

This is the accepted manuscript made available via CHORUS. The article has been published as:

Long-range magnetic order and interchain interactions in the $S=2$ chain system $\text{MnCl}_3(\text{bpy})$

Randy S. Fishman, Shin-ichi Shinozaki, Akira Okutani, Daichi Yoshizawa, Takanori Kida, Masayuki Hagiwara, and Mark W. Meisel

Phys. Rev. B **94**, 104435 — Published 28 September 2016

DOI: [10.1103/PhysRevB.94.104435](https://doi.org/10.1103/PhysRevB.94.104435)

Long-range magnetic order and interchain interactions in the $S = 2$ chain system $\text{MnCl}_3(\text{bpy})^*$

Randy S. Fishman,¹ Shin-ichi Shinozaki,² Akira Okutani,² Daichi Yoshizawa,²
Takanori Kida,² Masayuki Hagiwara,² and Mark W. Meisel^{3,4}

¹*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

²*Center for Advanced High Magnetic Field Science, Graduate School of Science,
Osaka University, Toyonaka, Osaka 560-0043, Japan*

³*Department of Physics and the National High Magnetic Field Laboratory,
University of Florida, Gainesville, Florida 32611-8440, USA*

⁴*Joint Institute for Neutron Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6453, USA*

(Dated: September 7, 2016)

A compound with very weakly interacting chains, $\text{MnCl}_3(\text{bpy})$, has attracted a great deal of attention as a possible $S = 2$ Haldane chain. However, long-range magnetic order of the chains prevents the Haldane gap from developing below 11.5 K. Based on a four-sublattice model, a description of the antiferromagnetic resonance (AFMR) spectrum up to frequencies of 1.5 THz and magnetic fields up to 50 T indicates that the interchain coupling is indeed quite small but that the Dzaloshinskii-Moriya interaction produced by broken inversion symmetry is substantial (0.12 meV). In addition, the antiferromagnetic, nearest-neighbor interaction within each chain (3.3 meV) is significantly stronger than previously reported. The excitation spectrum of this $S = 2$ compound is well-described by a $1/S$ expansion about the classical limit.

PACS numbers: 76.50.+g, 75.10.Jm, 75.50.Ee

INTRODUCTION

Magnetic chains composed of spin $S = 2$ ions have received considerable theoretical and numerical attention [1–8] due to their unique predicted behavior. Even- and odd-integer spin chains are distinct, with the latter in a symmetry-protected topological phase [3, 9]. Whereas the $S = 1$ Haldane phase [10–13] has been observed experimentally [14–20], formation of the $S = 2$ Haldane state has been prevented by long-range magnetic ordering due to interactions between the chains. Although some aspects of $S = 2$ chains have been observed in optical gasses [7, 21], the question remains whether a real chain can realize the $S = 2$ Haldane phase [22–27].

Portrayed in Fig. 1, our protagonist is the $S = 2$ antiferromagnetic chain of (2, 2'-bipyridine)trichloromanganese(III), $\text{MnCl}_3(\text{bpy})$, where $(\text{bpy}) = (2, 2'\text{-bipyridine}) = \text{C}_{10}\text{H}_8\text{N}_2$, [28, 29]. Due to the (bpy) molecules separating the chains, this material was believed to be an excellent candidate for observing the

$S = 2$ Haldane phase [30]. However, weak signatures from randomly-arranged microcrystals hinted that long-range order might appear at low temperatures [31, 32]. Recently, unambiguous long-range antiferromagnetic ordering was identified at $T_N = 11.5$ K [33, 34] in

