Critical properties of the $S=1$ spin dimer compound $\text{Ba}_3\text{Mn}_2\text{O}_8$

S. Suh, K. A. Al-Hassanieh, E. C. Samulon, J. S. Brooks, W. G. Clark, P. L. Kuhns, L. L. Lumata, A. Reyes, I. R. Fisher, S. E. Brown, and C. D. Batista

\textit{1Department of Physics and Astronomy, UCLA, Los Angeles, CA 90095-1547 USA}
\textit{2Theory Division, Los Alamos National Laboratory, Los Alamos, NM 87545 USA}
\textit{3Geballe Laboratory for Advanced Materials and Department of Applied Physics, Stanford University, Stanford, CA 94305 USA}
\textit{4Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310 USA}

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$\text{Ba}_3\text{Mn}_2\text{O}_8$ is a hexagonally coordinated Mn$^{5+}$ $S=1$ spin dimer system with small uniaxial single-ion anisotropy. $^{135,137}\text{Ba}$ NMR spectroscopy is used to establish the lower critical field $H_{c1}$ of distinct field-induced phases for $\mathbf{H} \parallel \mathbf{c}$, $\mathbf{H} \perp \mathbf{c}$, and to measure the longitudinal ($M_t$) and transverse ($M_\perp$) magnetizations in the vicinity of the quantum critical point (QCP). $M_t(T,H_{c1})$, $M_\perp(T,H_{c1})$ are reproduced by solving a low-energy model for a dilute gas of interacting bosons. $M_t(T \to 0,H = H_{c1})$ follows the expectation for a BEC (Ising-like) QCP.

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Recent investigations of field-induced phases in $S=1/2$ magnetic insulators typify the opportunities for studying the problem of Bose Einstein condensates (BEC’s) specifically $\mathbf{c}$, and quantum criticality more generally. In spin-dimer, and other spin-gapped systems, the ground state is a singlet while the lowest excited states are a mode of triplet excitations $\mathbf{2}$, $\mathbf{3}$. The magnetic field tunes the chemical potential for triplet excitations through zero at the critical field $H_{c1}$ producing a controlled density of triplets, that can either condense or crystallize into a superlattice depending on the balance between kinetic and potential energies $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$. The Hamiltonian has $U(1)$ rotational symmetry in the idealized case, and this symmetry is spontaneously broken in the condensed phase with the development of a finite transverse magnetization $M_t$.

From what is known about the spin-dimer system $\text{Ba}_3\text{Mn}_2\text{O}_8$ $\mathbf{a}$, these conditions hold for $\mathbf{H} \parallel \mathbf{c}$ $\mathbf{a}$, $\mathbf{b}$. However, the evolution of the phases in a magnetic field is known to deviate from the simplest $S=1/2$ isotropic case in a number of ways $\mathbf{c}$, $\mathbf{d}$, $\mathbf{e}$. Two magnetization plateaus with $\langle S_z \rangle = 1$ (per dimer) and $\langle S_z \rangle = 2$ are observed as a result of the $S=1$ state of the Mn$^{5+}$ ions $\mathbf{f}$, $\mathbf{g}$, $\mathbf{h}$. In addition, a small single-ion uniaxial anisotropy is understood to produce new boundaries in the ordered phases for $\mathbf{H}$ tilted from the $\mathbf{c}$-axis. While this anisotropy is not relevant for $\mathbf{H} \parallel \mathbf{c}$, its influence is most prominent for $\mathbf{H} \perp \mathbf{c}$, where there is evidence for an additional phase II, stabilized only near $H_{c1}$, and the other three critical fields. Further, the hexagonal coordination of the layers leads to geometric frustration. The near-neighbor transverse spin components would be rotated by $\alpha = 120^\circ$ in an isolated triangular layer $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$. However, interlayer coupling (Fig. $\mathbf{l}$) leads to $\alpha \to 120^\circ + \epsilon$ with $\epsilon \sim 9^\circ$, because incommensurate spin ordering partially releases the interlayer frustration.

