Spin-lattice Coupling and the Emergence of the Trimerized Phase in the S=1 Kagome Antiferromagnet Na_{2}Ti_{3}Cl_{8}

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Spin–lattice coupling and the emergence of the trimerized phase in the $S = 1$ Kagome antiferromagnet $Na_2Ti_3Cl_8$

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Spin-1 antiferromagnets are abundant in nature, but few theories exist to understand their properties and behavior when geometric frustration is present. Here we study the $S = 1$ Kagome compound $Na_2Ti_3Cl_8$ using a combination of Density Functional Theory, Exact Diagonalization, and Density Matrix Renormalization Group to achieve a first principles supported explanation of its exotic magnetic phases. We find that the effective magnetic Hamiltonian includes essential non-Heisenberg terms that do not stem from spin-orbit coupling, and both trimerized and spin-nematic magnetic phases are relevant. The experimentally observed structural transition to a breathing Kagome phase is driven by spin–lattice coupling, which favors the trimerized magnetic phase against the quadrupolar one. We thus show that lattice effects can be necessary to understand the magnetism in frustrated magnetic compounds, and surmise that $Na_2Ti_3Cl_8$ is a compound which cannot be understood from only electronic or only lattice Hamiltonians.

The search for exotic phases of matter in geometrical frustrated magnets has been an area of active research. Most effort has been focused on $S = 1/2$ 2D materials [1–3] which have seen a flurry of theoretical activity [4–10]. Less explored is the $S \geq 1$ case [11–17], where many candidate materials exist, but where the theoretical effort has not been proportionate to the experimental activity. This is partly based on the rationale that larger S systems magnetically order at low temperature, however, there are many counter-examples to this intuition. For example, it has been found that certain compounds do not conform to this scenario and instead form long-range non-magnetic states such as valence bond or "trimerized" (simplex solid) phases [13–15, 18, 19]. In some cases, a strongly quantum fluctuating phase or spin liquid is favored, as has been argued in the case of Heisenberg $S = 1$ pyrochlore [20–22], triangular lattices [16, 23–25], with second nearest neighbor and/or biquadratic couplings and possibly even the honeycomb lattice [26]. Further prohibiting deeper understanding of the physics of these materials is the coupling of magnetic degrees of freedom with the lattice, which provides an additional mechanism of relieving magnetic frustration [27, 28]. This work is thus motivated by the exploration of the interplay of magnetism with the lattice in $S = 1$ kagome materials, which have multiple reported experimental realizations [29, 30].

$Na_2Ti_3Cl_8$ has recently seen a resurgence of interest due to the underlying $S = 1$ kagome physics, and its relevance to understanding the interplay between magnetic and lattice degrees of freedom [31–33]. At room temperature, the compound has layers of titanium ions arranged in a kagome structure (Fig. 1). The titanium ions are in Ti^{2+} configuration, so Hund's rules dictate a $3d^2$ configuration with $S = 1$ magnetic moments. Experimentally, at low temperature (LT), $Na_2Ti_3Cl_8$ has the "breathing kagome" or "trimerized" structure [32] (Fig. 1c). On heating, around 200 K, a phase transition occurs to the undistorted kagome structure [32], which we refer to as the high temperature (HT) phase. On cooling the sample from the HT phase, one reproducibly gets trapped in a metastable "intermediate temperature" (IT) phase [32]. Magnetic susceptibility drops sharply with decreasing temperature below the HT phase, consistent with $S = 1$ atomic moments which are suppressed in the IT and LT phases due to trimer formation [31–33].

