Successive phase transitions and phase diagrams for the quasi-two-dimensional easy-axis triangular antiferromagnet \( \text{Rb}_4\text{Mn}(\text{MoO}_4)_3 \)

R. Ishii\(^{(a)}\), S. Tanaka\(^{1}\), K. Onuma\(^{2}\), Y. Nambu\(^{3,4}\), M. Tokunaga\(^{1}\), T. Sakakibara\(^{1}\), N. Kawashima\(^{1}\), Y. Maeno\(^{2}\), C. Broholm\(^{3,4}\), D. P. Gautreaux\(^{5}\), J. Y. Chan\(^{5}\) and S. Nakatsuji\(^{1}\)

\(^{1}\) Institute for Solid State Physics (ISSP), University of Tokyo, Kashiwa - Chiba 277-8581, Japan
\(^{2}\) Department of Physics, Kyoto University - Kyoto 606-8502, Japan
\(^{3}\) Institute for Quantum Matter and Department of Physics and Astronomy, Johns Hopkins University Baltimore, MD 21218, USA
\(^{4}\) NIST Center for Neutron Research, National Institute of Standards and Technology (NIST) Gaithersburg, MD 20899, USA
\(^{5}\) Department of Chemistry, Louisiana State University - Baton Rouge, LA 70803, USA

received 5 November 2010; accepted in final form 3 March 2011
published online 31 March 2011

PACS 75.10.Hk – Classical spin models
PACS 75.40.Cx – Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.)
PACS 75.50.Ee – Antiferromagnetics

Abstract – Using magnetic, thermal and neutron measurements we show that \( \text{Rb}_4\text{Mn}(\text{MoO}_4)_3 \) is a quasi-2D triangular Heisenberg antiferromagnet with easy-axis anisotropy and successive transitions bracketing an intermediate collinear phase. An accurate quantitative account of the phase diagram is achieved through Monte Carlo simulation of a spin Hamiltonian with easy-axis anisotropy \( D = 0.22J \).

Copyright © EPLA, 2011

Geometrically frustrated magnetism has been an active area of condensed-matter physics for more than two decades. Save the isolated examples of spin ice [1] and the Shastry-Sutherland lattice in \( \text{SrCu}_2(\text{BO}_3)_2 \) [2,3], full or semi-quantitative agreement between experiment and theory has, however, largely been elusive. Here we report a high-fidelity quantitative account of magnetism in a novel triangular lattice model system \( \text{Rb}_4\text{Mn}(\text{MoO}_4)_3 \) through Monte Carlo simulation of a simple spin Hamiltonian.

Originally the basis for Anderson’s resonating valence bond proposal [4], i.e. the two-dimensional (2D) triangular antiferromagnet (TAF), plays a special role in geometrically frustrated magnetism [5–8]. Theoretically, there is a consensus that the ground state for the nearest-neighbor antiferromagnetic (AF) Heisenberg model has \( 120^\circ \) spin order for any spin quantum number [9–11]. In such a non-collinear spin structure, the concept of vector chirality, the handedness by which the spins are rotated to form \( 120^\circ \) order on a given triangle, can be essential and lead to multiferroic phenomena [12] and phase transitions with a new universality class [13].

While the correlated behavior is complex, the Hamiltonian for the nearest-neighbor Heisenberg model on the triangular lattice is simply stated:

\[
\mathcal{H} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - D \sum_i (S_i^z)^2 - g \mu_B \sum_i \mathbf{H} \cdot \mathbf{S}_i. \tag{1}
\]

