Finite temperature thermodynamic properties of the spin-1 nematics in an applied magnetic field

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We study numerically the thermodynamic properties of the spin nematic phases in a magnetic field in the spin-1 bilinear-biquadratic model. When the field is applied, the director representing the axis of the quadrupolar rotator starts to lie in the plane perpendicular to the field. At finite temperature and in a small field, the director cant off the plane, which allows the spins to fluctuate thermally in one direction and quantum mechanically in two other directions. These fluctuations stabilize the ferroquadrupolar moment and slightly push up the transition temperature. Larger field suppresses the spin fluctuation and drives the transition temperature down to zero. This field-dependent reentrant behavior is detected by the peak-shift in the specific heat and serves as a fingerprint of the ferroquadrupolar phase, which is not observed for the case of antiferroquadrupoles.

Introduction. Among symmetry broken phases in solids, those of higher order multipolar degrees of freedom are hard to study and have been often referred to as “hidden orders”. This is because their order parameters are not linearly coupled to external fields or forces, and thus are extremely difficult to characterize by the conventional experimental probes. Famous examples include heavy fermion materials like CeB$_6$ [1, 2], URu$_2$Si$_2$ [3, 4]. It turned out that the electronic quadrupolar orderings in CeB$_6$ is detected by the elasticity measurements [5], since the deformation of the electronic wave functions couples to the crystal lattice distortion. New techniques such as elasto-resistivity measurements have been recently developed to clarify the relationships between orbital nematic orders and superconductivity in iron pnictides [6].

In quantum magnets, the quadrupolar orderings of localized spins are often referred to as spin nematics. Unlike the true hidden orders whose order parameters are not yet established, the quadrupolar spin moments are already well-defined in theories [7]. Nevertheless, the spin nematics are still “hidden” in the sense that they are often invisible to local magnetic probes like neutron scattering or magnetic resonances and only show featureless paramagnetic-like responses to static magnetic field. In order to capture the higher-rank orderings, efforts on measuring the dynamical quantities have been made [8–23], particularly through the nuclear magnetic resonance [10, 14, 16, 21], the inelastic neutron scattering [17, 19], or the electron spin resonance [20, 22], while experiments and theories are practically difficult to reconcile.

Spin nematics can resort to Landau’s approaches on second order phase transitions, where some anomalies are found in the the magnetocaloric and in the ac magnetic susceptibility measurements [24, 26]. In theories, finite temperature phase diagrams at zero field are studied for the square lattice [27, 28] and the triangular lattice [29, 30] by the quantum Monte Carlo simulation, and for the triangular lattice by the variational method [31]. However, the basic information on how the quadrupolar moments respond to a magnetic field and they modify the finite temperature properties remain unexplored. In this paper, we examine this issue by applying the Monte Carlo simulations to the spin-1 bilinear-biquadratic (BLBQ) model, a canonical model for spin nematics. A pure quadrupole is represented by a director $\mathbf{d}$, a real vector pointing perpendicular to the fluctuating spin moments, which does not couple to a magnetic field. However, the imaginary component of $\mathbf{d}$ relevant to the emergent dipole moment couples to the field, which modifies the shape of the quadrupole and confines $\mathbf{d}$ within a plane perpendicular to the field [8]. We find that the thermal fluctuation will cant $\mathbf{d}$ off this plane, that works to stabilize the ferroquadrupolar phase and raises the transition temperature. In a stronger field, fluctuations are suppressed overall and the transition temperature goes down to zero. This small reentrant behavior of the phase boundary is observed in the FQ phase but not in the antiferroquadrupolar (AFQ) spin nematic phases, and is detected by the shift of the peak in the specific heat and in the susceptibility.

Spin-1 bilinear-biquadratic model. We deal with the spin-1 bilinear-biquadratic (BLBQ) model on the triangular lattice in a magnetic field:

$$\mathcal{H} = \sum_{(i,j)} \left[J \hat{S}_i \cdot \hat{S}_j + K \left(\hat{S}_i \cdot \mathbf{S}_j\right)^2\right] - \hbar \sum_{i=1}^{N} \hat{S}_i^z,$$  \hspace{1cm} (1)

where $\hat{S}_i$ is the spin-1 operator on site-$i$ with $i = 1–N$, and $J$, $K$, and $\hbar$ denote the Heisenberg (bilinear) and the biquadratic interactions, and the magnetic field applied parallel to the $z$-axis, respectively.