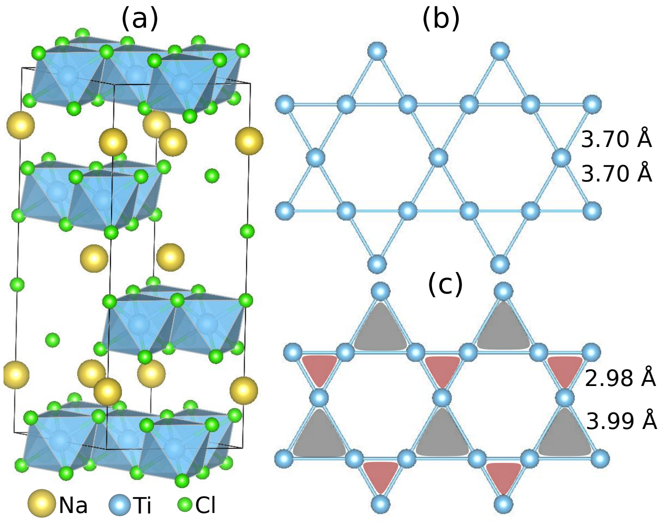

Figure 1. (Color online) (a) Crystal structure of $Na_2Ti_3Cl_8$ consists of layers of edge-sharing $TiCl_6$ octahedra, which are intercalated with Na ions. (b) At room temperature, Ti ions in each layer form ideal Kagome lattices (HT structure). (c) At low temperatures, a breathing distortion sets in, resulting in two different Ti-Ti bond lengths of 2.98 Åand 3.99 Å.

Here we elucidate the magnetic ground state and explicate the mechanism of the breathing distortion in $Na_2Ti_3Cl_8$

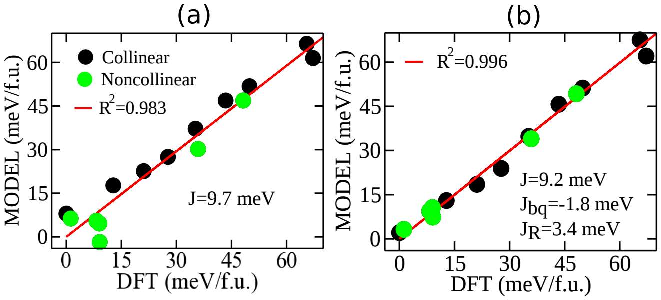

Figure 2. (Color online) Fits of different effective model spin Hamiltonians to density functional theory data for $U = 3$ eV. Each data point corresponds to a different magnetic configuration. The horizontal axis is the energy from the DFT calculation, and the vertical axis is the energy for the same configuration from the fitted model. (a) The fit to the model with only the nearest neighbor Heisenberg coupling. The energies of many non-collinear states are not reproduced well by the model. (b) The model with biquadratic and ring-exchange couplings. The agreement is enhanced, with no clear outliers in the data.

by a combination of first principles density functional theory (DFT), exact diagonalization (ED), and density matrix renormalization group (DMRG) approaches. We find that (i) the magnetic Hamiltonian in the HT phase includes non-Heisenberg terms (biquadratic and ring-like exchange) that stem from higher order processes, and (ii) due to the magnitude of these non-Heisenberg terms, the magnetic groundstate of the HT Hamiltonian is ferroquadrupolar (FQ)/spin-nematic instead of trimerized. The breathing distortion of the lattice is necessary to stabilize the trimerized phase. We also find that (iii) DFT calculations on the HT phase with Neel order give no lattice instability, which implies that the trimerized ground state is stabilized through spin-lattice coupling. In other words, neither the lattice nor the magnetic Hamiltonians by themselves are unstable towards trimerization, but their combination gives rise to a magnetic–structural transition.

Effective Hamiltonian— Lack of information on the low-energy effective Hamiltonian is often a limiting factor in studies of frustrated magnetic materials. While there has been progress in downfolding approaches using quantum mechanical expectation values [34, 35], here we adopt the classical fitting approach in conjunction with DFT that is now commonly used to extract magnetic Hamiltonians and parameters for real materials. (For example, Refs. [36–38].) We performed DFT calculations for multiple magnetic configurations, including various collinear and non-collinear states, and extracted the final spin configurations and energies at the DFT level. We then fit the parameters of various magnetic models to these energies. Errorbars of the fits were determined by statistical methods [39–42].

In Fig. 2, we present the results of our DFT calculations for the HT structure, performed using the PBEsol exchange correlation functional with the $+U$ correction with $U = 3$ eV [42–46]. A fit to a nearest-neighbor only Heisenberg Hamiltonian captures the main trend of the energy with an antiferromagnetic nearest neighbor coupling; but the agreement is far from perfect, and especially the non-collinear spin configurations' energy are not captured (Fig. 2a). The simplest extension of the Hamiltonian is the biquadratic term $\sim (S_i \cdot S_j)^2$ [47]. This term is allowed by symmetry, and emerges in various spin-1 models due to higher order ($\sim t^4$, where t is the hopping amplitude) perturbations which correspond to multiple electrons between two atoms [42, 48–50]. At the same order in nearest neighbor hopping t, there also exists a ring exchange on the triangles with the form $\sim (S_i \cdot S_j)(S_i \cdot S_k)$. We include both of these terms to get the Hamiltonian

