High-temperature thermodynamics of the honeycomb-lattice Kitaev-Heisenberg model: A high-temperature series expansion study

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High temperature thermodynamics of the honeycomb-lattice Kitaev-Heisenberg model: A high temperature series expansion study

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We develop high temperature series expansions for the thermodynamic properties of the honeycomb-lattice Kitaev-Heisenberg model. Numerical results for uniform susceptibility, heat capacity and entropy as a function of temperature for different values of the Kitaev coupling K and Heisenberg exachange coupling J (with $|J| \leq |K|$) are presented. These expansions show good convergence down to a temperature of a fraction of K and in some cases down to $T = K/10$. In the Kitaev exchange dominated regime, the inverse susceptibility has a nearly linear temperature dependence over a wide temperature range. However, we show that already at temperatures 10-times the Curie-Weiss temperature, the effective Curie-Weiss constant estimated from the data can be off by a factor of 2. We find that the magnitude of the heat capacity maximum at the short-range order peak, is substantially smaller for small J/K than for J of order or larger than K. We suggest that this itself represents a simple marker for the relative importance of the Kitaev terms in these systems. Somewhat surprisingly, both heat capacity and susceptibility data on Na_2IrO_3 are consistent with a dominant *antiferromagnetic* Kitaev exchange constant of about $300 - 400\ K$.

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INTRODUCTION

Kitaev's discovery of a class of honeycomb-lattice, anisotropic, spin-half models with gapped and gapless spin-liquid phases and Majorana fermion excitations [1], represents a major advance in the field of quantum magnetism. Furthermore, Jackeli and Khaliullin's demonstration that such special Kitaev-couplings can indeed be realized in real materials [2] has led to intense theoretical and experimental activity in the field. Several classes of materials dubbed 'Kitaev-materials'[3–5] have been synthesized and these now represent some of the most promising candidates for the much sought after quantum spin-liquid phase of matter [6]. Several neutron scattering and other experimental studies have been interpreted as evidence for proximate spin-liquid behavior, even though the true ground-state may often be long-range ordered [7–11].

Heisenberg exchange couplings are the most generic terms in modeling quantum magnetism. Even in Kitaev-materials, there is always varying degree of Heisenberg exchange couplings present, which can affect key properties including driving the system away from the spin-liquid phases and into various magnetically ordered phases [12–23]. The real materials may have additional exchange couplings other than Heisenberg and Kitaev couplings and possibly further neighbor interactions [3–5]. However, to keep things simple, in this paper, we confine ourselves to the nearest-neighbor Kitaev-Heisenberg model. One can regard this as a phenomenological approach to the Kitaev materials, where deviations from the pure Kitaev model are small. The high temperature properties are not so sensitive to details of the additional couplings and the Heisenberg-Kitaev model allows us to systematically explore the consequences of deviations from the pure Kitaev limit. Any Heisenberg coupling destroys the solubility of the model and necessitates numerical studies. Previously these models have been studied numerically by Monte Carlo simulations, Exact Diagonalization and other techniques based on finite-size clusters [12–23].

Here we present a study of the nearest-neighbor Kitaev-Heisenberg model using the high temperature series expansion (HTSE) method [27, 28]. These series expansions are formally defined in the thermodynamic limit and give accurate properties of the infinite system when the expansions are convergent typically at temperatures above the exchange energy scales. At lower temperatures, one can use Pade extrapolation methods to obtain the desired thermodynamic properties. We typically find good convergence up to and a little below the temperature of the peak in the heat capacity associated with short-range magnetic order in the system.

