Possible ferro-spin nematic order in $NiGa_2S_4$

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We explore the possibility that the spin-1 triangular lattice magnet $NiGa_2S_4$ may have a ferronematic ground state with no frozen magnetic moment but a uniform quadrupole moment. Such a state may be stabilized by biquadratic spin interactions. We describe the physical properties of this state and suggest experiments to help verify this proposal. We also contrast this state with a "noncollinear" nematic state proposed earlier by Tsunetsugu and Arikawa [J. Phys. Soc. Jpn. **75**, 083701 (2006)] for $NiGa_2S_4$.

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Spins on a lattice often develop some periodic order at low temperatures. It has been appreciated for some time that such ordering may be killed even at zero temperature by quantum fluctuations. This is particularly true of spin systems in low dimension and/or the presence of geometric frustration of the magnetic interactions. Indeed one of the earliest suggestions of a "resonating valance bond" spin liquid state was for the nearest-neighbor antiferromagnetic Heisenberg model on the triangular lattice.[1] Although the ground state of this system is now believed to be the "120° ordered" state (see Capriotti *et al.*[2] and references therein), the experimental search for low spin quantum magnets on a frustrated perfect triangular lattice has continued.

Recently, Nakatsuji *et al.*[3] reported an experimental realization of an insulating spin-1 quantum magnet on a perfect triangular lattice in the chalcogenide $NiGa_2S_4$. This is a layered material with alternating Ni-S and Ga-S planes. Each Ni^{2+} ion is in a (distorted) octahedral environment of six S^{2-} ions, and the Ni layer has Ni^{2+} ions arranged in a perfect triangular lattice. The system is an insulator; the only important electronic degree of freedom being the spin ($S=1$) on the Ni^{2+} ion which has an electronic configuration of $t_{2g}^6 e_g^2$ (due to the crystal field splitting brought about by the octahedral environment of the S^{2-} ions and the Hund coupling in the e_g sector). The compound shows unusual magnetic properties. The high temperature susceptibility is Curie-Weiss-like (with a Weiss temperature of −80 K), consistent with an $S=1$ moment on the Ni^{2+} ions. However, at around the Weiss temperature, the susceptibility begins to deviate smoothly from the Curie-Weiss law with decreasing temperature and reaches a finite value at $T=0$ indicating the absence of a spin gap. The magnetic specific heat shows two humps, one at around 10 K, and another broad hump at about 80 K (the Weiss temperature). However, there is no sign of any singular or discontinuous behavior suggesting a phase transition. The magnetic entropy per spin shows a plateau between 15 and 50 K at about a third of the high temperature entropy suggesting large degeneracy of low lying excitations above the ground state. The specific heat, up to 10 K, shows a T^2 power law suggesting the presence of linear dispersing gapless modes in the Ni planes. Moreover, this behavior of the specific heat was found to be robust to a nonmagnetic Zn substitution in the compound.[4] Intriguingly, despite this, no periodic spin order is detected in powder neutron scattering, and a broad (possibly incommensurate) peak is seen with a wavelength that is roughly twice that of the well-known 120° spin order on the antiferromagnetic triangular lattice. Furthermore, there is no indication of any lattice distortion associated with possible development of spin-Peierls order on cooling to low temperature.

Motivated by these experiments, Tsunetsugu and Arikawa[5] have recently proposed a spin nematic ground state for $NiGa_2S_4$. In such a state there is no average magnetic moment ($\langle \boldsymbol{S} \rangle = \mathbf{0}$) but there is a nonzero quadrupole moment characterized by a nonzero average of

$$\mathcal{Q}_i^{\alpha\beta} = \frac{1}{2}(S_i^\alpha S_i^\beta + S_i^\beta S_i^\alpha) - \frac{2}{3}\delta^{\alpha\beta}, \tag{1}$$

where S_i^α is the α-spin component operator at site i, and $\delta^{\alpha\beta}$ is the Kroneker delta symbol. In the state proposed in Ref. 5 the quadrupole order parameter has a three sublattice structure. Precisely, if one writes

$$\langle \mathcal{Q}_{\alpha\beta} \rangle = q\left(n^\alpha n^\beta - \frac{1}{3}\delta^{\alpha\beta}\right) \tag{2}$$

then the "director" $\boldsymbol{n}$ points along three orthogonal directions in the three sublattices of the triangular lattice.