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_{bq} \sum_{\langle ij \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j)^2 + \frac{J_R}{2} \sum_{\Delta = i,j,k} \left((\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_i \cdot \mathbf{S}_k) + (\mathbf{S}_i \cdot \mathbf{S}_k)(\mathbf{S}_i \cdot \mathbf{S}_j) \right) \quad (1)$$

where $\langle ij \rangle$ refers to nearest neighbor pairs and $J > 0$ is the Heisenberg coupling. Similar ring exchanges have been studied in square lattices [51], but to the best of our knowledge, this form of the Hamiltonian has not been considered for a Kagome system before. The additional terms make the fit better (Fig. 2b). We find that while the nearest neighbor antiferromagnetic Heisenberg coupling is the strongest term, both J_{bq} and J_R are nonzero and significant. [42].

Wannier function analysis provides insight into the reason that the Hamiltonian attains this complicated form, and also to how the J coefficients behave under the structural transition. In Fig. 3a, we show the t_{2g}-like Wannier functions on the Ti atoms. The Ti cations have site symmetry C_{2h}. This symmetry splits the t_{2g} orbitals into $t_{2g} \to A_g + B_g + B_g$, but the two B_g orbitals (xz and yz) are degenerate within numerical noise, and only the A_g (xy) orbital has a different energy. In Fig. 3b, we show the hoppings between the three t_{2g}-like orbitals in the HT phase. There are at least three different t values that are significant. While we do not solve this model explicitly, we note that it is rich enough to give rise to the biquadratic exchange. To derive a biquadratic term starting from an orbital model, Ref. 49 considered a model with 2 electrons on 3 orbitals, whereas Ref. 50 used a two orbital model with same-orbital hoppings. The Wannier model for $Na_2Ti_3Cl_8$ includes both of these terms and hence it is no surprise that a biquadratic term emerges. The ring exchange term $\sim (S_i \cdot S_j)(S_i \cdot S_k)$ can emerge from simultaneous hopping of two electrons from site i to sites j and k. Given that the largest hopping element (257 meV) is between alternating xz and yz orbitals in nearest neighbor atoms, this term can be proportional to the highest t^4 factor, and hence, significant.

Due to the low symmetry and very small Ti–Ti distances, it is technically challenging to stabilize many different magnetic states and calculate J's with high precision in the LT phase using DFT+U. Instead, in Fig. 3c, we present the evolution of the hopping parameters and the A_g–B_g splitting, obtained from the Wannier model, as the crystal structure is linearly interpolated between the HT and the LT phases. As the structure gets close to the LT phase, the Ti–Ti hoppings in the larger triangles go to zero. Two trends are evident: 1) The A_g–B_g energy