The uniform susceptibility is often used to obtain the first estimates of the exchange constants for magnetic materials. In the Kitaev coupling dominated regime, the inverse susceptibility appears to be nearly linear over a wide temperature range. Plots of inverse susceptibility versus temperature[24–26] can be extrapolated to obtain the Curie-Weiss constant. However, one needs to be careful in relating these to the microscopic exchange constants for these systems as already at temperatures 10 times the Curie-Weiss temperature the effective Curie-Weiss constant obtained from such an extrapolation can

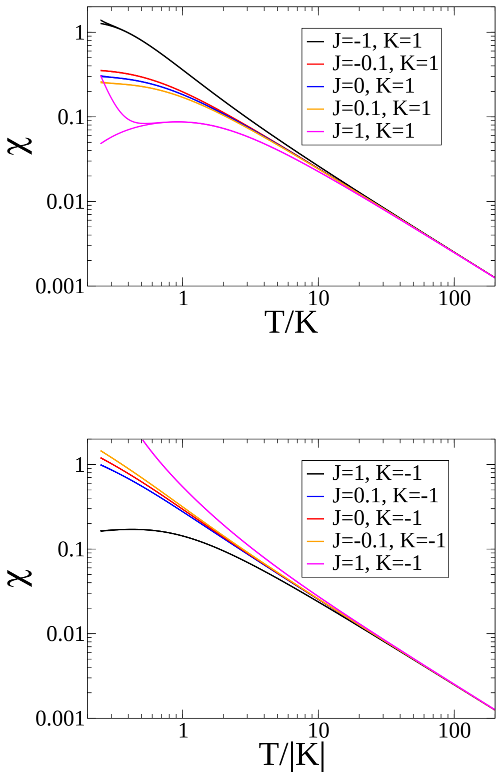

FIG. 1: A plot of the uniform susceptibility of the model as a function of temperature T for different values of exchange constants K and J. The upper plot corresponds to an antiferromagnetic Kitaev coupling and the lower plot to a ferromagnetic Kitaev coupling.

be off by a factor of 2.

The behavior of entropy and heat capacity in the Kitaev coupling dominated regime is qualitatively different from that in the Heisenberg coupling dominated regime and can serve as a simple marker for the importance of Kitaev couplings in a real material. In this regime, the entropy is realeased only partially at the onset of short-range order marking the beginning of a proximate Kitaev spin-liquid intermediate temperature regime. This is because the intermediate temperature regime has very short-range spin-correlations and still contains substantial entropy. In their Monte Carlo studies, Nasu et al [21] found a plateau in the entropy over a range of temperatures at a value of $\frac{1}{2}R\ln 2$. We are studying a model in which the Kitaev couplings are same along the three bond-directions of the Honeycomb lattice, where there may not be such a strict plateau. Our studies show only hints of a possible plateau formation not different from what is seen in some experiments [26].

Quite remarkably, the magnitude of the short-ranged peak in the heat capacity is itself a marker of whether the Kitaev terms are important or whether the system is dominated by Heisenberg exchange terms. In the Kitaev regime this peak is of significantly smaller magnitude. We suggest that this may itself provide a good experimental means to quickly characterize which materials are likely to be near the quantum spin-liquid phase.

MODELS

We study the honeycomb-lattice Kitaev-Heisenberg model with Hamiltonian

$$\mathcal{H} = J \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j + K \sum_{<i,j>_\alpha} S_i^\alpha S_j^\alpha, \tag{1}$$

where the sums run over all nearest neighbor pairs of the Honeycomb lattice. The second sum represents the Kitaev couplings. The bonds of the honeycomb lattice can be divided into 3 different types labelled by $\alpha = x$, y, or z. The Kitaev coupling along the bond type α involves bilinear spin-couplings involving only the spin operator S_i^α. We note that, in the literature, the opposite sign of the couplings as well as a factor of 2 in the definition of the Kitaev terms has sometimes been used. And, in fact, theory points towards a ferromagnetic Kitaev exchange, which in our notation corresponds to negative K. Also, in our study the strength of the Kitaev couplings are the same in all directions.

We develop high temperature series expansion for the logarithm of the partition function using the linked-cluster method. To illustrate the basic method [27], we expand the canonical partition function as,

$$\begin{aligned} Z = &\ Tr\ \exp\left(-\beta\mathcal{H}\right) \\ = &\ \textstyle\sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!}\ Tr\ \mathcal{H}^n, \end{aligned} \tag{2}$$

where the trace represents a sum over all states in the Hilbert space. Since $\mathcal{H}$ couples only pairs of sites, $\mathcal{H}^n$ can be expressed as a sum over terms each of which contains only a finite number of spin operators. Hence, the trace can be evaluated by considering finite sets of spins. When an extensive quantity such as the logarithm of the partition function is considered, the calculation can be reduced to one requiring only traces over connected clusters of spins. The linked cluster method [27] is a powerful computational technique that allows one to carry out such calculations to some order in β by an automated computer program resulting in the correct series coefficients for the system in the thermodynamic limit.