In this Brief Report we propose an alternate spin nematic state as a possible ground state of $NiGa_2S_4$. The particular state we propose may be dubbed a "ferronematic" in the sense that the average quadrupole moment is spatially uniform in the ground state. The director vector $\boldsymbol{n}$ is independent of site i. This is thus distinct from the Tsunetsugu-Arikawa (TA) state[5] which may be dubbed a noncollinear nematic. We discuss a number of different properties of the ferronematic state that makes it attractive as an explanation of the properties of $NiGa_2S_4$. We also point out differences with the TA state that may be used to distinguish them in experiments.

Microscopically the simplest nearest-neighbor antiferromagnetic Hamiltonian for a spin-1 triangular magnet is expected to have a 120° spin order which is not seen in $NiGa_2S_4$. Thus the Hamiltonian must apparently involve other terms that destabilize the magnetic order. This is further supported by the observation that *bulk* NiS_2 is close to a

Mott transition and hence may have significant charge fluctuations even when insulating. In $NiGa_2S_4$ the magnetic layers consist of NiS_2 sheets—an effective spin-only description of these may then plausibly have sizable interactions beyond the simplest near neighbor antiferromagnetic exchange.

Motivated by these considerations we will discuss the possibility of spin nematic order in the framework of the model Hamiltonian

$$H = H_0 + H_a, \tag{3}$$

$$H_0 = J\sum_{\langle i,j\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - K\sum_{\langle i,j\rangle} (\boldsymbol{S}_i \cdot \boldsymbol{S}_j)^2. \tag{4}$$

Here H_0 is the part of the Hamiltonian that is isotropic in spin space. H_a refers to small anisotropy terms which may be important in pinning any possible long range order. $\boldsymbol{S}_i$ is the spin-1 operator at the site i of a two-dimensional triangular lattice, and $J, K \geqslant 0$. Biquadratic interactions of some strength K will in general be present in spin-1 magnets and are known to favor nematic ordering.[6–10] In the present case where the bilinear exchange J is frustrated the effects of the biquadratic exchange are somewhat enhanced. We study the ground state of such a Hamiltonian in the mean field approximation and construct a zero temperature phase diagram. We find that at values larger than a critical value of the bi-quadratic exchange $K/J \sim 1.15$, there is a first order transition from a magnetic (120° order) state to a ferronematic ordered state. It is the latter that we propose to be a ground state of the $NiGa_2S_4$. We then study the expected properties of the ferronematic by including fluctuations beyond the mean field.

TA also invoked biquadratic interactions to stabilize their noncollinear nematic state. However, they chose $K<0$. Microscopically a biquadratic term may arise from a few different sources. First in an underlying two-band Hubbard type description of the e_g orbitals, the spin Hamiltonian arises and describes the gain of kinetic energy due to virtual fluctuations in a Mott insulating state. In this large-U perturbation theory the leading term is just the usual antiferromagnetic exchange. At higher orders a variety of terms will be induced which include the biquadratic exchange. The higher order exchanges are readily calculated by considering two sites and two orbitals at each site. The low energy sector of the four-electron Hilbert space for the two-site problem consists of one electron in each of the e_g orbitals at each site. The spins of the electrons in the two orbitals at a given site are aligned parallel due to the large Hund coupling J_H. The cost of double occupation of an orbital is U. Assuming that the energy scale for hopping between orbitals at different sites is t, we find via a perturbative calculation that

$$J = \frac{4t^2}{(U+2J_H)} - \frac{4t^4}{2(U+J_H)(U+2J_H)^2},$$

$$K = \frac{4t^4}{2(U+J_H)(U+2J_H)^2}, \tag{5}$$

with an effective Hamiltonian of the type (4) in the low energy sector. Note that $K>0$.

Biquadratic interactions may also be induced due to spin-phonon coupling. Indeed if an optical phonon couples to the spin bilinear in a bond, its effects can be approximately accounted for by integrating it out in favor of a biquadratic term. Again this leads to a positive K, and adds to the K already provided by the kinetic energy gain. We note that positive K tends to favor the ferronematic state.

We now proceed to obtain an approximate ground state of the isotropic part of the Hamiltonian H_0 adopting a mean field approach. Using the definition (1), the Hamiltonian H_0 can be rewritten as

$$H_0 = \left(J + \frac{K}{2}\right)\sum_{\langle ij\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - K\sum_{\langle ij\rangle} \mathcal{Q}_i^{\alpha\beta}\mathcal{Q}_j^{\alpha\beta}, \tag{6}$$

ignoring constant terms. The K term is thereby seen to favor ferronematic order. For small K we expect that the stable ground state will have spiral magnetic order which may give way to the ferronematic state as K is increased. We therefore calculate the mean field energies of spiral magnetic and ferronematic states to obtain the mean field phase diagram.