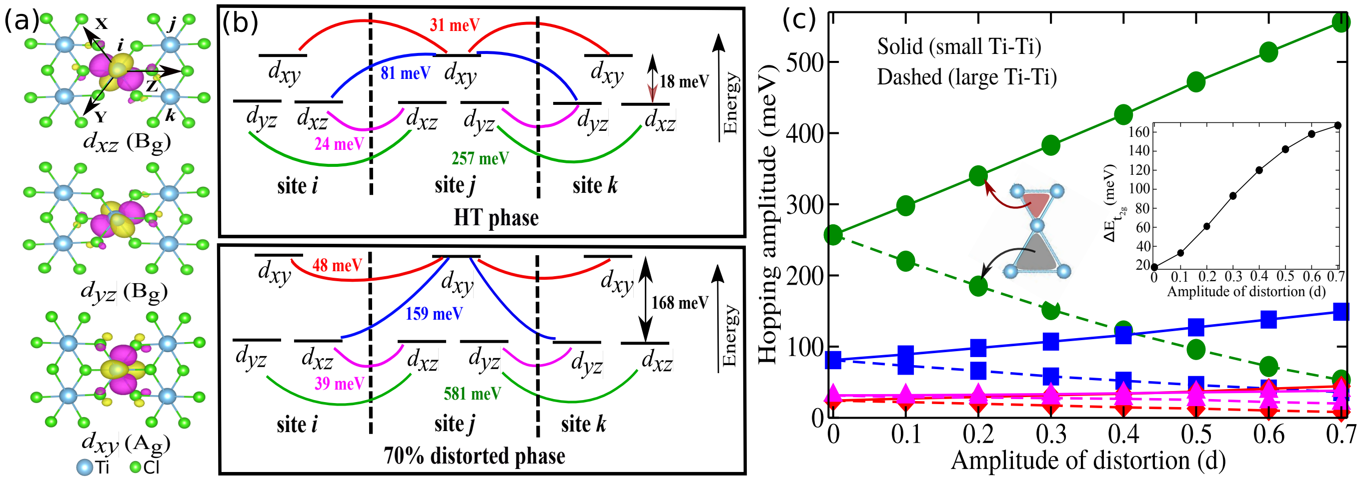

Figure 3. (Color online) (a) The t_{2g}-like Wannier functions obtained in the HT structure from nonmagnetic DFT calculations. While there is some hybridization with the Cl ions as expected, the Wannier orbitals have atomic character. (This is no longer the case in the LT structure, see SM for further details [42].) (b) Sketch of the three t_{2g} orbitals on a triangle and the hoppings between them in the HT phase (top), and in a hypothetical structure that is obtained by linearly interpolating the structural parameters (lattice constants and atomic positions) between the HT and LT phases. The values in the sketch are for the 70% distorted structure, where 100% distortion would correspond to the LT phase. For simplicity, only the hoppings in the smaller triangles are shown. (c) The hopping amplitudes between the orbitals on neighboring atoms and the splitting between the orbitals on the same atom as a function of distortion amplitude. Same colors correspond to the same hopping elements in panel (b).

separation increases by almost an order of magnitude in the LT phase. 2) The largest hopping amplitude (green) becomes even larger compared to all the other terms in the LT phase. Thus, in the LT phase, the antiferromagnetic exchange J is enhanced because of the increasing A_g–B_g separation makes the system an effectively half-filled system with increasing t. Also, J_{bq}/J should be suppressed, since a model with two half-filled orbitals per atom with significant hopping only between a pair of them cannot have biquadratic exchange according to the models proposed so far [48–50]. J_R/J, on the other hand, is not easy to predict, since there are multiple processes that contribute to this term, some of which (e.g. the one that involves hopping from xz or yz orbitals to xy orbital) are suppressed, whereas some of which (e.g. the one that involves hopping between xz and yz orbitals) are enhanced.

ED and DMRG— DFT provides estimates of the parameters of the effective Hamiltonian, but it does not tell the nature of the quantum many-body ground state. Thus we appeal to, and extend, previous results on the $S = 1$ kagome system which has been studied with a variety of approaches [15, 18, 19, 52]. For positive biquadratic interactions, the existence of a trimerized state was established [13, 14]. This state was found to persist to negative biquadratic interactions $J_{bq}/J \approx -0.16$ below which it transitions to a state with FQ order [15].

While the observation that J is large and J_{bq} and J_R have opposite signs is robust, the values of J_{bq}/J_R and J_R/J ratios depend on the choice of U employed in the DFT+U calculations [42]. For this reason, it is necessary to perform the ED calculations for a range of parameters. We scan the line in parameter space with J fixed to 9.2 meV, varying J_R with $J_{bq} = -0.529 J_R$. (Another scan for $J_R = -J_{bq}$, relevant for the $U = 4$ eV parameters gives similar results [42].) Fig. 4a shows the energy spectrum for the 18 site cluster as a function of J_R. There is a closing of energy scales, which signals the occurrence of a phase transition at $J_R \approx 1$ meV. The lowest excitation in the large J_R regime has $S = 2$; consistent with the FQ phase. Thus, the model with $J_{bq} = -0.529 J_R$ is qualitatively similar to the model with $J_R = 0$ and negative J_{bq}, and the magnetic ground state of $Na_2Ti_3Cl_8$ in HT structure is FQ.

To support these assertions further, we perform DMRG calculations on XC8-3 cylinders with the open (periodic) boundaries along the long (short) direction. The open boundaries are chosen to match the trimer order. We explicitly measure the trimerized order parameter (defined as the difference of bond energies on up and down triangles i.e. $\sum_{\Delta} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{\nabla} \mathbf{S}_i \cdot \mathbf{S}_j$) and the quadrupolar order parameter $\langle S_z^2 \rangle - \frac{2}{3}$. Results in Fig. 4b for $J_R/J = -J_{bq}/J = 0$ confirm that the ground state is trimerized in the absence of biquadratic coupling. On the other hand, for $J_R/J \approx -1.89 J_{bq}/J \approx 0.37$ (the same as in Fig. 2), a uniform nonzero FQ order parameter is observed throughout the bulk of our finite size sample, again confirming the ED results.