For our Hamiltonian, we have done these series expansions for the logarithm of the partition function to order β^{14}. Series coefficients for selected values of J and K are given in supplementary materials. From the logarithm of the partition function, the internal energy, heat capacity and entropy follows. In addition, we also apply an external-field along the x-axis, and calculate the uniform

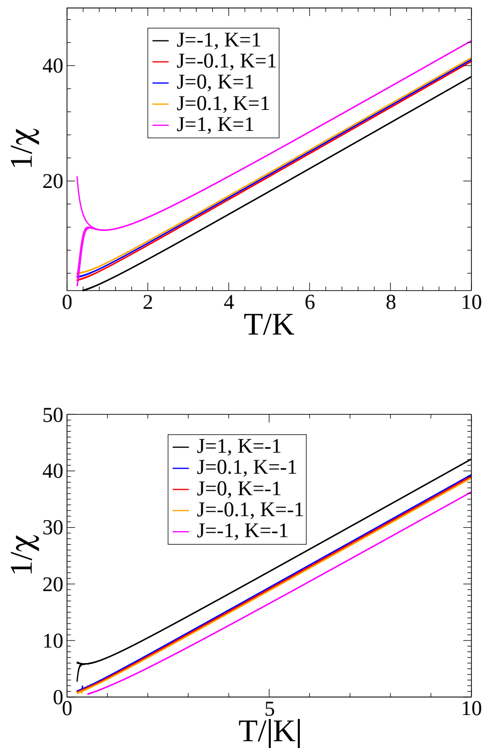

FIG. 2: A plot of the inverse susceptibility of the model as a function of temperature T for different values of exchange constants K and J. The linear temperature dependence of the inverse susceptibility seemingly extends well below $T = K$.

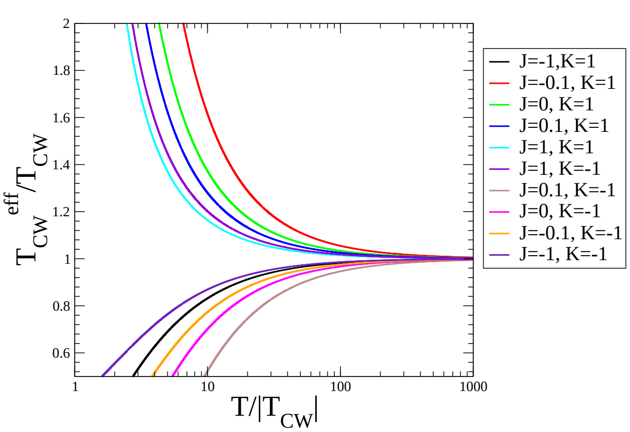

FIG. 3: The effective Curie-Weiss T_{cw}^{eff} constant obtained by a straight-line extrapolation of the inverse susceptibility locally from some temperature T as a function of temperature T. Note that in the Kitaev regime the effective Curie-Weiss constant can differ from the true Curie-Weiss T_{cw} constant by a factor of two already at a temperature 10 times the Curie-Weiss temperature.

susceptibility, in powers of β, as the second derivative of the free-energy with respect to this external field. These expansions are carried out for $T\chi$ to order β^{12}. The series coefficients for the susceptibilities are also given in the supplementary materials. We will present results for ferromagnetic and antiferromagnetic Kitaev coupling K as well as for J/K ratios of 0, ± 0.1 and ± 1 to cover a wide range of behaviors. Larger J values are closer to the $J/K = 1$ behavior so that the system is well in the Heisenberg dominated regime already when the two couplings are equal. We call the parameter range $|J/K| \leq 0.1$ as the Kitaev regime. At high temperatures the thermodynamic properties are not so sensitive to much smaller variations in parameters.