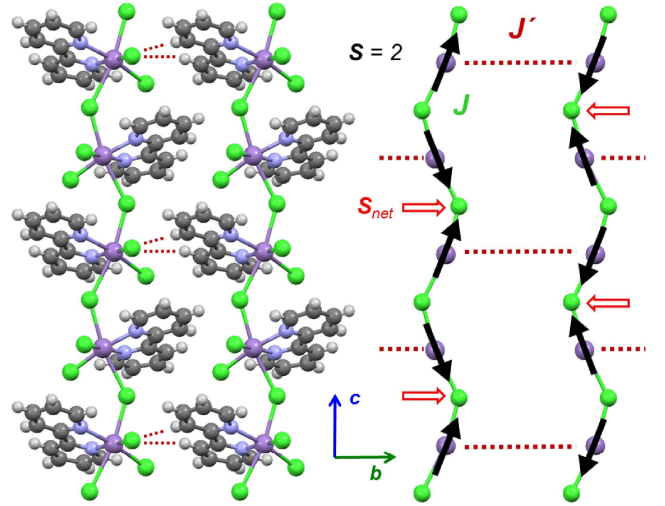


FIG. 1: (Color online) The left side shows the crystal structure of $\text{MnCl}_3(\text{bpy})$ [28] for two nearest-neighbor chains in the $b - c$ plane. The staggered chains of $\text{Mn(III)} S = 2$ ions are connected by Cl atoms, and the locations of the (bpy) cause an alternating $\text{Cl} \cdots \text{H}$ coupling indicated by the dotted lines. The right side shows only the $\text{Mn}-\text{Cl}$ chains and the interactions J and J' . The Mn magnetic moments are indicated by the dark arrows, while open arrows sketch the net moments arising from the canted spins.

*Copyright notice: This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

oriented single-crystals.

Although magnetic ordering appears in single crystals, the recently published antiferromagnetic resonance (AFMR) spectra of $\text{MnCl}_3(\text{bpy})$ [34] was not accurately described by a quasi-classical, two-sublattice calculation for isolated (non-interacting) chains [35–37]. Nevertheless, those results suggest that the classical Heisenberg model is an appropriate starting point for the Hamiltonian, which needs to also include other important interactions such as the Dzaloshinskii-Moriya (DM) interaction between neighboring spins and the exchange coupling between adjacent chains [38, 39].

The forthcoming analysis provides an excellent description of the magnetic field dependences of the AFMR mode frequencies in the presence of a sizable DM term. Strikingly, only an extremely weak interchain coupling is required to drive long-range antiferromagnetic order. Consequently, the $S = 2$ Haldane phase is unlikely to be detected in molecule-based magnets.

Our more sophisticated analysis of the AFMR spectrum includes both intrachain and interchain couplings J and J' , respectively, as well as the DM interaction D generated by broken inversion symmetry. From Fig. 1, the DM interaction vector lies along the $\pm \mathbf{a}^*$ directions, alternating in sign along each chain. Our description also includes the easy-axis anisotropy K , which favors spin alignment along the chain axis c ($K > 0$) or in the $a^* - b$ plane ($K < 0$), and the easy-plane anisotropy E , which favors spin alignment along \mathbf{b} ($E > 0$) or along \mathbf{a}^* ($E < 0$). As found earlier, the \underline{g} tensor will be taken to be slightly anisotropic with eigenvalues $g_{a^*a^*} = 2.09$, $g_{bb} = 1.92$ and $g_{cc} = 2.07$ [32, 34]. Note that we have modified the previous notation [34], where D was used to represent the single-ion anisotropy along c , now defined as K .

EXPERIMENTAL DETAILS

The high-field magnetization of some single crystal samples of $\text{MnCl}_3(\text{bpy})$ along the c axis was measured again in pulsed magnetic fields up to 47 T using a standard induction method with a pick-up coil arrangement. The signal response was calibrated by comparison with the data obtained with the SQUID magnetometer up to 7 T. High-field, multi-frequency electron-spin resonance data were taken from Ref.[34], where details of the sample preparation are given. Due to sample deterioration, the extrinsic magnetization was subtracted from the raw data to get the intrinsic magnetization curve by assuming a $S = 5/2$ Brillouin function as in Ref.[31]. The subtracted magnetization at 4.2 K and below 7 T then coincided with the magnetization measured previously with the SQUID magnetometer. The maximum error bar in the magnetization at 40 T is $\pm 10\%$.

TABLE I: Exchange and anisotropy parameters in meV (uncertainties discussed in text).