Emergence of trimerized phase and the role of lattice distortions— We now discuss what drives the instability towards the LT phase. The magnetic Hamiltonian of the HT phase by itself does not lead to such an instability, since both ED and DMRG calculations predict a nematic phase. It is possible that there is a lattice instability driven by not magnetism but rather by crystal chemistry, like those in ferroelectrics like $BaTiO_3$ [53]. This type of a instability in $Na_2Ti_3Cl_8$ would show up in DFT calculations as an unstable phonon that transforms as Γ_2^- irreducible representation [33]. (While DFT can

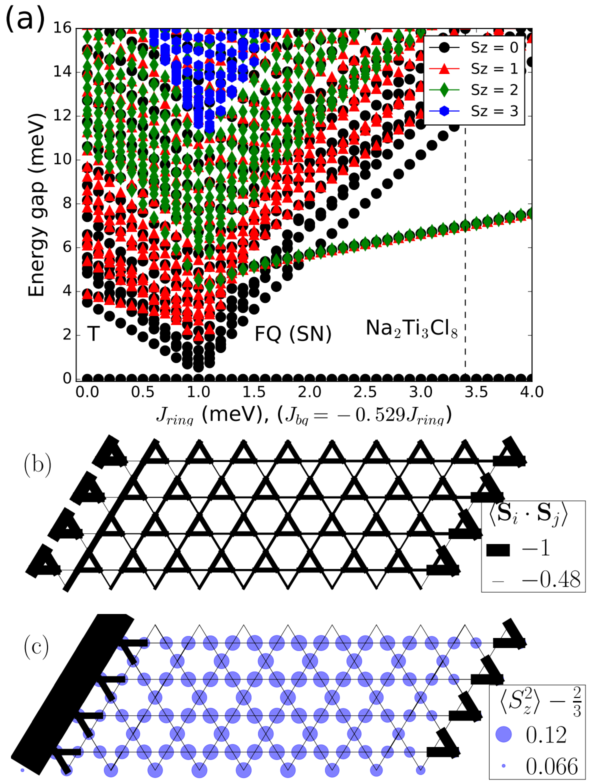

Figure 4. (Color online) (a) Spectrum of the 18b site cluster (organized by total S_z) from exact diagonalization, as a function of J_R with $J_{bq} = -0.529J_R$, fixing $J = 9.2$ meV. The trimerized (T) and ferroquadrupolar (FQ)/spin-nematic (SN) regions are indicated. The ground state in the HT structure is FQ and has a $S = 2$ excitation. (b,c) DMRG results for the trimerized and quadrupolar order parameters for the $S = 1$ model with bilinear, biquadratic and ring-exchange terms with (b) $J_R/J = J_{bq}/J = 0$ and (c) $J_R/J \approx -1.89J_{bq}/J \approx 0.37$ (the same as in Fig. 2). The width of the bonds (radius of the circles) are proportional to $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ ($\langle S_z^2 \rangle - \frac{2}{3}$). The reference values in the text boxes are valid for both cases.

not capture the quantum magnetic phases at play here, it is expected to reproduce hybridization between atoms etc. that gives rise to lattice instabilities.) Interestingly, our DFT calculations find no instability unless an unphysical electronic structure is imposed [42]. This suggests that there is no lattice-only instability towards trimerization.

What our calculations so far do not take into account is the spin–lattice coupling. Spin–lattice coupling is often considered in the context of materials with classical spin orders, where the changes in the crystal structure affects the magnetic energy through the dependence of exchange parameters to atomic positions [54, 55]. In Na$_2$Ti$_3$Cl$_8$, the Wannier models discussed previously suggest that in the trimerized LT crystal structure, the relative strength of the biquadratic exchange to Heisenberg exchange, J_{bq}/J, is suppressed, and hence, the trimerized magnetic phase is favored more strongly in the LT phase compared to the HT phase. In other words, *the spin–lattice coupling in Na$_2$Ti$_3$Cl$_8$ favors the trimerized phase*, and we surmise that it is the driving force of the trimerization in this compound. The phase transition of Na$_2$Ti$_3$Cl$_8$ driven by spin–lattice coupling can be considered as parallel to VO$_2$, where a "chicken and egg" debate is still ongoing; interactions between the correlated electronic states and the lattice give rise to concurrent electronic and crystal structural transitions [56–64]. We also note that in typical magnetic systems, spin Peierls distortions leads to only ∼1-3% change in the lattice constants, in contrast in Na$_2$Ti$_3$Cl$_8$ the change is of the order of 10%!