Presented here are results of $^{135,137}\text{Ba}$ NMR spectroscopy studies in the high symmetry phase near $H_{c1}$, and in the ordered phases I ($\mathbf{H} \parallel \mathbf{c}$, $\mathbf{H} \perp \mathbf{c}$) and II ($\mathbf{H} \perp \mathbf{c}$). The NMR shifts are used to establish the magnetization as a function of temperature at $H = H_{c1}$. For the case $\mathbf{H} \parallel \mathbf{c}$, the result is consistent with the expectations for a BEC-QCP, i.e., $M(T \to 0,H_{c1}) \sim T^{1.5}$. Both the universal and the non-universal ($T > 100\text{mK}$) regimes are quantitatively described using an effective low-energy theory for a dilute gas of bosons. Quantitative differences are observed for $\mathbf{H} \perp \mathbf{c}$, in agreement with the expectation for the Ising-like ($Z_2$) broken symmetry of phase II $\mathbf{a}$. Further, we investigate the longitudinal and transverse magnetization ($M_t$, $M_\perp$) of the ordered phases,
and establish that the field dependence of the transverse magnetization follows the expected mean-field behavior \((D = d + z \geq 4)\). We also conclude that the line of transitions dividing I/II is discontinuous.

The maximum temperature of the ordered phases is \(T_m = 0.9K\) \(3\), so the measurements reported here were performed on a single crystal placed inside the mixing chamber of a dilution refrigerator. \(135,137\)Ba \((135,137)I = 3/2\) NMR spectroscopy was performed in magnetic fields \(H \leq 120\)kOe using a top-tuned configuration. The platform holding the sample and coil is rotated by an Attocube piezoelectric motor. At the higher fields available at the NHMFL, we used a bottom-tuned \(^3\)He system.

The diagonal hyperfine couplings were determined by comparing high temperature measurements of the shift \((T \geq 20\)k) to susceptibility measurements \(3\). Orbital and quadrupolar couplings were determined from the shifts measured at the lowest temperatures for \(H < H_a\).

Some of the NMR parameters are summarized in Table I:

| Ba(1) | Ba(2) |
|-------|-------|
| \(A_{ax}\) | 0.26(1) | 0.26(1) |
| \(A_{\perp}\) | 0.35(2) | 0.35(2) |
| \(^{137}\nu_Q\) (MHz) | 54.7(2) | 10.8(2) |

The exchange constants \(13\) and the g-factors are \(J_1 = 0.118\)meV, \(J_2 - J_3 = 0.114\)meV, \(J_3 = 0.037\)meV, \(g_{cc} = 1.98\) and \(g_{aa} = 1.97\). The effective repulsive interaction \(\nu_a = \Gamma_a(\mathbf{Q}, \mathbf{Q})\) results for summing the ladder diagrams for the bare interaction vertex \(V_a\) \(14\):

\[
\Gamma_a(\mathbf{k}, \mathbf{k}') = V_a - \int_{-\infty}^{\infty} \frac{d^3p}{8\pi^3} V_{\mathbf{p}} \rho_{\mathbf{k}+\mathbf{p}} + \rho_{\mathbf{k}'-\mathbf{p}}
\]

For \(Ba_2\)Mn\(_2\)O\(_8\), we have \(V_a = U + (J_2 + J_3)\gamma_2^2 + J_1\gamma_1 q^2 + J_3\gamma_3 q^3\), where \(U \to \infty\) comes from the hard-core repulsion, while the rest of the terms correspond to the off-site repulsive interactions the result from the Ising terms of the inter-dimer exchange couplings. By solving Eq. (3), we obtain \(\nu_a = 0.9\)meV for \(J_2 + J_3 = 2.82\)K. The value of \(J_2 + J_3\) is obtained by fitting \(M_{c2} \approx 27\)T for \(H || c\). We note that the second term of \(H\) breaks the U(1) symmetry associated to the conservation of the total number of bosons (\(M_{\perp}\)) for \(H \perp c\). This term is originated by the effective exchange anisotropy found in Ref. \(3\). Consequently, we expect an Ising-like (broken \(Z_2\)) quantum phase transition (QPT) for \(H \perp c\) in contrast to the BEC-QPT that occurs for \(H || c\).

Magnetization results for \(H \parallel c\) are shown in Fig. 2, for several fields near \(H_a\). The curve measured at \(H = H_a = 89.3\)kOe is consistent with the expectation \(M_{\perp} \sim T^{3/2}\) for \(T \to 0\). The red line is the result of a Hartree-Fock decoupling of the last term of \(H\) that in the disordered phase has the effect of renormalizing the chemical potential \(\mu_{eff} = \mu - 2v_0\rho\) (\(\rho\) is the density of bosons) \(4\). Calculations for field values differing from \(H_a\), \(H = H_a - 1.3\)kOe (blue) and \(H = H_a + 1.5\)kOe (green), also match the NMR shift data well. There is a 20% disagreement if only the hard-core repulsion is included in Eq. (3).

