattice constant as a function of applied pressure. No structural transitions are observed. The low-temperature neutron spectroscopy measurements indicate a small change in magnetic scattering intensity in the vicinity of the spin gap for pressures up to $P = 0.6$ Gpa.

KEYWORDS: neutron scattering, pressure effect, spin-dimers, antiferromagnet

Quantum antiferromagnets are a good testing ground for examining and probing quantum critical points and phenomena.¹⁻³ One such system which we have been studying is $\text{Ba}_3\text{Mn}_2\text{O}_8$. This compound consists of coupled $S = 1$ Mn^{5+} spin dimers arranged on a hexagonal lattice.⁴ Dimer layers are separated from one another along the crystallographic c -axis by Ba sites. Thermodynamic measurements have examined the spin-gap and established that the ground state is a non-magnetic singlet.^{5,7} Inelastic neutron scattering measurements examining powders and single crystals determined the exchange connectivity and interactions.^{8,9}

Typical approaches to accessing quantum critical points in gapped spin liquid compounds include the application of applied magnetic fields and chemical substitution. Recently, non-magnetic substitution has also been studied in $\text{Ba}_3(\text{Mn}_{1-x}\text{V}_x)_2\text{O}_8$, and a potential disordered random singlet ground state has been found.^{10,11} Still another approach to perturbing the magnetic ground state of quantum antiferromagnets is to apply external pressure to the crystal structure. The distortion of the crystal structure via external pressure will affect the magnetic exchange interactions. Inelastic neutron scattering measurements are able to directly probe these effects by measuring the magnetic excitation cross-section. This has been done for the three dimensional dimer compound TlCuCl_3 ¹² and the two-dimensional spin dimer PHCC.¹⁷ For the case of TlCuCl_3 , which has an intradimer exchange of $J_0 \approx 5$ meV,¹³ it was found that an external pressure of 0.11 GPa can completely close the singlet-triplet spin-gap,¹⁴⁻¹⁶ whereas in PHCC the spin-gap is reduced by approximately 0.47 meV per GPa. The quantum spin ladder, IPA- CuCl_3 has also been examined as a function of pressure.¹⁸ For this system, it was found that the spin gap closed at a rate of approximately 0.23 meV per GPa. Here we examine the influence of pressure on the exchange interactions in the two-dimensional $S = 1$ disordered antiferromagnet $\text{Ba}_3\text{Mn}_2\text{O}_8$. $\text{Ba}_3\text{Mn}_2\text{O}_8$ has an intradimer exchange constant of $J_0 = 1.64$ meV with a series of weaker interdimer exchanges.⁹

Powder samples of $\text{Ba}_3\text{Mn}_2\text{O}_8$ were synthesized via a solid state reaction following the procedure previously de-

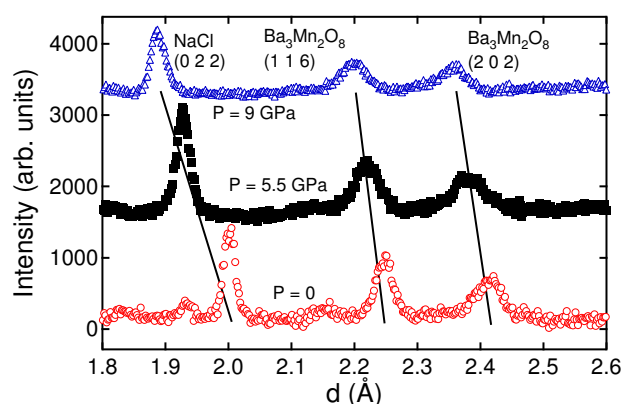


Fig. 1. Scattering intensity as a function of d -spacing for three applied pressures. Measurements were performed using the SNAP diffractometer as described in the text. Data are offset along the vertical axis for presentation. A NaCl calibration peak and two $\text{Ba}_3\text{Mn}_2\text{O}_8$ peaks are indexed in this portion of the spectrum.

scribed.^{5,8} Samples were examined for phase purity using a laboratory Cu anode x-ray powder diffractometer. No additional phases or unreacted materials were observed.

