Nematic ordering in pyrochlore antiferromagnets: high-field phase of chromium spinel oxides

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(Dated: October 9, 2015)

Motivated by recent observation of a new high field phase near saturation in chromium spinels $\text{ACr}_2\text{O}_4$ ($A = \text{Zn, Cd, Hg}$), we study the $S = 3/2$ pyrochlore Heisenberg antiferromagnet with biquadratic interactions. Magnon instability analysis at the saturation field reveals that a very small biquadratic interaction can induce magnon pairing in pyrochlore antiferromagnets, which leads to the emergence of a ferro-quadrupolar phase, or equivalently a spin nematic phase, below the saturation field. We present the magnetic phase diagram in an applied field, studying both $S = 3/2$ and $S = 1$ spin systems. The relevance of our result to chromium spinels is discussed.

PACS numbers: 75.10.Jm, 75.40.Cx

Highly frustrated magnets have been an active playground to find novel states of matter. Frustration suppresses long-range magnetic orders, leading to the possibility of quantum spin liquids [1] without any conventional order, or of other exotic states with unconventional orders. Among the latter, quantum multipolar states are of a particular interest. The simplest among them, the quadrupolar state is also known as the spin nematic state. This state does not have any conventional magnetic order with the spin vector as an order parameter. Instead, it has a directional order whose order parameters are the symmetric rank-2 spin tensors $\mathbf{S}$. Quantum mechanically, such a state can be understood as a result of condensation of bound magnon pairs. The presence of such an exotic state is theoretically proposed in various spin systems, including frustrated ferromagnets [4–6] and the one-dimensional $S = 1/2$ zigzag chain compound $\text{LiCuVO}_4$ [7,8]. The emergence of multipolar phases has been also theoretically well established in $S = 1$ spin systems with bilinear and biquadratic interactions on some lattices, such as square and cubic lattices, when the biquadratic interactions are strong enough [2,3,10]. Despite these theoretical results, the experimental confirmation of the spin nematic phase still remains difficult [11].

The ground states are infinitely degenerate in the classical limit [12] and it is believed that there is no spin long-range order at any temperature both in the classical ($S \rightarrow \infty$) [13] and quantum ($S = 1/2$) [14] models. In real materials this massive degeneracy can be often lifted by further neighbor interactions or by the order-by-distortion effect [15,18].

The magnetic structure of antiferromagnetic phases derived from the model (1) in the classical limit with the MF ansatz were found to be consistent with the available experimental
polarized ones. The dotted line shows the exact two-magnon instability line. The partially polarized uniform phase below this dotted line is a spin nematic phase. The overlap probability between the partially polarized and fully polarized (FP) magnetic moments and empty arrows partially arrowed ones. The dotted line shows the exact two-magnon instability line. The partially polarized uniform phase below this dotted line is a spin nematic phase. (b) Schematic figure of multipolar order in chromium spinels near the saturation field. The black dashed lines denote 1st (2nd) order phase boundaries.

In this Letter, motivated by the experimental discovery of the novel high-field phase, we study quantum effects in the $S = 3/2$ pyrochlore antiferromagnet $\mathfrak{I}$ with biquadratic interaction in an applied field. In fact, not much is known about multipolar order in $S > 1$ spin systems. In a MF approximation study of a $S = 3/2$ spin system on the cubic lattice at zero field, biquadratic interactions did not induce any multipolar order $\mathfrak{I}^3$. However, the possibility of the spin nematic phase for $S = 3/2$ has to be examined more carefully beyond these limitations, especially in the light of the experimental results on chromium spinels near the saturation field.

We first employ the site-decoupled MF approximation. The obtained magnetic phase diagram in this approximation is almost the same as the classical phase diagram. However, it reveals that quantum multipolar states exist close to the lowest energy state near the saturation field, and in fact become degenerate with the lowest energy state at the MF phase boundary. This suggests the possibility of an emergence of multipolar states near the saturation field, in more precise analysis. Indeed, in a magnon-instability analysis on the FP state, which is exact just below the saturation field, we find an emergence of a spin nematic phase. [See Fig. 1(a)].

