Spin-lattice Coupling and the Emergence of the Trimerized Phase in the $S=1$ Kagome Antiferromagnet $\text{Na}_2\text{Ti}_3\text{Cl}_8$

Arpita Paul, Chia-Min Chung, Turan Birol, and Hitesh J. Changlani

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Spin–lattice coupling and the emergence of the trimerized phase in the $S = 1$ Kagome antiferromagnet Na$_2$Ti$_3$Cl$_8$

Arpita Paul,1 Chia-Min Chung,2 Turan Birol,1,∗ and Hitesh J. Changlani3,4,†

1Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455, USA
2Department of Physics and Arnold Sommerfeld Center for Theoretical Physics, Ludwig-Maximilians-Universitat Munchen, Theresienstrasse 37, 80333 Munchen, Germany
3Department of Physics, Florida State University, Tallahassee, Florida 32306, USA
4National High Magnetic Field Laboratory, Tallahassee, Florida 32304, USA

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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$_2$Ti$_3$Cl$_8$ 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$_2$Ti$_3$Cl$_8$ 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$_2$Ti$_3$Cl$_8$ 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$_2$Ti$_3$Cl$_8$ 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].

Here we elucidate the magnetic ground state and elucidate the mechanism of the breathing distortion in Na$_2$Ti$_3$Cl$_8$.
We include both of these terms to get the Hamiltonian

\[
\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_{\text{bq}} \sum_{\langle ij \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j)^2 + \frac{J_R}{2} \sum_{\Delta \neq i,j,k} ((\mathbf{S}_i \cdot \mathbf{S}_j)(\mathbf{S}_i \cdot \mathbf{S}_k) + (\mathbf{S}_i \cdot \mathbf{S}_k)(\mathbf{S}_j \cdot \mathbf{S}_k))
\]

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 \(J_{\text{bq}}\) 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 \(C_{2v}\). This symmetry splits the \(t_{2g}\) orbitals into \(t_{2g} \rightarrow A_g + B_g + B_\delta\), but the two \(B_\delta\) orbitals \((xz\text{ and }yz)\) 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 energy \((257\text{ meV})\) 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...
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, $J_{bg}/J$ 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 $J_{bg}/J \approx -0.16$ below which it transitions to a state with FQ order [15].

While the observation that $J$ is large and $J_{bg}$ and $J_R$ have opposite signs is robust, the values of $J_{bg}/J_R$ 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 $J_{bg} = -0.529J_R$. (Another scan for $J_R = -J_{bg}$, 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 $J_{bg} = -0.529J_R$ is qualitatively similar to the model with $J_R = 0$ and negative $J_{bg}$, and the magnetic ground state of Na$_2$Ti$_3$Cl$_8$ in HT structure is FQ.

To support these assertions further, we perform DMRG calculations on XC8-3 cylinders with the open (periodic) boundary 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. $\sum_{\Delta}S_i \cdot S_j - \sum_\nabla S_i \cdot S_j$) and the quadrupolar order parameter $(\langle S^z_2 \rangle - \frac{2}{5})$. Results in Fig. 4b for $J_R/J = -J_{bg}/J = 0$ confirm that the ground state is trimerized in the absence of biquadratic coupling. On the other hand, for $J_R/J \approx -1.89 J_{bg}/J \approx 0.37$ (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$_2$Ti$_3$Cl$_8$ would show up in DFT calculations as an unstable phonon that transforms as $\Gamma_5$ irreducible representation [33]. (While DFT can...
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, $J_{0q}/J$, 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 $\sim$1-3% change in the lattice constants, in contrast in Na$_2$Ti$_3$Cl$_8$ the change is of the order of 10%!

An important feature of the $\Gamma_{1}^-$ 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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* tbirol@umn.edu
† hchanglani@fsu.edu

[42] See supplemental information for further details.