Neutron powder diffraction measurements were performed as a function of pressure using the SNAP instrument at the Spallation Neutron Source. NaCl powder was ground into the $\text{Ba}_3\text{Mn}_2\text{O}_8$ sample to use as a calibration standard for the applied pressure. The sample was loaded into a Paris-Edinburgh press fitted with single toroid cubic boron nitride anvils with the incident beam through the TiZr null scattering alloy gasket. Time-of-flight neutron diffraction measurements were performed using a wavelength band of 0.5 to 3.75 Angstrom neutrons. All measurements were performed at room temperature. The SNAP detector was kept in the 90 degree two theta configuration during the course of the measurements.

Inelastic neutron scattering measurements were performed using the SPINS cold neutron triple axis spectrometer at the NIST Center for Neutron Research. The sample consisted of approximately 1 cm³ of powder loaded into an aluminum

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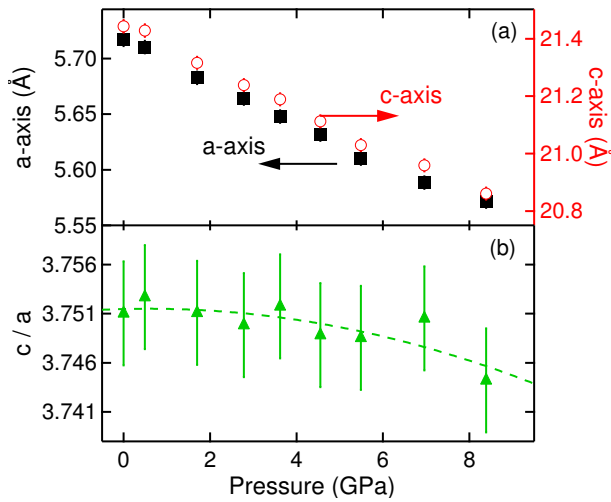


Fig. 2. (a) Lattice constants of $\text{Ba}_3\text{Mn}_2\text{O}_8$ as a function of applied pressure. (b) c/a as a function of applied pressure. Dashed line is a second order polynomial fit as a guide to the eye. Measurements were performed using the SNAP instrument with the sample at room temperature as described in the text. The vertical axes of panel (a) are shown with the same percentage change of lattice constant.

7075-T6 pressure cell. Pressure was controlled via condensation and pressurization of helium. A high pressure capillary was connected between the pressure cell and the pressure intensifier such that pressure could be controlled without removing the sample from the cryostat. Hydrostatic conditions were ensured by slow cooling under constant pressure and maintaining the capillary line heated above the P vs. T curve for helium. The sample and sample cell were placed inside a standard He gas flow cryostat for temperature control. An $80'$ collimator was placed between the monochromator and the sample, and an $80'$ radial collimator was placed between the sample and the analyzer. A cooled Be filter was used after the sample, and the final energy of the instrument was fixed to 5 meV. The analyzer was kept in a horizontal focusing configuration of seven 1.5 cm wide graphite blades throughout the measurement. Ambient pressure measurements were performed before and after the application of pressure. These data were averaged with one another for the constant wave vector, Q , scans shown later in the manuscript.

Figure 1 illustrates the time-of-flight neutron powder diffraction spectra measured using the SNAP instrument for three applied pressures.⁶⁾ Indexed peaks including those of the NaCl calibration are labeled in the figure. One can see a clear shift in nuclear peak position as a function of applied pressure. We refine these data for the a and c lattice constants for all of the pressures measured. The determined pressure dependent lattice constants are shown in Fig. 2(a). Both the lattice constants have a linear pressure dependence. $\text{Ba}_3\text{Mn}_2\text{O}_8$ is fairly isotropic and the a and c axis lattice constants have very similar compressibilities: $\frac{\Delta a}{a(P=0)\Delta P} = -0.00303$ and $\frac{\Delta c}{c(P=0)\Delta P} = -0.00324$. Figure 2(b) shows the ratio of c/a as a function of applied pressure. Although there may be an indication that there is a trend at larger pressures for this ratio to decrease, we would require higher pressure measurements to make this conclusion.