Here \( J > 0 \) and \( D \) parameterize the strength of the intralayer exchange interaction and the single-ion anisotropy, respectively. Depending on the sign of \( D \), the model exhibits three types of phase transitions affected by vector chirality. For Heisenberg spin with \( D = 0 \), a chiral point defect called a \( Z_2 \) vortex is possible, and a proposal has been made for a finite-temperature \( Z_2 \) vortex binding-unbinding transition at finite temperature [14]. For \( XY \)-type anisotropy \( (D < 0) \), long-range order (LRO) of the vector chirality without dipole magnetic order is expected at slightly higher temperature than the Kosterlitz-Thouless transition into \( 120^\circ \) quasi-LRO [15,16]. For the easy-axis case \( (D > 0) \), successive

\[^{(a)}\] E-mail: rmorisaki@issp.u-tokyo.ac.jp
transitions associated with respective ordering of the longitudinal and transverse spin components are expected [17,18]. Specifically on cooling, the system first forms a collinear intermediate phase (IMP) with the three-sublattice “uud” structure [19] before transitioning to 120° spin-order phase with a uniform vector chirality. A recent theoretical study has indicated another phase transition in the IMP, separating the lowertemperature “uud” phase and a higher-temperature collinear phase with three different sublattice moments. However, the latter phase is only stable in the purely 2D limit, and thus with finite interlayer coupling, the “uud” phase should become dominant throughout the collinear IMP [19]. For the easy-axis case, unlike the Heisenberg and XY, experiments have generally confirmed the theoretical predictions. Specifically, successive transitions and/or a 1/3 magnetization plateau have been observed for TAFs with easy-axis anisotropy such as VCl₃ [20], AGrO₂ (A = Li, Cu) [21,22], and a metallic TAF GdPd₂Al₂ [23]. However, neither a detailed study of the phase diagram under external field nor a quantitative comparison between experiment and theory has so far been possible, because of large values of J which preclude access to the high-field regime and/or magnetostriiction, which complicates quantitative comparison between theory and experiment. Here, we report a comprehensive study of the crystal structure, spin structure and thermo-dynamic properties of the quasi-2D Heisenberg TAF Rb₂Mn(MoO₄)₃. This material exhibits successive zero-field phase transitions and a 1/3 magnetization plateau, as a result of its easy-axis anisotropy. The relatively small exchange constant, J, allows us for the first time to determine the complete phase diagrams under field both parallel and perpendicular to the easy axis. In a rare case for geometrically frustrated magnetism, quantitative agreement between experiment and theory is achieved and establishes Rb₂Mn(MoO₄)₃ as an ideal model system for the 2D Heisenberg TAF described by eq. (1) with J = 1.2 K and D = 0.26 K.

Single crystals with typical dimensions 1 × 1 × 0.5 mm³ were synthesized by a flux method [24]. The structure was determined by single-crystal X-ray diffraction and is described by the space group P6₃/mmc (R₁ = 2.88%). powder neutron diffraction (PND) measurements were performed on BT1 at NIST, and confirmed this structure and its stability down to 1.5 K. Thus, Rb₂Mn(MoO₄)₃ contains an equilateral triangular lattice of Mn²⁺ ions. Each Mn²⁺ ion is located in a MoO₄ polyhedron and has a high-spin S = 5/2 Heisenberg spin. The dominant intralayer coupling J should result from the superexchange path Mn-O-O-Mn involving two oxygen atoms. The interlayer interaction is expected to be negligible because two Rb⁺ ions and two MoO₄ tetrahedra yield a large separation between neighboring planes.

DC magnetization (M) was measured by a commercial SQUID magnetometer above 1.8 K, and by a Faraday method for 0.37 K < T < 2 K [25]. Specific heat, Cₚ, was measured by a thermal relaxation method down to 0.4 K under fields up to 9 T. Pulsed-field measurements of M were performed up to 27 T. Classical Monte Carlo simulations (MCs) were carried out using the standard Metropolis method. The error bars of the MCs results are smaller than the symbol sizes used in all figures.