The site-decoupled MF approximation is a variational method within direct-product states of on-site quantum states $|\Psi\rangle = \bigotimes_i |\phi_i\rangle$. The arbitrary local states can be expressed by the linear combination of $|m\rangle$, where $|m\rangle$ is the eigenstate for the spin $z$ component $S^z$ on a single site with eigenvalue $m$. For spin 3/2, which is of our main interest in this Letter, the product states $|\Psi\rangle$ do include the nematic state $\otimes_i \left( \left| \frac{1}{2} \right\rangle + e^{i\gamma} \left| -\frac{1}{2} \right\rangle \right)$ $\mathfrak{I}^{31}$ [32]. Fixing the overall phase and normalization, one can describe the local spin-3/2 state $|\phi_i\rangle$ with 6 real parameters.

Furthermore, we assume that the system has 4-sublattice structure, $|\Psi\rangle = \bigotimes_a \bigotimes_i |\phi_{ai}\rangle$, where $a$ labels the sublattices and $i$-site belongs to the $a$-sublattice. In total, there are 6 x 4 = 24 real variational parameters. Minimizing the energy expectation value $\langle \Psi | \mathcal{H} | \Psi \rangle$, we obtain the phase diagram of antiferromagnetic phases in Fig. 1(a). The black dashed lines and the red solid lines, respectively, denote the second order and first order phase boundaries.

The magnetic characteristics of these antiferromagnetic phases are essentially the same as in the classical limit [18]. In the lower field regime, there appears canted antiferromagnetic phase with 2:2-sublattice structure. This state changes to higher field phases through first order phase transition. In higher field, the up-up-up-down plateau phase appears in a wide field range. When $J_z$ is relatively weak, this state continuously changes to a canted antiferromagnetic phase with 3:1 sublattice structure with increasing field and also to another canted antiferromagnetic phase with 2:1:1-sublattice structure with decreasing field. The upper boundary of the plateau phase expands to the higher field regime in comparison with the MF phase diagram in the classical spin model [18]. This is due to quantum effects originated from the biquadratic interaction. For strong $|J_z|$ regime, the plateau phase jumps to the FP phase through the first order phase transition with increasing field.

We should also note that multipolar states are also stable solutions in a finite magnetic field in the MF approximation under the condition that all sites are equivalent. These multipolar MF solutions are highly degenerate. Both purely quantum states such as a quadrupolar state $\bigotimes_i \left( a \left| \frac{1}{2} \right\rangle + c \left| -\frac{1}{2} \right\rangle \right)$ and a octupolar state $\bigotimes_i \left( a' \left| \frac{1}{2} \right\rangle + c' \left| -\frac{1}{2} \right\rangle \right)$ also a continuous deformation of these two states belong to the degenerate manifold of the MF solutions. In the site-decoupled MF approximation, these states generally have higher energy than the four-sublattice canted states and half-magnetization plateau.
state. However the MF energies of the degenerate multipolar states and the plateau state become identical exactly at the phase boundary between the plateau phase and the FP phase. This coincidence of the MF energies at the saturation field can open a possibility of emergence of multipolar phases above the plateau phase in a more precise analysis.

To investigate this possibility, we study instability induced by magnon excitations in the FP phase. Above the saturation field, all spins are perfectly polarized along the magnetic field. Below the saturation field, magnons, which are flipped spins in the FP state, are sparsely induced and their condensation leads to ordering of magnetic structure transverse to the applied field. Bose-Einstein condensation (BEC) of single magnons realizes the spin canting antiferromagnetic states [33]. The nature of the condensed magnons determine the magnetic structure.

For the single-magnon excitations in the FP state, we obtain four branches in the excitation energy spectrum: $E^\pm(p)$ and $E^0$, where $E^0$ is doubly degenerate and independent on the wave vector $i.e.$ it has a flat mode. The lowest excitation mode is $E^0$ for $2J_1 + 3J_2 \geq 0$ and $E^\pm(p)$ for $2J_1 + 3J_2 < 0$. The saturation field $h_{s1}$ given by the one-magnon instability is $h_{s1} = 6(2J_1 + 3J_2)$ in the parameter region $2J_1 + 3J_2 \geq 0$, whereas the ferromagnetic ground state is stable against single magnon excitations at zero field in $2J_1 + 3J_2 < 0$. In the pyrochlore antiferromagnetic Heisenberg model with $J_2 = 0$, it is known that the lowest-energy magnon states are localized [34]. This is also true for a finite $J_2$.