An important feature of the Γ_2^- structural distortion that connects the HT and LT structural phases is that it is polar [33], and hence it couples to external electric fields in bilinear order. It might be possible to use electric fields to change the crystal structure enough to induce a transition to the quadrupolar phase. We surmise that this might be a viable strategy to probe a possible quantum critical point between these two magnetic phases.

Conclusions— We performed a theoretical and numerical analysis of the spin-1 Kagome compound Na$_2$Ti$_3$Cl$_8$ using a combination of DFT, ED and DMRG. We found that this compound has a complex magnetic Hamiltonian, which includes biquadratic and ring exchange terms, in addition to strong antiferromagnetic Heisenberg interactions. ED and DMRG simulations agree on that depending on the strength of biquadratic and ring exchange terms, this Hamiltonian can give rise to either quadrupolar nematic or trimerized magnetic phases. We surmise that the magneto-structural transition observed in this compound is driven by the spin–lattice coupling, which favors the coexistence of the breathing distortion of the Kagome lattice and the trimerized magnetic phase.

Our study underlines the importance of non-Heisenberg terms and lattice effects in the study of quantum magnetic materials, and shows that the spin–lattice coupling can lead to phase transitions that cannot be understood by studying magnetic or lattice Hamiltonians by themselves. This is similar to the well studied correlated compound, VO$_2$, which cannot be understood by studying the electronic or lattice subsystems alone.

Finally, since lattice and spin degrees of freedom are strongly coupled in Na$_2$Ti$_3$Cl$_8$, it is desirable to go beyond our adopted downfolding procedure and instead fit our DFT data, for various crystal structures, directly to a spin-lattice Hamiltonian; then solve the latter with a strongly correlated lattice technique. While this is beyond the scope of the present work, we believe this direction will be useful for a large class of strongly correlated systems, including frustrated magnets, which show structural phase transitions driven by novel phases of electronic and magnetic matter.

Note added— At the time of acceptance of this paper, we became aware of Ref. [65] who presented a systematic derivation of the ring term used here in Eq. (1).

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[1] J. S. Helton, K. Matan, M. P. Shores, E. A. Nytko, B. M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D. G. Nocera, and Y. S. Lee, Phys. Rev. Lett. **98**, 107204 (2007).

[2] Tian-Heng Han, Joel S. Helton, Shaoyan Chu, Daniel G. Nocera, Jose A. Rodriguez-Rivera, Collin Broholm and Young S. Lee, *Nature* 492, 406-410 (2012).

[3] A. Zorko, M. Herak, M. Gomilšek, J. van Tol, M. Velázquez, P. Khuntia, F. Bert, and P. Mendels, Phys. Rev. Lett. **118**, 017202 (2017).

[4] S. Yan, D. A. Huse, and S. R. White, Science **332**, 1173 (2011), http://www.sciencemag.org/content/332/6034/1173.full.pdf.

[5] Y. Ran, M. Hermele, P. A. Lee, and X.-G. Wen, Phys. Rev. Lett. **98**, 117205 (2007).

[6] S. Depenbrock, I. P. McCulloch, and U. Schollwöck, Phys. Rev. Lett. **109**, 067201 (2012).

[7] Y. Iqbal, F. Becca, S. Sorella, and D. Poilblanc, Phys. Rev. B **87**, 060405 (2013).

[8] M. R. Norman, Rev. Mod. Phys. **88**, 041002 (2016).

[9] K. Kumar, H. J. Changlani, B. K. Clark, and E. Fradkin, Phys. Rev. B **94**, 134410 (2016).

[10] H. J. Changlani, D. Kochkov, K. Kumar, B. K. Clark, and E. Fradkin, Phys. Rev. Lett. **120**, 117202 (2018).

[11] K. Hida, Journal of the Physical Society of Japan **69**, 4003 (2000).

[12] O. Götze, D. J. J. Farnell, R. F. Bishop, P. H. Y. Li, and J. Richter, Phys. Rev. B **84**, 224428 (2011).