For an overview, we first present the T-H phase diagrams in figs. (1c) and (d). The qualitative nature of the phase diagram for μ₀H ∥ c is fully consistent with the pioneer theoretical works in refs. [17] and [18]. On the other hand, for μ₀H ∥ ab, this is the first report on the phase diagram for a quasi-2D TAF with an easy-axis-type anisotropy. For these two field directions, a total of six phases (A)–(F) are identified. Each symbol
represents a transition point determined by different probes. In the following, we describe details of the experiments used to construct the phase diagrams, and compare them to theory. Starting with the specific-heat data, a double-kink structure is observed in the temperature dependence of \( C_p / T \) at \( T \geq T_{N2} \) (Fig. 2(b)). A broad tail of the peak seen for \( C_p / T \) under a pulsed field (solid lines) and calculated using MCs (dashed lines) for \( \mu_0 H \parallel c \) and \( \mu_0 H \parallel ab \). Successive phase transitions and phase diagrams for the quasi-2D easy-axis TAF Rb$_2$Mn(MoO$_4$)$_3$ below \( \sim 10 \) K, suggesting that Rb$_2$Mn(MoO$_4$)$_3$ has easy-axis anisotropy.

Clear evidence for easy-axis anisotropy is found in the field dependence of \( M(H) \) measured under a pulsed field (solid lines) and calculated using MCs (dashed lines) for \( \mu_0 H \parallel c \) and \( \mu_0 H \parallel ab \). Quantitative agreement with the MCs' results is found except in the plateau region for \( \mu_0 H \parallel c \), where the experimental plateau is shallower than that of MCs possibly as a result of critical effects. By using the kink found in \( dM/dH \), we define the lower and upper critical fields of the plateau region, \( \mu_0 H_{c1} \) and \( \mu_0 H_{c2} \), and the critical field associated with the saturation of the magnetic moment, \( \mu_0 H_C \). The 1/3 plateau in \( M(H) \) for \( \mu_0 H \parallel c \) as well as the larger slope away from the plateau as compared to the \( ab \)-plane magnetization curve clearly indicates the easy-axis anisotropy. The phase diagram in fig. 1(c) shows that the plateau field region becomes wider with increasing temperature, and is smoothly connected with the IMP.
indicated by the temperature anomalies in both $C_p/T$ and $\chi$. In conjunction with the MCs data, this implies that phase (B) has the “$ud$” structure (fig. 1(c)).

By comparing experiment with theory in appropriate limits, we first estimate the parameters $J$ and $D$. The mean-field theory predicts that the $ab$-plane and $c$-axis magnetization data are linear in $H$ and follow $M = N_A g(\mu_B)^2 S H / (9 J - 2 D)$ up to $\mu_0 H_{c3}$ and $M = N_A g(\mu_B)^2 S H / (9 J - 6 D)$ up to $\mu_0 H_{c1}$, respectively [18]. The experimental results in figs. 4(a) and (b) are indeed $H$-linear and the fits give $J = 1.2 K$, $D = 0.28 K$ and thus $D/J = 0.23$. This value is consistent with the value of $J = 1.14(5) K$ derived from high-temperature susceptibility data. Fixing $J = 1.2 K$, and comparing zero field $T_{N1}$ and $T_{N2}$ with those obtained by MCs as a function of $D/J$, we estimate $D/J$ to be $0.22(2)$, as indicated by the vertical dotted line of fig. 2(c). The excellent agreement between these different routes to $D/J$ confirms each approach and the value obtained. Thus throughout the paper, we shall henceforth adopt $J = 1.2 K$ and $D/J = 0.22$.

We now proceed to a more comprehensive comparison of the phase diagrams obtained by experiment and by MCs of eq. (1) (figs. 1(c) and (d)). Considering that only two free parameters are involved, the agreement between experiment (symbols) and theory (dashed lines) for both field directions and including the magnetization plateau phase is remarkable. This suggests that the spin Hamiltonian for Rb$_4$Mn(MoO$_4$)$_3$ is well captured by eq. (1), while additional symmetry allowed terms such as the Dzyaloshinsky-Moriya interaction are inconsequential in comparison to the $J$ and $D$ terms. The three-sublattice spin structures inferred from comparison of thermo-magnetic data to theory are schematically presented by solid arrows in each region of phases (A)–(F).