	J	J'	K	E	D	χ^2
Ref.[34]	-2.69	0	0.129	0.015	0	0.211
This work	-3.3	0	0.102	0.018	0.12	0.035
uncertainties	± 0.7	± 0.0015	± 0.025	± 0.005	± 0.07	

MODEL

With magnetic field \mathbf{B} along \mathbf{m} , the Hamiltonian of $\text{MnCl}_3(\text{bpy})$ can be written as

$$\begin{aligned}
 \mathcal{H} = & -J \sum_{i,k} \mathbf{S}_i^{(k)} \cdot \mathbf{S}_{i+1}^{(k)} - J' \sum_{i,k} \mathbf{S}_i^{(k)} \cdot \mathbf{S}_i^{(k+1)} \\
 & - K \sum_{i,k} S_{iz}^{(k)2} + E \sum_{i,k} (S_{ix}^{(k)2} - S_{iy}^{(k)2}) \\
 & - D \sum_{i,k} (-1)^i \mathbf{a}^* \cdot (\mathbf{S}_i^{(k)} \times \mathbf{S}_{i+1}^{(k)}) \\
 & - \mu_B B \sum_{i,k} \mathbf{m} \cdot \underline{g} \cdot \mathbf{S}_i^{(k)}, \quad (1)
 \end{aligned}$$

where the chain index is given by k and the site index on each chain is given by i . The direction of the DM vector \mathbf{D} along \mathbf{a}^* was chosen to conform with the symmetry rules provided by Moriya [40] for materials with broken inversion symmetry. The factor $(-1)^i$ in front of the DM interaction reflects the alternation in the position of the (bpy) radical along the chain. We take $J < 0$ and $J' < 0$ for antiferromagnetic couplings.

The magnetic ground state of this Hamiltonian is obtained by minimizing the energy $\langle \mathcal{H} \rangle$ for the 8 angles of the four classical spins that form the magnetic unit cell, and the excitation spectrum is obtained by performing a $1/S$ expansion about the classical limit. Assuming a linear response for weak perturbation from equilibrium, solving the equations-of-motion requires the numerical diagonalization of a 8×8 matrix.

An earlier study of the AFMR excitation spectrum neglected both J' and D [34], while the value for the nearest-neighbor coupling J ($-2.69 \text{ meV} = -31.2 \text{ K}$) was estimated from the peak in temperature-dependence of the low-field magnetic susceptibility assuming $K = 0$ [32]. Using their values for the parameters (Table I), the calculated mode frequencies in Fig. 2(a) reproduce the ones reported by Shinozaki *et al.* [34]. In general, the experimental spectra are satisfactorily represented by those calculations, but the 10% overestimation of the spin-flop field B_{SF} and the error in the mode frequencies for $\mathbf{m} = \mathbf{c}$ and $B > B_{\text{SF}}$ are troubling issues.

NUMERICAL FITS

Due to the uncertainty in J , the other parameters in the Hamiltonian of Eq.(1) are calculated by fitting the AFMR data with fixed J . For $J < -2$ meV, the best fits are always obtained as $J' \rightarrow 0$. Of course, a small negative (antiferromagnetic) J' is required to cancel the moments on adjacent chains. The result of this analysis over a range of J values is shown in Fig. 3(a), where the DM coupling constant D becomes markedly smaller as $|J|$ decreases. For fixed J , the statistical uncertainties in J' , K , D , and E are evaluated from the variation in χ^2 . The anisotropies K and E are always positive, corresponding to one easy axis along **c** and a second easy axis along **b**. Both anisotropies grow as $|J|$ decreases.

The χ^2 value of the fits decreases from 0.0383 at $J = -5$ meV to a minimum of 0.0306 at $J = -2.3$ meV, as shown in Fig. 3(a). Because all χ^2 values in this range of J are acceptable, we use the magnetization as an additional constraint on J . The a^* -axis, b -axis, and c -axis magnetizations at 40 T are calculated as a function of J and plotted in Fig. 3(b). Since the magnetization is a function of $\mu_B B/|J|$, a smaller value of $|J|$ enhances both the effective field and the magnetization. Notice that the predicted values of M_{a^*} and M_b are quite close and cross at $J = -2.8$ meV. The experimental value for the magnetization $M_b^{\text{exp}} \approx 0.68 \mu_B$ with field along **b** is also indicated in this figure [34].

Figure 4 shows earlier magnetization curves [34] at 1.7 K along the a^* and b directions. The curve at 1.4 K along the c axis was remeasured to check the large deviation of the earlier measurements from the calculated magnetization. As before [34], the magnetization curve for $\mathbf{m} \parallel \mathbf{c}$ indicates a spin-flop transition at 22 T. Above this spin-flop field, the slope of the magnetization curve is larger than previously reported because the sample alignment along the c axis has now been corrected. The error in the experimental magnetizations given in Figs. 3(b) and 4 is $\pm 10\%$.