[13] D. P. Arovas, Phys. Rev. B **77**, 104404 (2008).

[14] P. Corboz, K. Penc, F. Mila, and A. M. Läuchli, Phys. Rev. B **86**, 041106 (2012).

[15] H. J. Changlani and A. M. Läuchli, Phys. Rev. B **91**, 100407 (2015).

[16] M. Serbyn, T. Senthil, and P. A. Lee, Phys. Rev. B **84**, 180403 (2011).

[17] H. Nakano and T. Sakai, Journal of the Physical Society of Japan **84**, 063705 (2015), https://doi.org/10.7566/JPSJ.84.063705.

[18] T. Liu, W. Li, A. Weichselbaum, J. von Delft, and G. Su, Phys. Rev. B **91**, 060403 (2015).

[19] P. Ghosh, A. K. Verma, and B. Kumar, Phys. Rev. B **93**, 014427 (2016).

[20] K. W. Plumb, H. J. Changlani, A. Scheie, S. Zhang, J. W. Krizan, J. A. Rodriguez-Rivera, Y. Qiu, B. Winn, R. J. Cava, and C. L. Broholm, Nature Physics **15**, 54 (2019).

[21] S. Zhang, H. J. Changlani, K. W. Plumb, O. Tchernyshyov, and R. Moessner, Phys. Rev. Lett. **122**, 167203 (2019).

[22] Y. Iqbal, T. Müller, P. Ghosh, M. J. P. Gingras, H. O. Jeschke, S. Rachel, J. Reuther, and R. Thomale, Phys. Rev. X **9**, 011005 (2019).

[23] S. Nakatsuji, Y. Nambu, H. Tonomura, O. Sakai, S. Jonas, C. Broholm, H. Tsunetsugu, Y. Qiu, and Y. Maeno, Science **309**, 1697 (2005), https://science.sciencemag.org/content/309/5741/1697.full.pdf.

[24] J. G. Cheng, G. Li, L. Balicas, J. S. Zhou, J. B. Goodenough, C. Xu, and H. D. Zhou, Phys. Rev. Lett. **107**, 197204 (2011).

[25] A. Läuchli, F. Mila, and K. Penc, Phys. Rev. Lett. **97**, 087205 (2006).

[26] R. Kumar, T. Dey, P. M. Ette, K. Ramesha, A. Chakraborty, I. Dasgupta, J. C. Orain, C. Baines, S. Tóth, A. Shahee, S. Kundu, M. Prinz-Zwick, A. A. Gippius, N. Büttgen, P. Gegenwart, and A. V. Mahajan, Phys. Rev. B **99**, 054417 (2019).

[27] O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. **88**, 067203 (2002).

[28] Y. Yamashita and K. Ueda, Phys. Rev. Lett. **85**, 4960 (2000).

[29] H. J. Silverstein, R. Sinclair, A. Sharma, Y. Qiu, I. Heinmaa, A. Leitmäe, C. R. Wiebe, R. Stern, and H. Zhou, Phys. Rev. Materials **2**, 044006 (2018).

[30] E. Takagi, T. Aoyama, S. Hara, H. Sato, T. Kimura, and Y. Wakabayashi, Phys. Rev. B **95**, 104416 (2017).

[31] D. J. Hinz, G. Meyer, T. Dedecke, and W. Urland, Angewandte Chemie International Edition in English **34**, 71 (1995).

[32] N. Hanni, M. D. Frontzek, J. Hauser, D. Cheptiakov, and K. Kramer, Zeitschrift fuer Anorganische und Allgemeine Chemie **643** (2017), 10.1002/zaac.201700331.

[33] Z. A. Kelly, T. T. Tran, and T. M. McQueen, Inorganic Chemistry , acs.inorgchem.9b01110 (2019).

[34] H. J. Changlani, H. Zheng, and L. K. Wagner, The Journal of Chemical Physics **143**, 102814 (2015), https://doi.org/10.1063/1.4927664.

[35] H. Zheng, H. J. Changlani, K. T. Williams, B. Busemeyer, and L. K. Wagner, Frontiers in Physics **6**, 43 (2018).

[36] N. S. Fedorova, C. Ederer, N. A. Spaldin, and A. Scaramucci, Phys. Rev. B **91**, 165122 (2015).