We introduce the expectation values of the spin and nematic operators respectively, as $\langle \boldsymbol{S}_i\rangle$ and $\langle \mathcal{Q}_i^{\alpha\beta}\rangle$ at each site and obtain the local Hamiltonian at site i as

$$H_{MF}^i = (J + K/2)\sum_{\delta}\left(\boldsymbol{S}_i \cdot \langle \boldsymbol{S}_{i+\delta}\rangle - \frac{1}{2}\langle \boldsymbol{S}_i\rangle \cdot \langle \boldsymbol{S}_{i+\delta}\rangle\right)$$
$$- K\sum_{\delta}\left(\mathcal{Q}_i^{\alpha\beta}\langle \mathcal{Q}_{i+\delta}^{\alpha\beta}\rangle - \frac{1}{2}\langle \mathcal{Q}_i^{\alpha\beta}\rangle\langle \mathcal{Q}_{i+\delta}^{\alpha\beta}\rangle\right), \tag{7}$$

where δ runs over all the neighbors of the site i.

For the ferronematic state the mean spin at any site is zero, and the $\langle \mathcal{Q}^{\alpha\beta}\rangle_i$ has the form

$$\langle \mathcal{Q}^{\alpha\beta}\rangle_i = q\left(n^\alpha n^\beta - \frac{1}{3}\delta^{\alpha\beta}\right), \tag{8}$$

with $\boldsymbol{n}$ independent of the site index i. The mean field value of q is readily calculated to be -1 corresponding to an energy per spin -2 K. This energy must be compared with that of the spiral state.

For the spiral state the mean spin at the site i is taken to be of the form

$$\langle \boldsymbol{S}_i\rangle = m\boldsymbol{s}_i \tag{9}$$

with $\boldsymbol{s}_i$ a unit vector defined at the site i with position vector $\boldsymbol{r}_i$ as

$$\boldsymbol{s}_i = \cos(\boldsymbol{q}\cdot\boldsymbol{r}_i)\boldsymbol{e}_x + \sin(\boldsymbol{q}\cdot\boldsymbol{r}_i)\boldsymbol{e}_y \tag{10}$$

where m and $\boldsymbol{q}$ are, as yet undetermined, magnitude and wave vector, respectively, and $\boldsymbol{e}$'s are two orthogonal basis vectors in the plane of spiral ordering. The spin ordering will induce a nonzero $\langle \mathcal{Q}_i^{\alpha\beta}\rangle$ of the form

$$\langle \mathcal{Q}_i^{\alpha\beta}\rangle = Q\left(s_i^\alpha s_i^\beta - \frac{1}{3}\delta^{\alpha\beta}\right) \tag{11}$$

with Q satisfying $\frac{3}{2}m - 1 \leqslant Q \leqslant 1$. The four variational parameters m, q_x, q_y, Q are determined by minimizing the ground state energy of the mean field Hamiltonian (7).