RESULTS

We analyze the series by using Pade approximants. As long as different approximants agree with each other, those usually imply convergence in the thermodynamic limit. At least two approximants are plotted in each case. Some times Pade approximants have nearby pole-zero pairs around some temperature. That spoils the convergence around that temperature and shows up as a sharp glitch in our plots. Such a glitch need not affect the convergence of the approximants away from the neighborhood of that temperature. However, at low temperatures different approximants clearly start diverging from each other. This shows up as a fork in the plots of various properties, with some growing and others diminishing in magnitude. Then, the series analysis can no longer be relied upon.

We begin in Fig. 1 with a plot of the uniform susceptibility as a function of temperature on a log-log scale. We see that in the Kitaev regime the plots remain close to each other. Note that for $J = 0$, even though the entropy and heat capacity do not depend on the sign of K, the susceptibility very much does.

The asymptotic Curie-Weiss constant for the model can be obtained from the very first order of the high temperature expansion as:

$$T_{cw} = 0.75J + 0.25K. \tag{3}$$

In Fig. 2, we show the Curie-Weiss plot of inverse susceptibility versus temperature. In the Kitaev regime, the plot looks linear over a wide temperature range. Following Kouvel and Fisher [29, 30] one can define an effective Curie-Weiss temperature as

$$T_{cw}^{eff} = -T - \frac{\chi}{d\chi/dT} \tag{4}$$

If we draw a straight-line to the inverse susceptibility plot at some temperature T, T_{cw}^{eff} would be the intercept. In other words, if one obtains Curie-Weiss constant from experimental data up to some temperature

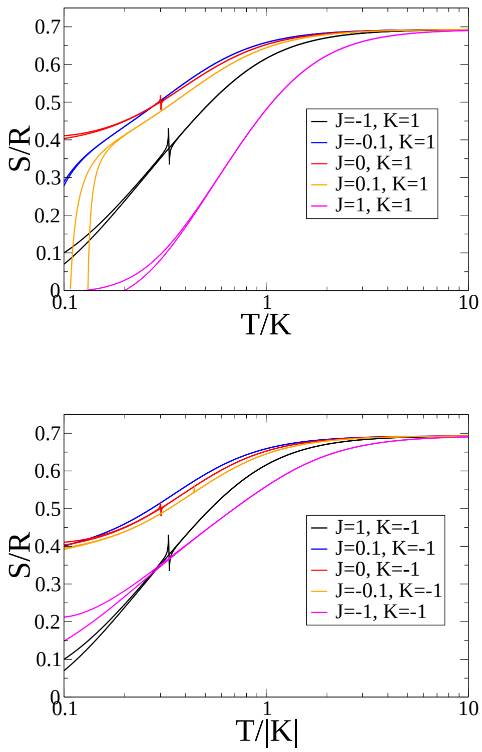

FIG. 4: A plot of the entropy per mole of the model as a function of temperature T for different values of the Heisenberg coupling J and the Kitaev coupling K. The upper plot corresponds to an antiferromagnetic Kitaev coupling and the lower plot to a ferromagnetic Kitaev coupling. Some of the Pade approximants have nearby pole-zero pair around some temperature, that shows as a sharp glitch in the plots. These approximants do not converge near that temperature, but should be fine away from that temperature.