Semiclassical approaches using the variational method revealed that in the absence of a magnetic field, the ground state of Eq. 1 has a ferroquadrupolar order for $J > 0$ and $K/J \leq \tan^{-1}(\frac{-2}{\sqrt{2}})$, or $K < J \leq 0$ [8, 22], which agree qualitatively well with those from the fully quantum approaches. When a magnetic field is applied along the $z$-axis, the ferroquadrupolar state acquires a small but finite magnetic moment along the $z$-axis while retains its quadrupolar moment in the $xy$-plane, but finally turns into a fully polarized magnetic phase at
Monte Carlo method with semiclassical SU(3) approximation. We employ the semiclassical SU(3) approximation combined with classical Monte Carlo methods (sSU(3)-MC) \cite{31}. The wave functions are approximated by the direct product form of the one-body wave functions as

$$|\Psi\rangle = \bigotimes_{i=1}^{N} |\psi_i\rangle, \quad |\psi_i\rangle = \sum_{\alpha=x,y,z} d_{i,\alpha} |\alpha\rangle,$$

(2)

where $d_{i,\alpha}$ is the complex coefficient satisfying $|d_i| = 1$. The time-reversal invariant basis states $|\alpha\rangle$ are given as

$$|x\rangle = \frac{1}{\sqrt{2}} (|+1\rangle - |−1\rangle), \quad |y\rangle = \frac{1}{\sqrt{2}} (|+1\rangle + |−1\rangle), \quad |z\rangle = i |0\rangle,$$

(3)

where $|n\rangle$ $(n = 0, \pm 1)$ is the spin-1 state with $S^z = n$. The energy evaluated using this wave function is given as

$$E_{\text{sSU}(3)} = \langle \Psi | H | \Psi \rangle = \sum_{(i,j)} [J |d_i^* \cdot d_j|^2 + (B-J) |d_i \cdot d_j|^2]$$

$$+ i\hbar \sum_{i=1}^{N} (d_i^* \times d_i)^2 + \text{const.} \tag{4}$$

A set of order parameters $\{d_{i,\alpha}\}_{i=1,\ldots,N}$ are updated by the standard classical Monte Carlo sampling with the canonical ensemble of $\exp(-\beta E_{\text{sSU}(3)})$, where $\beta = (k_B T)^{-1}$ is the inverse temperature. Spin moment whose $z$-element appears in the Zeeman term of Eq. (4) is given explicitly as

$$S_i = \langle \psi_i | \hat{S}_z | \psi_i \rangle = -i \left( \begin{array}{ccc} d_{i,y} d_{i,z} - d_{i,z} d_{i,y} & d_{i,x} d_{i,z} & d_{i,x} d_{i,y} \\ d_{i,x} d_{i,z} & d_{i,y} d_{i,z} - d_{i,z} d_{i,y} & d_{i,x} d_{i,z} \\ d_{i,x} d_{i,y} & d_{i,x} d_{i,z} & d_{i,y} d_{i,z} - d_{i,z} d_{i,y} \end{array} \right).$$

(5)

Spin quadrupolar operator, $\hat{Q}_{i}^{\alpha\beta} = \hat{S}_i^\alpha \hat{S}_i^\beta + \hat{S}_i^\beta \hat{S}_i^\alpha - 2S(S+1)/3\delta_{\alpha\beta}$, is a rank-2 traceless symmetric tensor, and its vector representation for five linearly independent components, $Q_i = (Q_i^{x^2-y^2}, Q_i^{z^2-r^2}, Q_i^{xy}, Q_i^{yz}, Q_i^{zx})$, is generally applied, which are evaluated as

$$Q_i = \langle \psi_i | \hat{Q}_i | \psi_i \rangle = \left( \begin{array}{c} -\left(|d_{i,x}|^2 - |d_{i,y}|^2\right) \\ \frac{1}{\sqrt{3}} \left(2 |d_{i,z}|^2 - |d_{i,x}|^2 - |d_{i,y}|^2\right) \\ - (d_{i,x} d_{i,y} + d_{i,y} d_{i,x}) \\ - (d_{i,y} d_{i,z} + d_{i,z} d_{i,y}) \\ - (d_{i,z} d_{i,x} + d_{i,x} d_{i,z}) \end{array} \right).$$

(6)

Our simulation is performed on the lattice of $N = L \times L$, with $L = 12 - 36$ under the periodic boundary condition. We combine the conventional Metropolis method with single spin rotations and replica exchange method \cite{34}, taking averages over the independent initial configurations using the jackknife resampling, each run consisting of $10^8 - 10^9$ Monte Carlo steps for thermalization and measurements, respectively.