Recently it was found that significant changes in the vi-

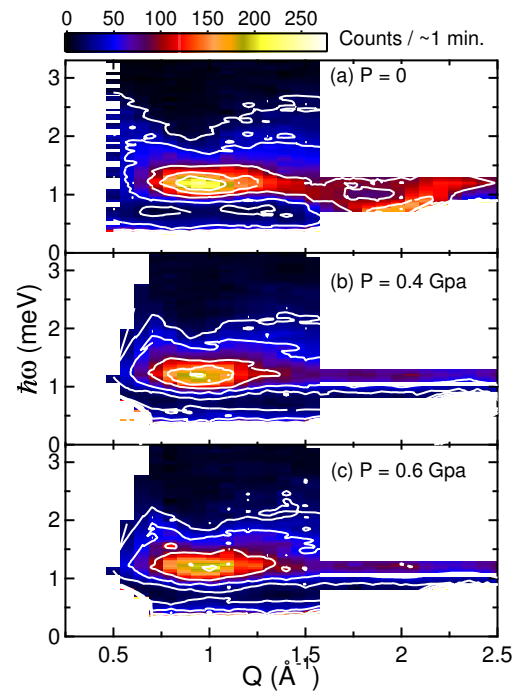


Fig. 3. Inelastic neutron scattering measurements of $\text{Ba}_3\text{Mn}_2\text{O}_8$ as a function of applied pressure for $T = 1.4$ K. Contour plots were made from individual constant Q and $\hbar\omega$ scans as described in the text. Contour lines are shown at intensities intervals of {25, 50, 100, 150, 200, 250}.

brational modes of the similar compounds $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Ba}_3(\text{VO}_4)_2$ occurred at elevated pressures.¹⁹⁾ These changes occurred at pressures greater than approximately 15 GPa. The changes in the vibrational spectra are likely associated with pressure induced changes in the lattice. Although we observe no structural phase transition up to $P = 9$ GPa, the trend we observe in c/a at large pressure is possibly signaling the approach of a similar pressure induced transition as was observed in $\text{Sr}_3(\text{VO}_4)_2$ and $\text{Ba}_3(\text{VO}_4)_2$.

Figure 3 shows the inelastic spectrum for ambient pressure and $P = 0.4$ and $P = 0.6$ GPa acquired at $T = 1.4$ K. This figure was produced from the combination of a series of constant wave vector and constant energy scans. For all pressures, one can see the magnetic excitations in the vicinity of $Q = 1 \text{ \AA}^{-1}$ and $\hbar\omega = 1$ meV. The magnetic excitations extend to higher energy transfers in a smeared “V” pattern for larger and smaller wave vectors. For $P = 0$, one can see the roton mode of liquid helium contributing to the measured scattering intensity at larger wave vector transfers. Because of this contamination, we restrict our quantitative analysis to smaller values of Q . The multi-phonon cross-section of the liquid helium in the sample cell increased the overall background for the ambient pressure measurements. We determine an overall constant background based upon the difference in scattering intensity for $P = 0$ and $P \neq 0$ for energy transfers greater than 2 meV and wave vector $Q = 0.9 \text{ \AA}^{-1}$. Examination of the contour lines shown in Fig. 3(a)–(c) illustrates that for applied pressures there is a potential decrease in the scattering intensity in the vicinity of $\hbar\omega = 1$ meV, and that the intensity at larger energy transfers also slightly decreases.

Figure 4 shows a constant $\hbar\omega = 1.2$ meV scan for $T = 1.4$ K for ambient and applied pressures. For larger values

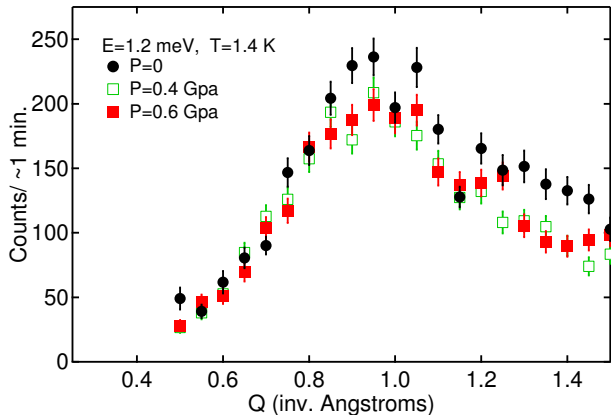


Fig. 4. Intensity as a function of Q for $T = 1.4$ K and $\hbar\omega = 1.2$ meV for ambient and applied pressures. The $P = 0$ data have been background subtracted as described in the text.