Ground states of dilute magnons are highly degenerate, since the single-magnon eigenstates are localized. In this case, even a weak perturbation can change the nature of the ground state drastically. Actually, the biquadratic interaction has a pair hopping process $(S_i^+ S_j^+ + h.c.)$, which can induce a dynamical process of two magnons. A similar dynamical energy gain happens to two magnons in frustrated ferromagnets [5], where two-magnons become stable bound states and these bound magnon pairs condense in the ground state [4,8].

Such an unconventional magnon condensed state is nothing but the spin nematic state, where the order parameter is given by quadrupolar operators $(S_i^+ S_j^+ + S_j^+ S_i^+ + S_j^+ S_i^+ + S_i^+ S_j^+)$ defined on single sites $(i = j)$ or on neighboring sites. To analyze the emergence of bound-magnon condensation below the saturation field, we study multiple-magnon instability to the FP state at the saturation field in the following.

We first consider the two-magnon excited states. Two-magnon excited states are generally expressed as $|2\rangle = \sum_{(i,j)} \phi_{ij} S_i^+ S_j^+ |0\rangle$, where the summation is taken over all pairs of lattice sites. We solve the Schrödinger equation for this wave function exactly, extending the previous method [35] to a system with plural sites in the unit cells. The energy spectrum contains a branch of stable two magnon bound state, which has a lower energy than two independent localized magnons at the saturation field for $J_2 < -0.043 J_1$. The dynamical process effectively gives the attractive interaction between two magnons. The lowest excitation mode is dispersive and non-degenerate, and has the minimum energy at $k = (0,0,0)$, where $k$ is the center-of-mass wave vector. It means that the magnon pairs can move around on the lattice. From the lowest excitation energy, we obtain the saturation field $h_{s2}$ at which the lowest two-magnon bound state becomes gapless. The values of $h_{s2}$ are plotted in Fig. 1(a).

For $J_2 < -0.043 J_1$, $h_{s2}$ is larger than both $h_{s1}$ and the upper boundary field of $1/2$-plateau phase. We thus find that a nematic phase is expected to appear below $h_{s2}$ induced by the two-magnon instability.

We can identify the nature of the quadrupolar order from the structure of the magnon pair. The wave-function of the lowest-energy bound magnon pair is uniform, i.e. it has the wave vector $k = (0,0,0)$, and fully symmetric $(A_1)$ under the space symmetry group $O_h$. Hence that is simply represented in the form $|\psi\rangle = \phi_{\text{on-site}} S_i^+ S_j^+ |0\rangle + \phi_{1st} \sum_{(i,j)} S_i^+ S_j^+ |0\rangle + \phi_{2nd} \sum_{(i,j)} S_i^+ S_j^+ |0\rangle + \cdots$, where $\sum_{(i,j)}$ is taken over the $n$-th neighboring pairs and the coefficients $\phi$ are equal for all the pairs in each type. We show the ratios of these coefficients $\phi$ in Fig. 2. The two bound magnons are almost confined to the same site or to the nearest neighbor sites for large $J_2$. However, for small $|J_2|$ the two magnons are more weakly bound, occupying farther sites, and the size of the pair diverges as $J_2 \rightarrow 0$. We note that, if we restrict the Hilbert space of magnon pairs to on-site pairs, the estimated saturation field reduces to that from the MF approximation. Thus the correction to the MF approximation originates from the fact that the bound magnon pairs are not totally confined on single sites.

The condensate of these magnon pairs is characterized by ferro-quadrupolar order $(S_i^+ S_j^+) = \sqrt{\rho} e^{i \rho \theta}$ on the single sites [see Fig. 1(b)] and also $(S_i^+ S_j^+) = -\sqrt{\rho} e^{i \rho \theta}$ on the nearest-neighbor bonds $(j,k)$. We note that the stability of the bi-magnon condensate depends on the correlation effects between magnon pairs, which remain to be studied.