The method is theoretically equivalent to the approximation leaving only the leading terms in the cumulant expansion of the partition function \cite{31}. Since it works qualitatively well for the analysis of the ground states of spin-1 BLBQ model on a triangular lattice \cite{8,32}, one can also extend it to finite temperature with enough reliability. It should be mentioned that the sSU(3)-MC has distinct advantages over the simple classical approximation which treats the spin moments as vectors \cite{35}. In the sSU(3)-MC, the BQ interaction favors the quadrupolar orderings because the spins can fluctuate in-plane quantum mechanically, whereas the same interaction in classical method favors the collinear spin orderings which is unphysical \cite{31}.

Ferroquadrupolar phase. We first present the finite-temperature properties of the ferroquadrupolar state at $(J, K) = (0, -1)$ \cite{8}. Figure 1(a) shows the $T-h$ phase diagram where the boundary between the paramagnetic and ferroquadrupolar phases, $T_c$, decreases with $h$. Here, we determine $T_c$ as the peak position of the specific heat $C$; temperature dependence of $C/N$ in various magnetic fields are shown in Fig. 1(b). The peak position first slightly shifts to higher temperature and at $h \gtrsim 1$ starts to move rapidly toward lower temperature. We plot the results of $L = 12$ and 36 together in the same panel in order to show that the finite size effects are small enough, although $T_c$ is always slightly lower and the peak-height increases for larger $L$ for all values of $h$ we examined.

Figures 2(a) and (b) show the magnetic susceptibilities of the spin component perpendicular and parallel to the magnetic field, $\chi^\perp = (\chi^x + \chi^y)/2$, and $\chi^z$, respect-
tively, where $\chi^a = \beta N \left( \langle (S^a)^2 \rangle - \langle S^a \rangle^2 \right)$. One finds that $\chi^z$ starts to develop a small peak at $T_c$ when $h$ is applied, indicating that the finite magnetic moment is induced along the $z$-axis. The value of $\chi^z$ remains almost featureless, but a small structure appears at the same position as $\chi^z$ for larger $L$. The magnetization $\langle S^z \rangle$ does not depend much on $T$ and its value in the FQ phase is in good agreement with the ground state ones, $m = h/|6(J-K)| = h/6$ (see inset of Fig. 2(b)).

We next examine the field-dependence of the quadrupolar moments. In the ground state, the magnetic field confines the $d$-vector within the $xy$-plane, namely, $|\Psi\rangle = \bigotimes_{i=1}^N |d_i\rangle$ with $|d_i\rangle = d_x |x\rangle + d_y |y\rangle$. This is because $h$ couples to $d_x^2d_y^2 - d_y^2d_x$ but not with $d_z$ (see Eq. (1)). When $d$ is real, a pure quadrupole is formed $O(2)$-symmetric about the director $d$, as shown in the first column of Fig. 3(a). At $h \neq 0$ the emergent imaginary component of $d$ will distort it by shifting its fluctuation center toward the $+z$-direction (see the second and third columns of Fig. 3(a)).

The relationship between $d$ and the shape of the quadrupole is understood more clearly from Eq. (10) as follows; when $d_z$ is zero so do $\langle Q^{yz} \rangle$ and $\langle Q^{zx} \rangle$, while $\langle Q^{x^2-y^2} \rangle$ and $\langle Q^{xy} \rangle$ which consist only of $x$ and $y$ elements of $d$ can respond to $h$. Based on this consideration, we define two kinds of squared quadrupolar moments,

$$Q^2_{\text{in}} = \frac{1}{2} \left( \langle Q^{x^2-y^2} \rangle^2 + \langle Q^{xy} \rangle^2 \right),$$

$$Q^2_{\text{out}} = \frac{1}{2} \left( \langle Q^{y^2-x^2} \rangle^2 + \langle Q^{xy} \rangle^2 \right),$$

where we straightforwardly find $Q^2_{\text{in}} \neq 0$ and $Q^2_{\text{out}} = 0$ at $T = 0$.