Based on M_b^{exp} , the best value for the nearest-neighbor interaction is $J \approx -3.60$ meV. However, our new results indicate that $M_c^{\text{exp}} \approx 0.9 \mu_B$, suggesting that $J \approx -2.95$ meV. It is important to recognize that these values reflect anisotropy contributions that were neglected in the earlier estimate $J \approx -2.69$ meV [34].

Comparison with the experimental magnetizations accounting for experimental error suggests that $J = -3.3 \pm 0.7$ meV. The corresponding anisotropy and DM parameters from Fig. 3 are $K = 0.102 \pm 0.025$ meV, $E = 0.018 \pm 0.005$ meV, and $D = 0.12 \pm 0.07$ meV. Within an uncertainty of $\pm 1.5 \times 10^{-3}$ meV, J' is zero. All parameters and their uncertainties are given in Table I. Compared with earlier fits [34], K is smaller but E is slightly larger.

The value $D = 0.12$ meV for the DM interaction cor-

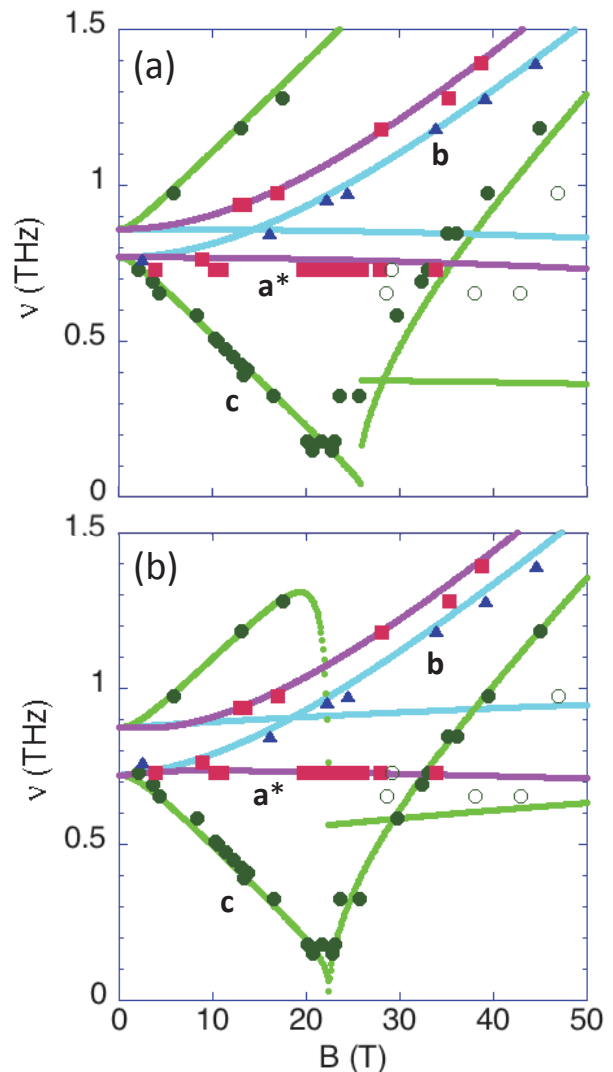


FIG. 2: (Color online) The magnetic field dependences of the AFMR frequencies of $\text{MnCl}_3(\text{bpy})$ for $T \approx 1.3$ K ($\mathbf{m} \parallel \mathbf{a}^*$ and $\mathbf{m} \parallel \mathbf{b}$) or 1.3, 1.5, and 1.7 K ($\mathbf{m} \parallel \mathbf{c}$). The data points are from the experimentally observed resonances [34] for magnetic field $B\mathbf{m}$ applied parallel to \mathbf{a}^* (red squares), \mathbf{b} (blue triangles), and \mathbf{c} (green circles). (a) The lines are the results of the calculations reported by Shinozaki *et al.* [34] and reproduced here with the values for the parameters listed in Table I. (b) The results of this work using Eq.(1) and the analysis presented in Fig. 3 to determine the parameters given in Table I. Open circles are “outlier” points for the field along the c -axis (see discussion in the text).