At zero temperature and field, the theory predicts a 120° structure with slight canting toward the $c$-axis due to easy-axis anisotropy, and as schematically shown in phase (A) of fig. 1(c). The canting angle $\theta$ is estimated to be 2.7° for $H = 0$ by the relation $\cos(\pi/3 - \theta) = 3J/(6J - 2D)$ [18]. Such canting causes an increase in $\chi(T)$ below $T_{N1}$, as consistently seen in both experiment and theory (figs. 3(a) and (b) and their insets). According to theory, the canted structure is stable under $\mu_0 H \parallel c$ in phase (A). With further increasing $\mu_0 H \parallel c$, however, the “$ud$” structure with a 1/3 magnetization plateau takes over in phase (B) as observed in the magnetization data, and then should transit to the “oblique” phase (C) with two parallel spins and one pointing to a different direction. Finally, in phase (D), the moments are fully polarized.

Because $D/J < 1$, the low-$T$ canted structure at 0T should be nearly degenerate with a fan-shape structure that has one spin in the $ab$-plane [18]. This fan-shape structure has a weak ferromagnetic component in the $ab$-plane, and can be easily stabilized under a weak in-plane field in phase (E). This should induce an enhancement of $\chi(T)$ below $T_{N1}$. Here as well, we find quantitative agreement between experiment and theory (fig. 3(b) and its inset). Notably, the fan-shape structure in phase (E) has uniform vector chirality directed along an in-plane direction perpendicular to the field. Under $\mu_0 H \parallel ab$, the IMP (F) narrows in temperature where the theory predicts that a collinear spin structure becomes inclined toward the field direction (fig. 1(d)). Although unlikely, the possibility of the umbrella state cannot be ruled out in phases (C) and (E) from our experiment and MCs. To clarify this possibility, single-crystal neutron diffraction measurements in magnetic fields will be necessary to confirm the magnetic structure in more detail in phases (A)–(F).

To confirm the 120° structure under zero field, we performed PND measurements on B'T7 at NIST. Figure 5 shows the difference between the PND spectra obtained at 1.5 K and 10 K with no final energy analysis. A magnetic peak at the wave vector $\sim (1/3, 1/3, 1)$ indicates a 120° in-plane spin structure as well as AF interlayer correlations. The absence of a strong peak at (1,1,1) is consistent with a near fan-like structure at low $T$ as opposed to a “$ud$” structure. We fit the data to the analytical formula for the spherical average of magnetic scattering from a quasi-2D 120° magnetic structure with small canting component as predicted for phase (A). The out-of-plane correlations are described by a Lorentzian and the in-plane correlations by a Lorentzian squared [8]. The inferred in-plane and out-of-plane correlation lengths are $\xi_{ab} > 53.7a(6) \approx 9a$ and $\xi_c > 19.1(6) \approx 0.8c$, respectively, indicating quasi-2D magnetism of the variety anticipated by MCs. The weak interlayer correlations justify the use of a two-dimensional model to account for the thermo-magnetic data.

Our study has established a rare case of detailed quantitative agreement between experiment and theory for a geometrically frustrated magnet. Especially for $\mu_0 H \parallel ab$, fig. 1(d) provides the first experimental and theoretical case of a magnetic phase diagram on the easy-axis triangular antiferromagnet. It has also established Rb$_4$Mn(MoO$_4$)$_3$ as an ideal model system to explore many unusual aspects of 2D frustrated magnetism, such as
critical dynamics associated with vector chirality [13], multiferroic non-collinear magnetism, and instability of conventional magnon excitations [26]. In addition, quantum effects, which are particularly important for smaller-size spins with $S \leq 1$, are left as a subject for future studies.