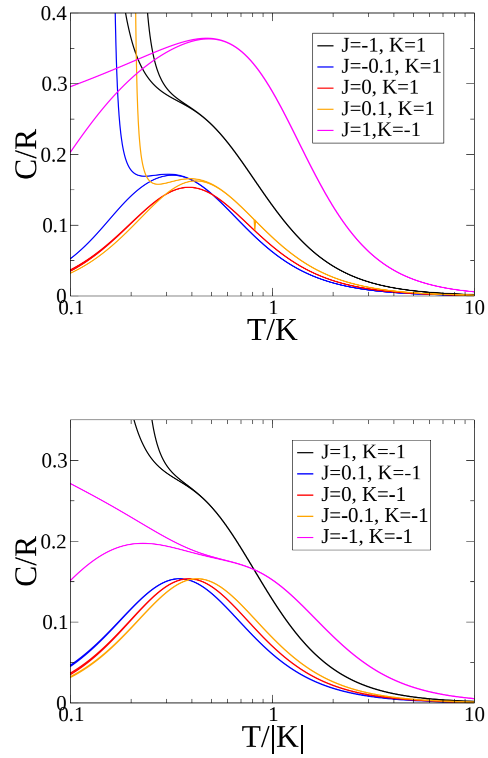

FIG. 5: A plot of the heat capacity per mole of the model in units of the gas constant R as a function of temperature T for different values of the Heisenberg coupling J and the Kitaev coupling K. The upper plot corresponds to an antiferromagnetic Kitaev coupling and the lower plot to a ferromagnetic Kitaev coupling. Note that a fork-like split of approximants shows that the convergence is breaking down at lower temperatures. For small Heisenberg couplings, the convergence is better for ferromagnetic Kitaev coupling than for antiferromagnetic Kitaev coupling.

only an effective Curie-Weiss constant will result. In Fig 3, we show the effective Curie-Weiss constant as a function of temperature. The temperature scale itself is normalized by the magnitude of the Curie-Weiss constant for the given exchange values. Note that when the Curie-Weiss constant is antiferromagnetic, the effective Curie-Weiss constant increases in magnitude as temperature goes down whereas when the Curie-Weiss constant is ferromagnetic it decreases in magnitude as the temperature is lowered. The Kitaev regime shows very substantial deviations from the high temperature behavior already at a temperature 10 times T_{cw}. This needs to be taken into account in obtaining exchange constants from such measurements.

Plots of the molar entropy as a function of temperature is shown in Fig. 4 and the heat capacity in Fig. 5, with the temperature on a logarithmic scale. The main message in these plots is very simple. The Kitaev regime corresponding to small J/K has very different temperature dependence of heat capacity and entropy than Heisenberg systems where most of the entropy is released in the development of short-range order. That is not the case in the Kitaev regime. Nasu et al have emphasized a plateau in the entropy at a value of $ln 2/2$ in the gapped spin-liquid models and a plateau-like feature in the gapless spin-liquid models [21]. This is consistent with the idea of a two step release of entropy and the development of an intermedaite proximate spin-liquid regime.

We are studying here the gapless spin-liquid model only as the Kitaev couplings are taken to be equal along all three bond-directions of the honeycomb lattice. We do not see a plateau in the entropy plots. But, for the pure Kitaev model and a range of Heisenberg couplings the development of a plateau-like feature at still lower temperature is plausible. Note that the entropy at the lowest temperatures we show is still above $1/2 \ln 2$. This feature seems more robust when the Kitaev exchange is ferromagnetic than when it is antiferromagnetic. Hence, we would conclude that if a plateau actually develops that would be at temperatures below $T/|K| = 0.1$.

Pade extrapolations for the heat capacity are shown in Fig. 5. Some of the Pade approximants have nearby pole-zero pair [31] around some temperature, that shows as a sharp glitch in the plots. These approximants do not converge near that temperature, but should be fine away from that temperature. A striking thing about the plots is that the magnitude of the heat capacity peak at high-temperatures where the short-range order develops is significantly smaller in the Kitaev regime than that when the system is dominated by the Heisenberg coupling and is likely to be deep in the long-range ordered phase at $T = 0$. Although our results are not always well converged below the short-range order peak, we can clearly say that the magnitude of this peak remains roughly unchanged in the Kitaev regime.

In the absence of a finite temperature phase transition, it should be possible, in principle, to extrapolate thermodynamic properties all the way down to $T = 0$. However, that usually does not work well [27, 32]. Bernu and Misguich have suggested a very different extrapolation procedure for the heat capacity [33] that takes advantage of known zero-temperature properties. While this may be helpful for the pure Kitaev model, low temperature properties of the infinite system are not known well enough for the Kitaev-Heisenberg model. And, the extrapolations can be highly sensitive to the exact $T = 0$ properties as well as to the full details of the model parameters. We leave such extrapolations for a later study.