responds to a tilt of each spin at zero field by about 1° towards the b axis. This canting is associated with a net moment $\mathbf{M}_{\text{net}} \approx \pm 0.07 \mu_B \mathbf{b}$, alternating in sign on neighboring chains. The new fits provide a χ^2 value about 6 times smaller than the fits in Ref.[34]. The five points indicated by open circles in Fig. 2, all obtained with field along **c**, are not included in this analysis. These points seem to be “outliers” with respect to the main c -axis mode for $B > B_{\text{SF}}$ and may be associated with other

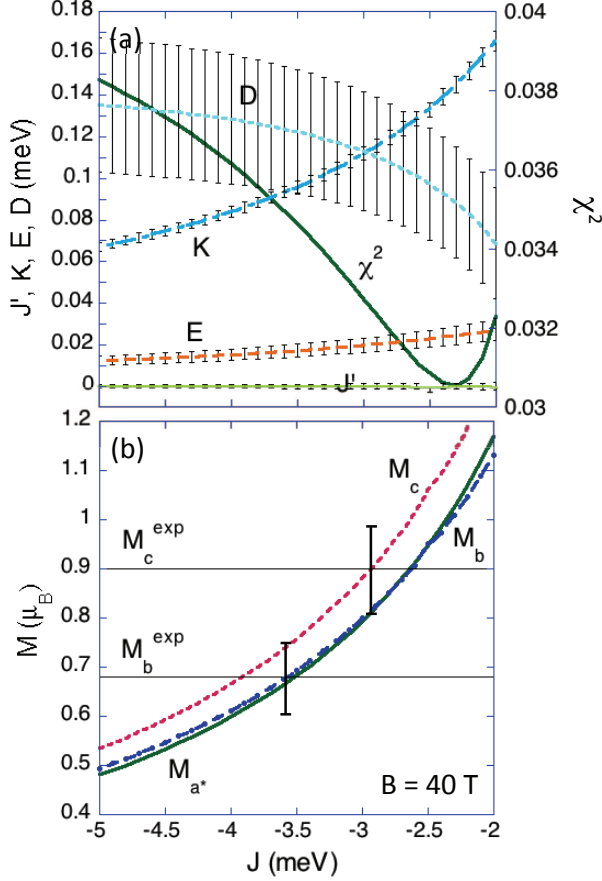


FIG. 3: (Color online) (a) The anisotropy, DM interactions, χ^2 , and (b) the magnetizations at 40 T versus J . Horizontal lines in (b) show the experimental magnetizations, with their corresponding uncertainties denoted by vertical bars, for a 40 T field along **b** or **c**.

flat branches due to a small misalignment of the crystal. Including these “outliers” would increase χ^2 but would not change the fitting parameters in Table I.

The resulting fits to the AFMR spectrum are plotted in Fig. 2(b), where excellent agreement now exists between the calculated value for $B_{\text{SF}} = 22.4$ T and the experimentally determined one. In addition, the predicted mode frequencies are in much better agreement with the measured mode frequencies when $\mathbf{m} = \mathbf{c}$. The lower predicted mode frequency reaches a minimum of about 3×10^{-3} THz at B_{SF} , and it is noteworthy that both branches of the excitation spectrum soften as B approaches B_{SF} . Aside from $\mathbf{m} = \mathbf{a}^*$, the other predicted “flat” modes are too weak to be observed, but they are included in Fig. 2 for completeness.

CONCLUSION

Surprisingly, the expansion about the classical limit or linear spin-wave theory works very well for this putative

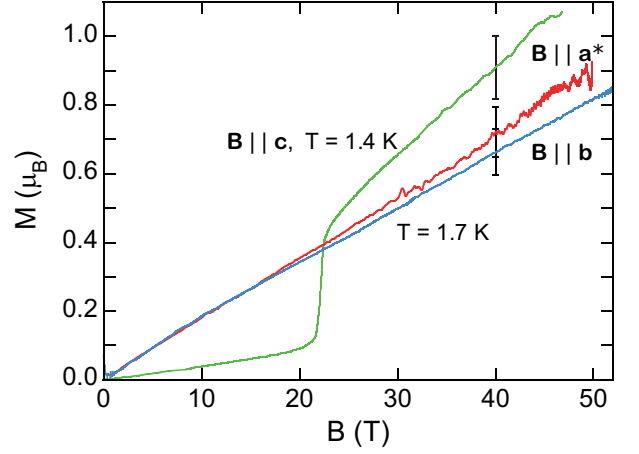


FIG. 4: (Color online) The magnetization curves for field along the \mathbf{a}^* , \mathbf{b} , or \mathbf{c} crystalline axes. The magnetization along the \mathbf{c} axis was remeasured and those along the other directions are taken from Ref.[34]. Error bars are shown at 40 T.