When the applied field is rotated to the \(ab\) plane, the ordered phase II bordering the paramagnet is believed to be Ising-like, with transverse spins confined to the \(c\) direction. In this case, we expect \(M_{\perp} \approx T^2\) for \(T \to 0\) and \(H = H_a\). The NMR results in Fig. 2 agree well with the mean field treatment of \(H\). The anisotropy term also has the effect of lowering the critical field \(H_{c1}\). In confining the transverse spins to the \(c\)-axis, the energy gain associated with the broken symmetry is reduced slightly, and consequently \(M_{\perp} < M_{\parallel}\). The outcome is consistent with the anisotropy parameter \(D = 32\)meV as established by electron paramagnetic resonance \(15\).

Turning to the transverse magnetization, Fig. 3 shows two field-swept spectra in the condensed phase for \(H \parallel c\). The blue segment in the inset shows the location in the phase diagram where these spectra were recorded. The spectrum of the Ba(1) site is well reproduced by assuming a simple plane wave incommensurate modulation of the longitudinal field (dashed red line). The functional form is independent of \(H\) for \(H \parallel c\); only the spectral width and overall shift vary. The Ba(2) spectra are composed of two parts of equal intensity, and there appears

\[
\begin{array}{|c|c|c|}
\hline
\text{site} & A_{ax} & A_{\perp} & \nu_Q (MHz) \\
\hline
\text{Ba(1)} & 0.26(1) & 0.35(2) & 54.7(2) \\
\text{Ba(2)} & 0.18(1) & 0.11(1) & 10.8(2) \\
\hline
\end{array}
\]
The incommensurate modulation arises from the incommensurability. The Ba(2) sites have lower ($C_{3h}$) symmetry, with the three nearest-neighbor Mn forming a triangle of specific chirality.

The spectrum broadens and shifts near $H_{c1}$. Unlike for $H \parallel c$, the spectra are distinctly asymmetric at all fields in the range of phase II. Still, the spectrum remains relatively simple up to $H \approx 100-105$ kOe. The spectrum becomes particularly complicated over a range of fields extending to approximately $115$ kOe, then simplifies once again, for $H \geq 115$ kOe. We take this observation as evidence for a line of first order phase transitions dividing phases II and I, consistent with recent neutron scattering experiments carried out independent of this work [17].

It is useful to consider the prediction for the nature of phase II to interpret the significance of the lineshapes. At low temperatures and $H > H_{c1}$, the transverse magnetization oscillates with wavevector $\mathbf{Q}$ out of the plane, $M_t \parallel c$. The longitudinal component is modulated with $M_l \parallel c$...
wavevector $2Q$. The behavior is parameterized as

$$S^y_{j\mu} = (-1)^\mu \frac{1}{\sqrt{3}} \sin 2\theta \cos (r_j \cdot Q), \quad S^y_{j\mu} = 0$$

$$S^z_{j\mu} = \frac{1}{4} \pm \frac{1}{4} \sqrt{\cos^2 2\theta + \sin^2 2\theta \sin^2 (r_j \cdot Q)},$$

where $j$ is a dimer index, $\mu = 1, 2$ labels the two sites of each dimer, $H$ defines the z-axis, and $\theta = [0, \pi]$. The results of model simulations indicate that the lineshapes for $H < 105\text{kOe}$ are qualitatively consistent with phase II, provided that both isotropic and anisotropic hyperfine coupling terms are included.[10]

The $^{135,137}$Ba spectroscopy reported here summarized the behavior around the critical point $H = H_{c1}$ for two directions of $H$. For the longitudinal magnetization, the data is well described by including interdimer (near-neighbor) repulsions in the ladder calculation. In particular, the BEC universality class applies for the case $H \parallel c$, whereas Ising-like criticality applies to $H \perp c$. Our data also establishes the presence of incommensurate order parameters. However, some parameters, which are relevant to the analysis of the Ba(2) site hyperfine coupling for $H \parallel c$, remain unknown. For example, the shifts of the sites located near Mn triangles of opposite chirality are different in the condensed phase, and it is not clear why this should be the case. A possible explanation could originate with spin-orbit interactions indirectly impacting the hyperfine fields in Ba(2) sites of different chirality.

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