We turn now to experimental systems. Various researchers have discussed the possibility of exchange constants other than Kitaev and Heisenberg terms as well as various anisotropies and further neighbor terms in the Hamiltonian. The high temperature thermodynamics are not very sensitive to the full details of the model. Looking at the data of Mehlawat et al [26], for Na_2IrO_3 the peak in the heat capacity occurs at a temperature of about 110 K. In the Kitaev regime, the peak occurs at a temperature of 0.3 to 0.4 in units of the Kitaev coupling. That translates into a Kitaev coupling of about $275 - 370$ K. So far, the Kitaev couplings can have either sign. The Curie-Weiss fit gives an antiferromagnetic Curie-Weiss temperature of about 125 K. This value of the Curie-Weiss constant would imply an antiferromagnetic Kitaev exchange of approximately 500 K. However, once we take into account that the measured Curie-Weiss constant is roughly 1.2-1.8 times too large, once again the Kitaev exchange constant is in the range of $280 - 400$ K. Thus, the high temperature thermodynamics of this material is in good agreement with the Kitaev regime, with a single *antiferromagnetic* Kitaev coupling. The data is similar but more erratic for Li_2IrO_3, where both quantities are about 20 percent smaller. These results are surprising as theory points to a ferromagnetic Kitaev exchange. And, in that case, explaining the susceptibility data requires invoking strong second and third neighbor interactions.

CONCLUSIONS

In conclusion, in this paper we have studied the honeycomb-lattice Kitaev-Heisenberg model using the high temperature series expansion method. We have presented results for thermodynamic properties including the entropy, the heat capacity and the uniform susceptibility for a range of Kitaev and Heisenberg exchange couplings. We showed that the usual Curie-Weiss plot of inverse susceptibility looks linear in temperature over a wide temperature range in the Kitaev regime. But it shows significant deviations from the asymptotic high temperature behavior, which means one needs to be careful in obtaining exchange constants from such a Curie-Weiss plot. Comparison of our results with experiments on Na_2IrO_3 gives a dominant *antiferromagnetic* Kitaev exchange constant of $280 - 400$ K.

The heat capacity and entropy show very distinct behavior in the Kitaev-exchange dominated regime. The heat capacity peak has a much smaller value in this regime and is effectively constant as J/K is varied. This itself may be used as a marker in experimental studies for an early determination of the importance of Kitaev couplings in the materials. Furthermore, the entropy is released more gradually as the temperature is lowered creating a very distinct and characteristic experimental signature. While we do not see clear evidence of an entropy plateau, our results are consistent with the development of such a plateau-like feature at still lower temperature. Clearly, the entropy release in these systems is like a two step process, where the higher temperature heat capacity peak only gives rise to an intermediate proximate spin-liquid phase at intermediate temperatures. Somewhat surprisingly, a single *antiferromagnetic* Kitaev exchange in the range of $275 - 400$ K gives a reasonable account of both heat capacity and susceptibility data in sodium and lithium iridates.

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[1] A. Kitaev, Annals of Physics, 321, 2 (2006).
[2] G. Jackeli and G. Khaliullin, Phys. Rev. Lett. 102, 017205 (2009).
[3] S. Trebst arxiv:1701.07315 and references therein.
[4] S. M. Winter, A. A. Tsirlin, M. Daghofer, J. van den Brink, Y. Singh, P. Gegenwart, R. Valenti, arXiv:1706.06113 and references therein.