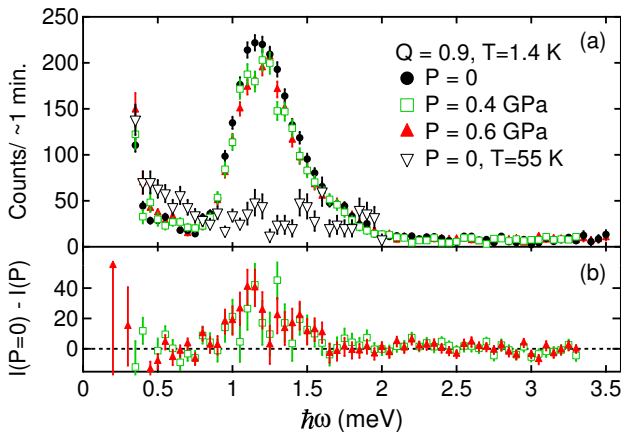


Fig. 5. Inelastic measurements of the singlet-triplet excitation in $\text{Ba}_3\text{Mn}_2\text{O}_8$ as a function of applied pressure. These data correspond to a constant wave-vector scan performed at $Q = 0.9$ Å. Measurements were performed at $T = 1.4$ K. Panel (a) are the data from the constant wave-vector scans at the pressures indicated. (b) is the difference between the $P = 0$ and $P \neq 0$ measurements.

of Q , the $P = 0$ measurement has an elevated intensity at larger wave-vectors. This is due to the increased background from the liquid helium phonon-roton spectrum as shown in Fig. 3(a). The peak in Q for all three measurements is at the identical location indicating that the strongly coupled spin dimer remains persistent as a function of pressure.⁸⁾ In the vicinity of this peak, the decrease in scattering intensity with applied pressure indicates that either there is a suppression of the triplet excitation or a change in the excitation spectrum.

Figures 5(a) and 6(a) show constant Q scans through the singlet-triplet excitation for the three pressures measured at $T = 1.4$ K for $Q = 0.9$ Å⁻¹ and $Q = 0.7$ Å⁻¹ respectively. The ambient pressure measurement has a greater scattering intensity than the applied pressure measurements. A high temperature, $T = 55$ K, measurement is also shown in Fig. 5 for ambient pressure. This illustrates the magnetic nature of the low-energy excitations.

Figures 5(b) and 6(b) show the difference between the ambient pressure measurement and the applied pressure measurements. The pressure induced changes in the spectrum

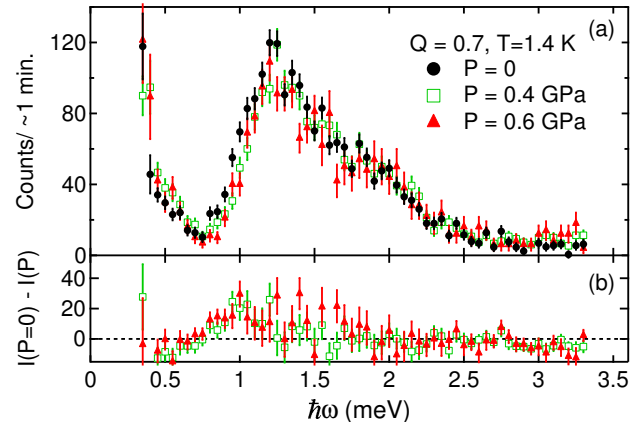


Fig. 6. Inelastic measurements of the singlet-triplet excitation in $\text{Ba}_3\text{Mn}_2\text{O}_8$ as a function of applied pressure. These data correspond to a constant wave-vector scan performed at $Q = 0.7$ Å. Measurements were performed at $T = 1.4$ K. Panel (a) are the data from the constant wave-vector scans at the pressures indicated. (b) is the difference between the $P = 0$ and $P \neq 0$ measurements.

appear between 0.8 and 1.75 meV. These changes may reflect a small increase in the spin gap with no change in the spectrum at larger energy transfers. Unfortunately, the current state of the art for low-temperature high pressure inelastic neutron scattering measurements makes it difficult to see a large change in the spectrum for the $\text{Ba}_3\text{Mn}_2\text{O}_8$ compound. The reduction in scattering intensity may also reflect an increased exchange connectivity within the $a - b$ plane relative to the connectivity between the dimer planes. That is, interdimer correlations may be changing relative to the intradimer correlations. This would suppress triplet propagation along the c -axis relative to the ambient pressure measurements, and potentially decrease the number of singlet-triplet excitations.