Temperature dependences of $Q^2_{\text{in}}$ and $Q^2_{\text{out}}$ are shown in Figs. 3(b) and 3(c). In a weak field, $Q^2_{\text{in}}$ increases first and then at around $h \gtrsim 1$ starts to decrease with $h$. Whereas, $Q^2_{\text{out}}$ takes a small but finite value at small $h$ and $T \neq 0$ because of the thermal fluctuation, and becomes $Q^2_{\text{out}} = 0$ at $T = 0$. Notice that the apparently large values of $Q^2_{\text{out}}$ at $h = 0$ simply because the moments are decoupled to the spatial coordinate. Once the field increases to $h \gtrsim 1$, $Q^2_{\text{out}}$ is suppressed to zero for all temperatures, which is the tendency similar to what we saw in $Q^2_{\text{in}}$. These results indicate that there is a crossover at $h \sim 1$ from the thermal fluctuation dominant low-field regime to the high field regime where both the quantum and thermal fluctuations are gradually suppressed. It apparently links with the reentrant behavior of $T_c$ at $h \lesssim 1$.

Such particular field-dependence of the quadrupolar moment is visualized in Fig. 3(d). Compared to the ones at $T = 0$, the quadrupoles at $h = 1$ and $T = 0.2$ has a gourd-shape which indicates that $d$ cant slightly off the $xy$-plane. Here, the MC simulation keeps the $O(2)$ symmetry so that the directors are not pointing in the particular $xy$-directions, and the quadrupoles are the their averages. Strictly speaking, the true thermody-
namic transitions breaking such O(2) symmetry are not present in the pure two-dimensional system because of the Mermin-Wagner theorem \[36\]. However, a one-body approximation in Eq. \[4\] practically allows it, and provides a divergent specific heat at $T_c$, which shall give an realistic interpretation when considering the inter-layer couplings in actual materials.

**Antiferroquadrupolar phase.** Finally, we briefly discuss the finite temperature properties and its field dependence for the AFQ phase. In the ground state of the triangular lattice, the AFQ is realized at $0 < J < K$ \[8\]. The quadrupolar moments form a three-sublattice structure \[\mathbf{d}_{\alpha}\] defined, and two of three components, \(\mathbf{d}_{\alpha} = |x\rangle\) and \(\mathbf{d}_{\alpha} = |y\rangle\), behave similarly to the $d$-vector of the FQ phase in a magnetic field, i.e., $d_x$ and $d_y$ become complex numbers, while $\mathbf{d}_{\alpha} = |z\rangle$ remains unchanged \[8\]. In the field range of $h = 3/\sqrt{5} \approx 1.34$ to $3(1 - 1/\sqrt{5}) \approx 1.658$, a $2/3$ plateau phase appears, where the $\mathbf{d}_{\alpha} = |z\rangle$ remains and the spins on A and B sublattices are fully polarized. We here focus on the phase below this plateau where the quadrupoles on the A and B-sublattices gradually develops a magnetic moment similarly to that of the aforementioned FQ phase at $T = 0$.

We fix the parameter values to $K/J = 2$, where $J, K > 0$ are normalized as $J^2 + K^2 = 1$ \[37\]. Figure 4(a) shows the $T$–$h$ phase diagram; $T_c$ decreases with increasing $h$, which can be detected clearly by the temperature dependence of the specific heat in Fig. 4(b) for the different values of $h$ in $L = 12$ and 36 samples. Figures 4(c) and (d) are the temperature dependences of $\chi^x$ and $\chi^z$ for the different values of $h$, respectively. As in the case for the FQ phase, the $xy$-components remain almost featureless, and the $z$-component starts to develop a moderate peak structure.

Although the quadrupoles on the A- and B-sublattices behave similar to that of the FQ phase, the difference lies in that they do not acquire a finite $d_z$ and continue pointing within the $xy$-plane. In fact, the slight increase in $T_c$ at small $h$ is not observed in the case of AFQ. This is because the correlation between the quadrupoles of different sublattices do not allow the directors to cant off the original angle, which rather works as a suppression of the thermal fluctuation effect.

**Conclusion.** We disclosed the way how the quadrupolar order parameters of the spin nematics are deformed at finite temperature in a magnetic field. The semiclassical SU(3) Monte Carlo simulation that takes account of the quantum fluctuation indispensable for the description of such higher order nonmagnetic phases, turned out to describe precisely the finely field-controlled temperature-dependent behavior of the quadrupolar ordering. The reentrant behavior of the FQ phase boundary in a low field reflects the interplay of thermal and quantum fluctuation which can be detected by the specific heat and susceptibility measurements.

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