Meanwhile in the MF approximation mentioned above, an octupolar state also has the same energy as a quadrupolar state for a finite $|J_2|$ at the saturation field. The octupolar ordering can be regarded as a condensation of three-magnon bound states [36]. To see how the degeneracy of the MF energies of quadrupolar and octupolar states is lifted, we also
study the three-magnon excitations. We calculated the energy of three-magnon bound states using a trial wave function. We prepared on-site type bases, bond type bases, and plane type bases, which respectively contain three magnons on the same sites, on the nearest neighbor two sites (bonds), and on the nearest neighbor three sites (planes). Diagonalizing the $32 \times 32$ matrix, we find that three-magnon bound states are also stable and have a lower energy than three independent magnons for large negative $J_2$. For small $|J_2|$, bound two-magnons are more stable than bound three-magnons, but for large $|J_2|$, bound three-magnons become the most stable and the saturation field is given by the instability line of bound three magnons [see Fig. 3(a)]. In this approximation the lowest bound three magnons have a flat mode, which is doubly degenerate for $J_2 < 0$, reflecting the existence of localized three-magnon bound states. If we include more Hilbert space for three magnons or fluctuations around the degenerate ground states, new quantum states for example an octupolar state might appear. This also remains to be a future problem.

Figure 3(a) shows the obtained whole phase diagram in a wider range of negative $J_2$, in the notation $J_1 = J \cos \theta$ and $J_2 = J \sin \theta$ with $J > 0$. We find that a small biquadratic interaction can arise magnon pairing in $S = 3/2$ pyrochlore antiferromagnets and it gives the possibilities for the appearance of the magnon-pairing BEC phase, i.e., a spin nematic phase.

Lastly, we study the spin size dependence in the phase diagram, changing the spins $S = 3/2$ to $S = 1$. As we have discussed earlier, multipolar phases have been found in $S = 1$ spin systems on various lattices. However, the $S = 1$ bilinear-biquadratic model [1] on the pyrochlore lattice has not been well investigated. Following our study for $S = 3/2$, we obtained the phase diagram for $S = 1$ in a similar manner, with the MF approximation and the magnon instability analysis. The obtained phase diagram is shown in Fig. 3(b). It clearly shows that the region of the nematic phase is much wider in the $S = 1$ system than in the $S = 3/2$ case. Moreover, the nematic phase is enlarged, also compared to the $S = 1$ triangular lattice bilinear-biquadratic model [17,38]. Therefore, if an $S = 1$ pyrochlore Heisenberg antiferromagnet can be synthesized, it would be a very good candidate for realization of the spin nematic phase, even better than the $S = 1$ triangular lattice or the $S = 3/2$ pyrochlore lattice.

To summarize, we investigated how quantum effects change magnetic phases in pyrochlore antiferromagnets in applied magnetic field. We find that a very small biquadratic interaction can induce magnon pairing near the saturation, in $S = 3/2$ pyrochlore antiferromagnets. These magnon pairs give rise to a spin nematic phase below the saturation field. This spin nematic phase does not involve any lattice distortion. The characteristics of this state are consistent with the results from ESR measurements [24] and magneto-optical absorption in the novel phase found experimentally in chromium spinel oxides near the saturation field [25,38]. We hence expect it is indeed a realization of the spin nematic phase.

It is our pleasure to acknowledge stimulating discussions with Atsuhiko Miyata, Karlo Penc, Nic Shannon, and Shojiro Takeyama. This work was supported by Grants-in-Aid for Scientific Research (Grants Nos. 25103706, 15H02113, and 23540397) from MEXT of Japan and by the RIKEN iTHES Project. A part of this work was performed at the Aspen Center for Physics, which is supported by US National Science Foundation grant PHY-1066293.

![FIG. 3. (Color online) Magnetic phase diagrams of the $S = 3/2$ (a) and $S = 1$ (b) pyrochlore antiferromagnets with the biquadratic interaction in a field $h$. The symbols and notations are the same as Fig. 1. The dotted dashed line denotes the approximate boundary due to a three-magnon instability, which induces an octupolar phase. The couplings are scaled as $J_1 = J \cos \theta$ and $J_2 = J \sin \theta$ with $J > 0$.](image-url)
[23] In fact, the ground state of the classical Hamiltonian [1] has a macroscopic degeneracy as in the original pyrochlore Heisenberg antiferromagnet [13, 14]. The macroscopic degeneracy would be lifted by a weak inter-tetrahedral interaction, such as the third-neighbor ferromagnetic exchange [39], resulting in a ground state which may match with that within the mean-field ansatz [18]. For simplicity, in this Letter, we implicitly assume the presence of such a weak interaction. We emphasize that, the spin nematic phase, which is our main focus in this Letter, is stable without such an interaction; our conclusion thus stands as long as the inter-tetrahedral interaction is sufficiently weak.

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