This work is partially supported by Grant-in-Aid for Scientific Research (Nos. 19052004, 19340109, 21684019, 21840021, 22340111) from JSPS, by Grant-in-Aid for Scientific Research on Priority Areas (Nos. 17071003, 19052003, 17072001) from MEXT, Japan, and by US-Japan Cooperative Program, ISSP. The computation is executed at the Supercomputer Center, ISSP. Work at IQM is supported by the US DOE office of Basic Energy Sciences through DE-FG02-08ER46544.

REFERENCES

[1] Bramwell S. T. and Gingras M. J. P., Science, 294 (2001) 1495.
[2] Kageyama H., Yoshimura K., Stern R., Mushnikov N. V., Kato M., Kosuge K., Sliechter C. P., Goto T. and Ueda Y., Phys. Rev. Lett., 82 (1999) 3168.
[3] Miyahara S. and Ueda K., Phys. Rev. Lett., 82 (1999) 3701.
[4] Anderson P. W., Mater. Res. Bull., 8 (1973) 153.
[5] Collins M. F. and Petrenko O. A., Can. J. Phys., 75 (1997) 605.
[6] Shimizu Y., Miyagawa K., Kanoda K., Maesato M. and Saito G., Phys. Rev. Lett., 91 (2003) 107001.
[7] Misguich G. and Lhuillier C., in Frustrated Spin Systems, edited by Diep H. T. (World Scientific, Singapore) 2004.
[8] Nakatsuji S., Nambu Y., Tonomura H., Sakai O., Jonas S., Broholm C., Tsunetsugu H., Qiu Y. and Maeno Y., Science, 309 (2005) 1697.
[9] Huse D. A. and Elser V., Phys. Rev. Lett., 60 (1988) 2531.
[10] Bernu B., Lhuillier C. and Pierre L., Phys. Rev. Lett., 69 (1992) 2590.
[11] Capriotti L., Trumper A. E. and Sorella S., Phys. Rev. Lett., 82 (1999) 3899.
[12] Kimura T. and Tokura Y., J. Phys.: Condens. Matter, 20 (2008) 434204.
[13] Kawamura H., J. Phys.: Condens. Matter, 10 (1998) 4707.
[14] Kawamura H. and Miyashita S., J. Phys. Soc. Jpn., 53 (1984) 4138.
[15] Miyashita S. and Shibata H., J. Phys. Soc. Jpn., 53 (1984) 1145.
[16] Capriotti L., Vail R., Cuccoli A. and Tognetti V., Phys. Rev. B, 58 (1998) 273.
[17] Miyashita S. and Kawamura H., J. Phys. Soc. Jpn., 54 (1985) 3385.
[18] Miyashita S., J. Phys. Soc. Jpn., 55 (1986) 3605.
[19] Melchy P.-E. and Zhitomirsky M. E., Phys. Rev. B, 80 (2009) 064411.
[20] Kadowaki H., Uebuki K., Hirakawa K., Martinez J. L. and Shirane G., J. Phys. Soc. Jpn., 56 (1987) 4027.
[21] Kadowaki H., Takei H. and Motoyama K., J. Phys.: Condens. Matter, 7 (1995) 6869.
[22] Kimura K., Nakamura H., Ohgushi K. and Kimura T., Phys. Rev. B, 78 (2008) 144041(R).
[23] Kitazawa H., Suzuki H., Abe H., Tan H. and Kido G., Physica B, 259 (1999) 890.
[24] Solodovnikov S. F. and Klevtsova R. F., Sov. Phys. Crystallogr., 33 (1988) 820.
[25] Sakakibara T., Mitamura H., Tayama T. and Amitsuka H., Jpn. J. Appl. Phys., 33 (1994) 5067.
[26] Chernyshev A. L. and Zhitomirsky M. E., Phys. Rev. Lett., 97 (2006) 207202.