We have observed small changes in the magnetic spectrum of the $S = 1$ dimer antiferromagnet as a function of applied pressure. Single crystal higher resolution inelastic neutron scattering measurements at pressures of $P \geq 1$ GPa would be useful to look for potential changes in the dispersion of the singlet-triplet excitation in $\text{Ba}_3\text{Mn}_2\text{O}_8$. Given the trend we observe in c/a , higher pressure ($P > 10$ GPa) neutron or x-ray diffraction measurements or raman spectra of $\text{Ba}_3\text{Mn}_2\text{O}_8$ are appropriate for further investigations of a potential high pressure phase transition as observed in similar compounds.¹⁹⁾ Unfortunately, current inelastic neutron scattering techniques do not allow for such high pressures to be reached at temperatures as low as $T \approx 2$ K.

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1) S. E. Sebastian *et al.*: Nature (London) **441** (2006) 617.
 2) C. D. Batista *et al.*: Phys. Rev. Lett. **98** (2007) 257201.

- 3) J. Schmalian and C. D. Batista: Phys. Rev. B **77** (2008) 094406.
- 4) M. T. Weller and S. J. Skinner: Acta Crystallogr., Sect. C **55** (1999) 154.
- 5) M. Uchida *et al.*: J. Phys. Soc. Jpn. **70** (2001) 1790.
- 6) Unless otherwise noted, error bars represent one standard deviation uncertainty.
- 7) E. C. Samulon, Y.-J. Jo, P. Sengupta, C. D. Batista, M. Jaime, L. Balicas, and I. R. Fisher: Phys. Rev. B **77** (2008) 214441.
- 8) M. B. Stone, M. D. Lumsden, Y. Qiu, E. C. Samulon, C. D. Batista, and I. R. Fisher: Phys. Rev. B **77** (2008) 134406.
- 9) M. B. Stone, M. D. Lumsden, S. Chang, E. C. Samulon, C. D. Batista, and I. R. Fisher: Phys. Rev. Lett. **100** (2008) 237201.
- 10) E. C. Samulon, M. C. Shapiro, and I. R. Fisher: Phys. Rev. B **84** (2011) 054417.
- 11) M. B. Stone, A. A. Podlesnyak, G. Ehlers, A. Huq, E. C. Samulon, M. C. Shapiro, and I. R. Fisher: J. Phys.: Condens. Matter **23** (2011) 416003
- 12) Ch. Rüegg, B. Normand, M. Matsumoto, A. Furrer, D.F. McMorrow, K. W. Krämer, H.-U. Güdel, S. Gvasaliya, H. Mutka, and M. Boehm: Phys. Rev. Lett. **100** (2008) 205701; Ch. Rüegg, A. Furrer, D. Sheptyakov, Th. Strässle, K. W. Krämer, H.-U. Güdel, and L. Mélési: Phys. Rev. Lett. **93** (2004) 257201.
- 13) B. Normand, M. Matsumoto, O. Nohadani, S. Wessel, S. Haas, T. M. Rice, and M. Sigrist: J. Phys.: Condens. Matter **16** (2004) S867.
- 14) H. Tanaka, K. Goto, M. Fujisawa, T. Ono, and Y. Uwatoko: Physica B **329-333** (2003) 697.
- 15) N. Johannsen, A. Oosawa, J. Tanaka, A. Vasiliev, and T. Lorenz: Physica B **378-380** (2006) 1043.
- 16) K. Goto, T. Ono, H. Tanaka, and Y. Uwatoko: Prog. Theor. Phys. **159** (2005) 397.
- 17) T. Hong, C. Stock, I. Cabera, C. Broholm, Y. Qiu, J. B. Leao, S. J. Poulton, and J. R. D. Copley: Phys. Rev. B **82** (2010) 184424.
- 18) T. Hong, V. O. Garlea, A. Zheludev, J. A. Fernandez-Baca, H. Manaka, S. Chang, J. B. Leao, and S. J. Poulton: Phys. Rev. B **78** (2008) 224409.
- 19) A. Grzechnik and P. F. McMillan: J. Solid State Chem. **132** (1997) 156.