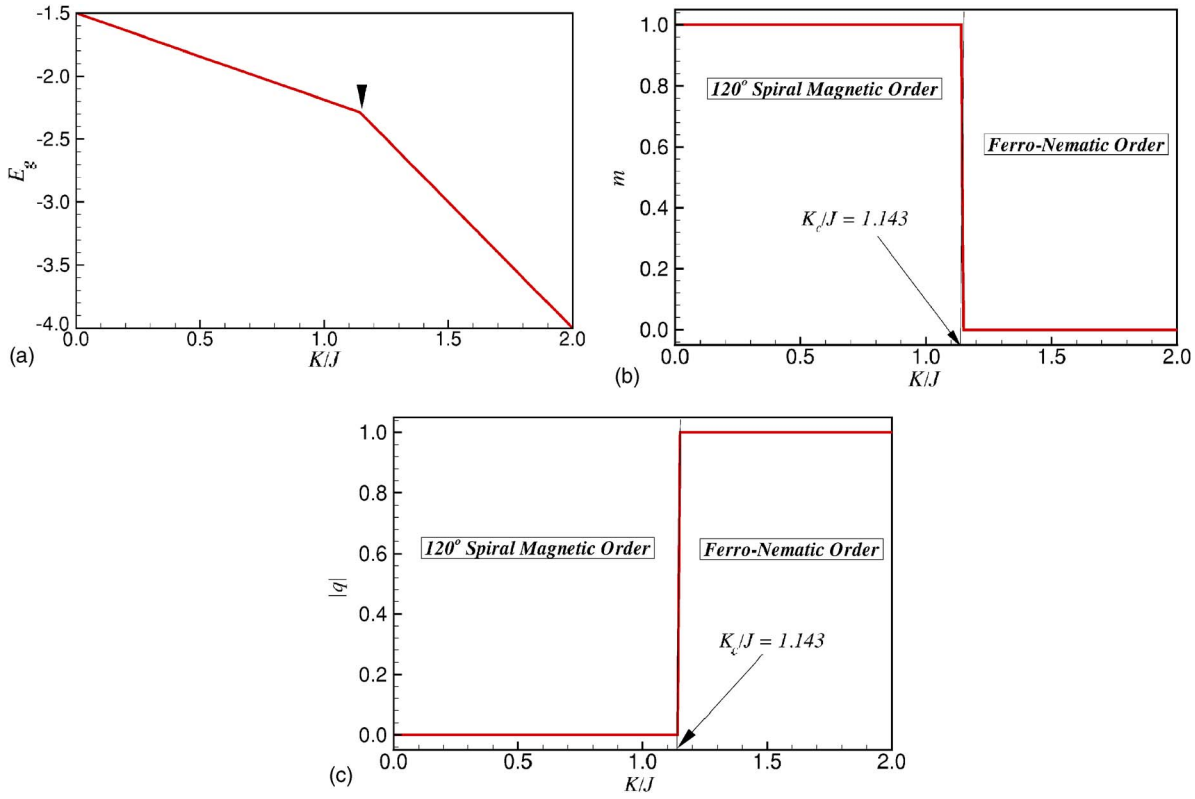

FIG. 1. (Color online) (a) Variation of the mean field ground state energy E_g per site with K/J. Note the "level crossing" at $(K/J)_c = 1.143$. (b) The variation of m with K/J. A first order phase transition occurs at $(K/J)_c = 1.143$ at which m vanishes. (c) The variation of q with K/J. There is a jump in q at $(K/J) = 0^+$, and another at the critical value of $(K/J)_c = 1.143$.

Figure 1(a) shows the variation of the ground state energy as a function of K/J. The standard spiral state with 120° three sublattice order is obtained as the ground state for $(K/J)_c \leqslant \frac{8}{7} \approx 1.143$. Beyond this value the ferronematic state is found to have lower energy. A study of the spin order parameter m [Fig. 1(b)] shows that it jumps at the transition point indicating a first order transition.

The structure of the fluctuations beyond the mean field in the spiral state are well-known and consist of three gapless spin wave modes. The ferronematic state also breaks global spin SU (2) symmetry despite the absence of a frozen magnetic moment. Indeed the director $\boldsymbol{n}$ picks out a single direction in spin space. Thus this state will have gapless Goldstone modes corresponding to slow transverse fluctuations of the director. A straightforward calculation shows the existence of two such gapless modes (coresponding to the two independent transverse directions in which the director can tilt) centered at wave vector $\boldsymbol{k} = \boldsymbol{0}$. At low energies the dispersion is linear $\omega = c|\boldsymbol{k}|$ with velocity

$$c = \frac{1}{\hbar}\sqrt{6K\left(J + \frac{K}{2}\right)}. \tag{12}$$

We now consider various physical properties of the ferronematic state with an eye toward interpreting experiments in $NiGa_2S_4$. In thinking about experiments it is important to allow for the possibility of small spin anisotropies that pin the nematic order parameter. The most important of these is single ion anisotropy that selects out a particular direction in spin space. Specifically consider

$$H_a = D\sum_i (S_i^z)^2 \tag{13}$$

with $D > 0$. The natural choice is to have the hard axis point perpendicular to the Ni-S layers. Note that this anisotropy couples directly to the ferronematic order parameter. Thus a nonzero D even if small will generally pin the director to a point perpendicular to the layers. Then in the ferronematic state even though there is no magnetic order the spins will predominantly fluctuate parallel to the layers at low temperature.

In the presence of a nonzero D the linear dispersion of the small $|\boldsymbol{k}|$ director fluctuation modes will be cut off—instead a gap of order D will develop as $\boldsymbol{k} \to 0$. For the specific heat this implies that

$$C \sim T^2 \tag{14}$$

so long as $T > T_D \sim D$. In $NiGa_2S_4$, this behavior is precisely seen in the range $0.35\ \mathrm{K} < T < 10\ \mathrm{K}$. Thus the ferronematic state can explain the low temperature specific heat provided D is smaller than about 0.35 K.