quantum-spin system. Since $J'/J \lesssim 5 \times 10^{-4}$, the coupling between chains is very weak in $\text{MnCl}_3(\text{bpy})$. Nevertheless, the ordering temperature of $\text{MnCl}_3(\text{bpy})$ is about 11.5 K [33, 34]. For a quasi-two-dimensional system with small exchange J' between planes, the critical temperature scales like $|J|\log(J'/J)$ [41]. For a two-dimensional antiferromagnet with easy-axis anisotropy K , the critical temperature scales like $|J|\log(K/|J|)$ [42]. Since no long range order is possible in one dimension, even with anisotropy, it is unclear how the critical temperature scales with J'/J . Certainly, T_N must vanish as $J'/J \rightarrow 0$. If T_N scales like $|J|\log(J'/J)$, then even a very small value of J' can stabilize long-range magnetic order with a Néel temperature of 10 K. If instead, T_N scales like $\sqrt{J'J}$, then $J' = 5 \times 10^{-4}J$ would correspond to a Néel temperature of order $z\sqrt{J'J}S(S+1) = 21$ K in the absence of anisotropy. Either scaling may explain the magnetic ordering in $\text{MnCl}_3(\text{bpy})$.

To summarize, we have used linear spin wave theory to obtain an excellent description of the AFMR spectrum in $\text{MnCl}_3(\text{bpy})$. Since an expansion about the classical limit works very well for $\text{MnCl}_3(\text{bpy})$, researchers searching for an $S = 2$ Haldane chain should explore other options.

We thank Sasha Chernyshev for useful conversations. Research sponsored by the Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division (RSF), by Grants-in-Aid for Scientific Research (Grants No. 24240590, No. 25246006, and No. 25220803) from the MEXT, Japan (MH), and by the National Science Foundation through Grant No. DMR-1202033 (MWM). A part of this work was conducted under the foreign visiting professor program of the Center for Advanced High Magnetic Field Science.