[5] J. G. Rau, E. K. Lee and H. Y. Kee, Phys. Rev. Lett. 112, 077204 (2014); *ibid.* Annual Review of Condensed Matter Physics, 7, 195 (2016).
[6] L. Balents, Nature 464, 199 (2010).
[7] A. Banerjee, C.A. Bridges, J-Q. Yan, A.A. Aczel, L. Li, M.B. Stone, G.E. Granroth, M.D. Lumsden, Y. Yiu, J. Knolle, D.L. Kovrizhin, S. Bhattacharjee, R. Moessner, D.A. Tennant, D.G. Mandrus, S.E. Nagler, Nature Materials, 15, 733 (2016).
[8] S, H. Chun, J.-W. Kim, J. Kim, H. Zheng, C. C. Stoumpos, C. D. Malliakas, J. F. Mitchell, K. Mehlawat, Y. Singh, Y. Choi, T. Gog, A. Al-Zein, M. M. Sala, M. Krisch, J. Chaloupka, G. Jackeli, G. Khaliullin, B. J. Kim, Nature Phys. 11, 462 (2015).
[9] J. Knolle, G.W. Chern, D. L. Kovrizhin, R. Moessner and N. B. Perkins, Phys. Rev. Lett. 113, 187201 (2014).
[10] J. Knolle, D. L. Kovrizhin, J. T. Chalker and R. Moessner, Phys. Rev. Lett. 112, 207203 (2014).
[11] N. P. Breznay, A. Ruiz, A. Frano, W. Bi, R. J. Birgeneau, D. Haskel, J. G. Analytis, arXiv:1703.00499.
[12] J. Chaloupka, G. Jackeli, G. Khaliullin, Phys.Rev.Lett. 105, 027204 (2010).
[13] J. Chaloupka, G. Jackeli and G. Khaliullin, Phys. Rev. Lett. 110, 097204 (2013).
[14] J. Reuther, R. Thomale and S. Trebst, Phys. Rev. B 84, 100406 (2011).
[15] H. C. Jiang, Z. C. Gu, X. L. Qi and S. Trebst, Phys. Rev. B 83, 245104 (2011).
[16] I. Kimchi and Y.Z. You, Phys. Rev. B 84, 180047 (2011).
[17] R. Schaffer, S. Bhattacharjee and Y. B. Kim, Phys. Rev. B 86, 224417 (2012).
[18] X. Y. Song, Y. Z. You and L. Balents, Phys. Rev. Lett. 117, 037209 (2016).
[19] C. C. Price and N. B. Perkins, Phys. Rev. Lett. 109, 187201 (2012).
[20] J. Yoshitake, J. Nasu and Y. Motome, Phys. Rev. Lett. 117, 157203 (2016).
[21] J. Nasu, M. Udagawa and Y. Motome, Phys. Rev. B 92, 115122 (2015); *ibid.* Phys. Rev. Lett. 113, 197205 (2014).
[22] I. Kimchi and A. Vishwanath, Phys. Rev. B 89. 014414 (2014).
[23] G. B. Halasz, N. B. Perkins and J. van den Brink, Phys. Rev. Lett. 117, 127203 (2016).
[24] Y. Singh and P. Gegenwart, Phys. Rev. B 82, 064412 (2010).
[25] Y. Singh, S. Manni, J. Reuther, T. Berlijn, R. Thomale, W. Ku, S. Trebst, P. Gegenwart, Phys. Rev. Lett. 108, 127203 (2012).
[26] K. Mehlawat, A. Thamizhavel, Y. Singh, Phys. Rev. B 95, 144406 (2017).
[27] J. Oitmaa, C. Hamer and W. Zheng, *Series Expansion Methods for strongly interacting lattice models* (Cambridge University Press, Cambridge 2006).
[28] M. P. Gelfand and R. R. P. Singh, Adv. Phys. **49**, 93(2000).
[29] J. S. Kouvel and M. E. Fisher Phys. Rev. 136, A1626 (1964).
[30] W. Zheng, R. R. P. Singh, R. H. McKenzie, and R. Coldea, Phys. Rev. B 71, 134422 (2005).
[31] George A. Baker and Peter Graves-Morris, *Pade Approximants*, (Cambridge University Press, Cambridge 1996).
[32] N. Elstner, R. R. P. Singh, and A. P. Young Phys. Rev. Lett. 71, 1629 (1993); N. Elstner and A. P. Young Phys. Rev. B 50, 6871 (1994).
[33] B. Bernu and G. Misguich, Phys. Rev. B 63, 134409 (2001).