[37] H. O. Jeschke, F. Salvat-Pujol, and R. Valentí, Phys. Rev. B **88**, 075106 (2013).

[38] T. Birol, K. Haule, and D. Vanderbilt, Physical Review B **98**, 134432 (2018).

[39] M. H. Quenouille, Ann. Math. Statist. **20**, 355 (1949).

[40] M. H. Quenouille, Biometrika **43**, 353 (1956).

[41] J. W. Tukey, Ann. Math. Statist. **29**, 614 (1958).

[42] See supplemental information for further details.

[43] G. Kresse and J. Furthmuller, Computational Materials Science **6**, 15 (1996).

[44] G. Kresse and J. Furthmüller, Physical Review B **54**, 11169 (1996).

[45] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Physical Review Letters **100**, 136406 (2008).

[46] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Physical Review B **57**, 1505 (1998).

[47] M. Blume and Y. Y. Hsieh, Journal of Applied Physics **40**, 1249 (1969), https://doi.org/10.1063/1.1657616.

[48] R. N. Bhatt and K. Yang, Journal of Applied Physics **83**, 7231

(1998), https://doi.org/10.1063/1.367612.

[49] F. Mila and F.-C. Zhang, European Physical Journal B **16**, 7 (2000), arXiv:cond-mat/0006068 [cond-mat.str-el].

[50] P. Fazekas, *Lecture notes on electron correlation and magnetism*, Vol. 5 (World scientific, 1999).

[51] N. Desai and R. Kaul, arXiv e-prints , arXiv:1904.09629 (2019), arXiv:1904.09629 [cond-mat.str-el].

[52] J. Oitmaa and R. R. P. Singh, Phys. Rev. B **93**, 014424 (2016).

[53] R. E. Cohen, Nature **358**, 136 (1992).

[54] T. Birol, N. A. Benedek, H. Das, A. L. Wysocki, A. T. Mulder, B. M. Abbett, E. H. Smith, S. Ghosh, and C. J. Fennie, Current Opinion in Solid State and Materials Science **16**, 227 (2012).

[55] A. L. Wysocki and T. Birol, Physical Review B **93**, 134425 (2016), arXiv:1508.00834v1.

[56] A. Zylbersztejn and N. F. Mott, Physical Review B **11**, 4383 (1975).

[57] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Physical Review Letters **72**, 3389 (1994).

[58] M. W. Haverkort, Z. Hu, A. Tanaka, W. Reichelt, S. V. Streltsov, M. A. Korotin, V. I. Anisimov, H. H. Hsieh, H.-J. Lin, C. T. Chen, D. I. Khomskii, and L. H. Tjeng, Physical Review Letters **95**, 196404 (2005).

[59] S. Biermann, A. Poteryaev, A. I. Lichtenstein, and A. Georges, Physical Review Letters **94**, 026404 (2005).

[60] C. Weber, D. D. O'Regan, N. D. M. Hine, M. C. Payne, G. Kotliar, and P. B. Littlewood, Physical Review Letters **108**, 256402 (2012).

[61] A. X. Gray, J. Jeong, N. P. Aetukuri, P. Granitzka, Z. Chen, R. Kukreja, D. Higley, T. Chase, A. H. Reid, H. Ohldag, M. A. Marcus, A. Scholl, A. T. Young, A. Doran, C. A. Jenkins, P. Shafer, E. Arenholz, M. G. Samant, S. S. P. Parkin, and H. A. Dürr, Physical Review Letters **116**, 116403 (2016).

[62] N. F. Quackenbush, J. W. Tashman, J. A. Mundy, S. Sallis, H. Paik, R. Misra, J. A. Moyer, J.-H. Guo, D. A. Fischer, J. C. Woicik, D. A. Muller, D. G. Schlom, and L. F. J. Piper, Nano Letters **13**, 4857 (2013).

[63] T. J. Huffman, C. Hendriks, E. J. Walter, J. Yoon, H. Ju, R. Smith, G. L. Carr, H. Krakauer, and M. M. Qazilbash, Physical Review B **95**, 075125 (2017).

[64] O. Nájera, M. Civelli, V. Dobrosavljević, and M. J. Rozenberg, Phys. Rev. B **95**, 035113 (2017).

[65] M. Hoffmann and S. Blügel, Phys. Rev. B **101**, 024418 (2020).

[66] M. Stoudenmire and S.R. White, www.itensor.org.