-
- [1] T. Tonegawa, K. Okamoto, H. Nakano, T. Sakai, K. Nomura, and M. Kaburagi, *Journal of the Physical Society of Japan* **80**, 043001 (2011), URL <http://journals.jps.jp/doi/abs/10.1143/JPSJ.80.043001>.
- [2] H.-H. Tu and R. Orús, *Phys. Rev. B* **84**, 140407 (2011), URL <http://link.aps.org/doi/10.1103/PhysRevB.84.140407>.
- [3] F. Pollmann, E. Berg, A. M. Turner, and M. Oshikawa, *Phys. Rev. B* **85**, 075125 (2012), URL <http://link.aps.org/doi/10.1103/PhysRevB.85.075125>.
- [4] Y.-C. Tzeng, *Phys. Rev. B* **86**, 024403 (2012), URL <http://link.aps.org/doi/10.1103/PhysRevB.86.024403>.
- [5] K. Hasebe and K. Totsuka, *Phys. Rev. B* **87**, 045115 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevB.87.045115>.
- [6] J. A. Kjäll, M. P. Zaletel, R. S. K. Mong, J. H. Bardarson, and F. Pollmann, *Phys. Rev. B* **87**, 235106 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevB.87.235106>.
- [7] P. Chen, Z.-L. Xue, I. P. McCulloch, M.-C. Chung, C.-C. Huang, and S.-K. Yip, *Phys. Rev. Lett.* **114**, 145301 (2015), URL <http://link.aps.org/doi/10.1103/PhysRevLett.114.145301>.
- [8] A. Kshetrimayum, H.-H. Tu, and R. Orús, *Phys. Rev. B* **91**, 205118 (2015), URL <http://link.aps.org/doi/10.1103/PhysRevB.91.205118>.
- [9] F. Pollmann, A. M. Turner, E. Berg, and M. Oshikawa, *Phys. Rev. B* **81**, 064439 (2010), URL <http://link.aps.org/doi/10.1103/PhysRevB.81.064439>.
- [10] F. Haldane, *Physics Letters A* **93**, 464 (1983), ISSN 0375-9601, URL <http://www.sciencedirect.com/science/article/pii/037596018390631X>.
- [11] F. D. M. Haldane, *Phys. Rev. Lett.* **50**, 1153 (1983), URL <http://link.aps.org/doi/10.1103/PhysRevLett.50.1153>.
- [12] H. J. Schulz, *Phys. Rev. B* **34**, 6372 (1986), URL <http://link.aps.org/doi/10.1103/PhysRevB.34.6372>.
- [13] I. Affleck, *Journal of Physics: Condensed Matter* **1**, 3047 (1989), URL <http://stacks.iop.org/0953-8984/1/i=19/a=001>.
- [14] J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, *EPL (Europhysics Letters)* **3**, 945 (1987), URL <http://stacks.iop.org/0295-5075/3/i=8/a=013>.
- [15] M. Hagiwara, K. Katsumata, I. Affleck, B. I. Halperin, and J. P. Renard, *Phys. Rev. Lett.* **65**, 3181 (1990), URL <http://link.aps.org/doi/10.1103/PhysRevLett.65.3181>.
- [16] S. H. Glarum, S. Geschwind, K. M. Lee, M. L. Kaplan, and J. Michel, *Phys. Rev. Lett.* **67**, 1614 (1991), URL <http://link.aps.org/doi/10.1103/PhysRevLett.67.1614>.
- [17] O. Avenel, J. Xu, J. S. Xia, M.-F. Xu, B. Andraka, T. Lang, P. L. Moyland, W. Ni, P. J. C. Signore, C. M. C. M. van Woerkens, et al., *Phys. Rev. B* **46**, 8655 (1992), URL <http://link.aps.org/doi/10.1103/PhysRevB.46.8655>.
- [18] O. Avenel, J. Xu, J. Xia, M.-F. Xu, B. Andraka, T. Lang, P. Moyland, W. Ni, P. Signore, C. Woerkens, et al., *Journal of Low Temperature Physics* **89**, 547 (1992), ISSN 0022-2291, URL <http://dx.doi.org/10.1007/BF00694084>.
- [19] M. Yamashita, T. Ishii, and H. Matsuzaka, *Coordination Chemistry Reviews* **198**, 347 (2000), ISSN 0010-8545, URL <http://www.sciencedirect.com/science/article/pii/S001085459900212X>.
- [20] H. Huang and I. Affleck, *Phys. Rev. B* **69**, 184414 (2004), URL <http://link.aps.org/doi/10.1103/PhysRevB.69.184414>.
- [21] M. Lewenstein, A. Sanpera, V. Ahufinger, B. Damski, A. Sen(De), and U. Sen, *Advances in Physics* **56**, 243 (2007), URL <http://dx.doi.org/10.1080/00018730701223200>.
- [22] Y. Matsushita and Y. Ueda, *Inorganic Chemistry* **42**, 7830 (2003), URL <http://dx.doi.org/10.1021/ic034634t>.
- [23] P. Lone, G. Andr, C. Doussier, and Y. Molo, *Journal of Magnetism and Magnetic Materials* **284**, 92 (2004), ISSN 0304-8853, URL <http://www.sciencedirect.com/science/article/pii/S0304885304006882>.
- [24] E. Čížmár, J.-H. Park, S. Gamble, B. Ward, D. Talham, J. Tol, L.-C. Brunel, M. Orendáč, A. Feher, J. Šebek, et al., *Journal of Magnetism and Magnetic Materials* **272-276**, Part 2, 874 (2004), ISSN 0304-8853, URL <http://www.sciencedirect.com/science/article/pii/S0304885303012873>.
- [25] C. Stock, L. C. Chapon, O. Adamopoulos, A. Lappas, M. Giot, J. W. Taylor, M. A. Green, C. M. Brown, and P. G. Radaelli, *Phys. Rev. Lett.* **103**, 077202 (2009), URL <http://link.aps.org/doi/10.1103/PhysRevLett.103.077202>.
- [26] M. B. Stone, G. Ehlers, and G. E. Granroth, *Phys. Rev. B* **88**, 104413 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevB.88.104413>.
- [27] E. Čížmár, O. N. Risset, T. Wang, M. Botko, A. R. Ahir, M. J. Andrus, J.-H. Park, K. A. Abboud, D. R. Talham, M. W. Meisel, et al., *Journal of Physics: Condensed Matter* **28**, 236003 (2016), URL <http://stacks.iop.org/0953-8984/28/i=23/a=236003>.
- [28] S. P. Perlepes, A. G. Blackman, J. C. Huffman, and G. Christou, *Inorganic Chemistry* **30**, 1665 (1991), URL <http://pubs.acs.org/doi/abs/10.1021/ic00007a046>.
- [29] H. A. Goodwin and R. N. Sylva, *Australian Journal of Chemistry* **20**, 629 (1967), URL <http://www.publish.csiro.au/paper/CH9670629>.
- [30] G. E. Granroth, M. W. Meisel, M. Chaparala, T. Jolicoeur, B. H. Ward, and D. R. Talham, *Phys. Rev. Lett.* **77**, 1616 (1996), URL <http://link.aps.org/doi/10.1103/PhysRevLett.77.1616>.
- [31] M. Hagiwara, Y. Idutsu, Z. Honda, and S. Yamamoto, *Journal of Physics: Conference Series* **400**, 032014 (2012), URL <http://stacks.iop.org/1742-6596/400/i=3/a=032014>.
- [32] M. Hagiwara, M. Ikeda, Y. Idutsu, S. Kimura, and Z. Honda, *Journal of the Korean Physical Society* **62**, 2046 (2013), ISSN 0374-4884, URL <http://dx.doi.org/10.3938/jkps.62.2046>.
- [33] M. Hagiwara, S.-i. Shinozaki, A. Okutani, D. Yoshizawa, T. Kida, T. Takeuchi, O. N. Risset, D. R. Talham, and M. W. Meisel, *Physics Procedia* **75**, 106 (2015), ISSN 1875-3892, URL <http://www.sciencedirect.com/science/article/pii/S1875389215016545>.
- [34] S.-i. Shinozaki, A. Okutani, D. Yoshizawa, T. Kida, T. Takeuchi, S. Yamamoto, O. N. Risset, D. R. Tal-