Let us now consider the magnetic susceptibility. In a single domain sample assuming that the director is fixed the pure ferronematic state has strongly anisotropic magnetic susceptibility. The system is spin-gapped for magnetic fields aligned precisely along the nematic director, but has finite

susceptibility for fields applied perpendicular to the director. A straightforward calculation shows that the susceptibility tensor (per site) is

$$\chi^{\alpha\beta} = \frac{g^2\mu_B^2}{3K}(\delta^{\alpha\beta} - n^\alpha n^\beta), \tag{15}$$

where n^α is the direction of the nematic director (now ferroaligned at all sites), g is the gyromagnetic ratio, and μ_B is the Bohr magneton. If the director is not fixed, however, and is free to rotate it would prefer to orient itself in a direction perpendicular to the external field, and the susceptibility would be a constant. In the real system the detailed behavior therefore depends sensitively on the competition between the pinning due to the spin anisotropy D and the reorientation energy in a field. At very low fields the pinning will win and the susceptibility will be anisotropic. At higher fields the pinning will be overcome and the susceptibility will be a constant independent of the field orientation. As the pinning energy per site is $\sim D$ while the reorientation energy is $\sim B^2$ the crossover occurs at a field strength $B_D \sim \sqrt{D/\chi} \sim \sqrt{KD}$. Therefore the energy scale associated with the depinning field B_D is much larger than D since $K \gg D$ (K is expected to be of the order of 100 K and $D < 0.35$ K), and thus B_D is expected to be a measurably large field.

In a single crystal sample, the susceptibility at a measuring field $B \ll B_D$ will therefore be strongly anisotropic while at higher fields a constant susceptibility independent of field orientation will be obtained. In polycrystalline samples (where the existing experiments have been done), due to the existence of domains with differing orientations of the pinning axis, the susceptibility will be independent of field orientation even at low fields ($< B_D$). However, as the field increases beyond B_D domains with pinning direction parallel to the field will reorient their directors thereby increasing the net magnetization. We therefore expect significant increase in the magnetization on field strengths on the scale of B_D.

The constant low-T susceptibility and the T^2 specific heat of the ferronematic are consistent with the experiments. However, these properties are also shared by the TA state. What experiments may distinguish the two states? A useful and direct signature is the polarization of the spin fluctuation spectrum. In the ferronematic state (with director perpendicular to the Ni-S planes) the spins should primarily fluctuate in the directions along the planes at low temperature. In the TA state, on the other hand, there should be no such strong preference for the spins to lie along the planes. Thus spin polarized neutron scattering experiments on single crystals may be able to determine which (if either) of these two spin nematic states is realized in $NiGa_2S_4$. Another useful experiment that could distinguish the ferronematic state from the TA state is the direction dependent susceptibility measurement in single crystals. As noted above a vanishing susceptibility is expected for a field smaller than B_D along the pinning direction in the ferronematic state, with a significant increase in the susceptibility when the field exceeds B_D. A field in a direction perpendicular to the pinning direction would obtain a constant susceptibility independent of the field strength over field scales of order B_D and above. On the other hand, in the TA state the anisotropy in the susceptibility is expected to be much smaller for small fields, and the susceptibility is expected to remain constant with increasing field.

In this Brief Report we have proposed that $NiGa_2S_4$ may have a ferronematic ground state characterized by a uniform quadrupole moment. We discussed some of the experimental properties of this state and suggested experiments to distinguish it from the alternate proposal of Tsunetsugu and Arikawa.[5] In a simple model for a spin-1 triangular magnet with bilinear and biquadratic terms, the latter promotes nematic order. We suggest that the naturally expected sign for the biquadratic term prefers ferronematic order and not the noncollinear nematic. We note that while many properties of either spin nematic state (specific heat, susceptibility) resemble that seen in experiments neither proposal directly addresses the short ranged incommensurate spin fluctuations inferred from powder neutron data. This feature of the spin fluctuation spectrum presumably depends on the details of the microscopic spin Hamiltonian which are not known at present.

Just prior to submission of this Brief Report Ref. 11 appeared which also studies the ferronematic state in the J-K spin-1 triangular magnet, and suggests this as a possible ground state in $NiGa_2S_4$.

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