- ham, M. W. Meisel, and M. Hagiwara, Phys. Rev. B **93**, 014407 (2016), URL <http://link.aps.org/doi/10.1103/PhysRevB.93.014407>.
- [35] J. Kanamori and H. Minatono, Journal of the Physical Society of Japan **17**, 1759 (1962), URL <http://dx.doi.org/10.1143/JPSJ.17.1759>.
- [36] M. Date and M. Motokawa, Journal of the Physical Society of Japan **22**, 165 (1967), URL <http://dx.doi.org/10.1143/JPSJ.22.165>.
- [37] M. Hagiwara and K. Katsumata, RIKEN Review **24**, 13 (1999), URL <http://citeseerx.ist.psu.edu/viewdoc/summary?doi=10.1.1.222.6545>.
- [38] H. Huang and I. Affleck, Phys. Rev. B **69**, 184414 (2004), URL <http://link.aps.org/doi/10.1103/PhysRevB.69.184414>.
- [39] M. Herak, A. Zorko, M. Pregelj, O. Zaharko, G. Posnjak, Z. Jagličić, A. Potočnik, H. Luetkens, J. van Tol, A. Ozarowski, et al., Phys. Rev. B **87**, 104413 (2013), URL <http://link.aps.org/doi/10.1103/PhysRevB.87.104413>.
- [40] T. Moriya, Phys. Rev. **120**, 91 (1960), URL <http://link.aps.org/doi/10.1103/PhysRev.120.91>.
- [41] A. Yasuda, S. Todo, K. Hukushima, F. Alet, M. Keller, M. Troyer, and H. Takayama, Phys. Rev. Lett. **94**, 217201 (2005), URL <http://link.aps.org/doi/10.1103/PhysRevLett.94.217201>.
- [42] K. Yosida, *Theory of Magnetism* (Springer-Verlag, Berlin, 1996).