Possible ferro-spin nematic order in NiGa$_2$S$_4$

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We explore the possibility that the spin-1 triangular lattice magnet NiGa$_2$S$_4$ may have a ferro-nematic 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 'non-collinear' nematic state proposed earlier by Tsunetsugu and Arikawa for NiGa$_2$S$_4$.

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I. INTRODUCTION

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 suggestion of a “resonating valence bond” spin liquid state was for the nearest neighbor antiferromagnetic Heisenberg on the triangular lattice. Although, the ground state of this system is now believed to be the “120° ordered” state (see Capriotti et al. and references therein), the experimental search for low spin quantum magnets on a frustrated perfect triangular lattice has continued.

Recently, Nakatsuji et al. reported an experimental realization of an insulating spin-1 quantum magnet on a perfect triangular lattice in the chalcogenide NiGa$_2$S$_4$. 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 on the Ni$^{2+}$ ions. How-ever at around the Weiss temperature, the susceptibility begins to drop smoothly, 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 Kelvin, and another broad hump at about 80 Kelvin (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 to 50 Kelvin 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 non-magnetic Zn substitution in the compound. Intriguingly despite this no periodic spin order is detected in powder neutron scattering, and a broad (possibly in-commensurate) 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 have recently proposed a spin nematic ground state for NiGa$_2$S$_4$. In such a state there is no average magnetic moment $\langle S \rangle = 0$ but there is a non-zero quadrupole moment characterized by a non-zero average of

$$Q_{\alpha \beta}^\circ = \frac{1}{2}(S_i^\alpha S_i^\beta + S_i^\beta S_i^\alpha) - \frac{2}{3}\delta_{\alpha \beta}$$

where $S_i^\alpha$ is the $\alpha$-spin component operator at site $i$, $\delta_{\alpha \beta}$ is the Kronecker delta symbol. In the state proposed in Ref. $^1$, the quadrupole order parameter has a three sublattice structure. Precisely if one writes

$$\langle Q_{\alpha \beta} \rangle = q \left( n^\alpha n^\beta - \frac{1}{3}\delta_{\alpha \beta} \right)$$

then the “director” $\mathbf{n}$ points along three orthogonal directions in the three sublattices of the triangular lattice.

In this paper we propose an alternate spin nematic state as a possible ground state of NiGa$_2$S$_4$. The particular state we propose may be dubbed a ‘ferro-nematic’ in the sense that the average quadrupole moment is spatially uniform in the ground state. The director vector $\mathbf{n}$ is independent of site $i$. This is thus distinct from the...
Tsunetsugu-Arikawa (TA) state, which may be dubbed a non-collinear nematic. We discuss a number of different properties of the ferro-nematic state that makes it attractive as an explanation of the properties of NiGa₂S₄. 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 NiGa₂S₄. Thus the Hamiltonian must apparently involve other terms that destabilize the magnetic order. This is further supported by the observation that bulk NiS₂ is close to a Mott transition and hence may have significant charge fluctuations even when insulating. In NiGa₂S₄ the magnetic layers consist of NiS₂ 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

\[ H = H_0 + H_a \]

\[ H_0 = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - K \sum_{\langle i,j \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \]

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. \( S_i \) is the spin-1 operator at the site \( i \) of a two dimensional triangular lattice, and \( J, K \geq 0 \). Biquadratic interactions of some strength \( K \) will in general be present in spin-1 magnets and are known to favor nematic ordering. 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 that the biquadratic exchange \( K/J \sim 1.15 \), there is a first order transition from a magnetic(120° order) state to a ferro-nematic ordered state. It is the latter that we propose to be ground state of the NiGa₂S₄. We then study the expected properties of the ferro-nematic by including fluctuations beyond the mean field.

\[ H_{MF}^i = (J + K/2) \sum_{\delta} (\mathbf{S}_i \cdot \langle \mathbf{S}_{i+\delta} \rangle - \frac{1}{2} \langle \mathbf{S}_i \rangle \cdot \langle \mathbf{S}_{i+\delta} \rangle) - K \sum_{\delta} \langle \mathbf{Q}_{i}^{\alpha \beta} \rangle \langle \mathbf{Q}_{i+\delta}^{\alpha \beta} \rangle - \frac{1}{2} \langle \mathbf{Q}_{i}^{\alpha \beta} \rangle \langle \mathbf{Q}_{i+\delta}^{\alpha \beta} \rangle \]

where \( \delta \) runs over all the neighbors of the site \( i \).

For the ferro-nematic state the mean spin at any site is zero, and the \( \langle \mathbf{Q}_{i}^{\alpha \beta} \rangle \) has the form

\[ \langle \mathbf{Q}_{i}^{\alpha \beta} \rangle = q \left( n_{i}^{\alpha} n_{i}^{\beta} - \frac{1}{3} \delta^{\alpha \beta} \right) \]
with \( n \) independent of the site index \( i \). The mean field value of \( q \) is readily calculated to be \(-1\) corresponding to an energy per spin \(-2K\). 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

\[
\langle S_i \rangle = ms_i
\]  

with \( s_i \) a unit vector defined at the site \( i \) with position vector \( r_i \) as

\[
s_i = \cos (q \cdot r_i) e_x + \sin (q \cdot r_i) e_y
\]  

where \( m \) and \( q \) are, as yet undetermined, magnitude and wave vector respectively, and \( e_s \) are two orthogonal basis vectors in the plane of spiral ordering.

The spin ordering will induce a non-zero \( \langle Q^{\alpha \beta}_i \rangle \) of the form

\[
\langle Q^{\alpha \beta}_i \rangle = Q \left( s_\alpha^{s_i} s_\beta^{s_i} - \frac{1}{3} \delta^{\alpha \beta} \right)
\]  

with \( Q \) satisfying \( \frac{3}{2} m - 1 \leq Q \leq 1 \). The four variational parameters \( m, q_x, q_y, Q \) are determined by minimizing the ground state energy of the mean field Hamiltonian (6).

Fig. 1(a) shows the variation of the ground state energy as a function of \( K/J \). The standard spiral state with \( 120^\circ \) three sublattice order is obtained as the ground state for \((K/J)_c \leq 1.143\). Beyond this value the ferro-nematic 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 ferro-nematic state also breaks global spin \( SU(2) \) symmetry despite the absence of a frozen magnetic moment. Indeed the director \( n \) 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 (corresponding to the two independent transverse directions in which the director can tilt) centered at wavevector \( k = 0 \). At low energies the dispersion is linear \( \omega = c|k| \) with velocity

\[
c = \frac{1}{\hbar} \sqrt{\frac{12K(J + K/2)}{}}
\]  

III. PHYSICAL PROPERTIES OF THE FERRO-NEMATIC STATE

We now consider various physical properties of the ferro-nematic 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

$$H_n = D \sum_i (S_i^z)^2$$  \hspace{1cm} (12)

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 ferro-nematic order parameter. Thus a non-zero $D$ even if small will generally pin the director to point perpendicular to the layers. Then in the ferro-nematic 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 non-zero $D$ the linear dispersion of the small $|k|$ director fluctuation modes will be cut-off - instead a gap of order $D$ will develop as $k \to 0$. For the specific heat this implies that

$$C \sim T^2$$  \hspace{1cm} (13)

so long as $T > T_D \sim D$. In NiGa$_2$S$_4$, precisely this behavior is seen in the range $0.35 \, K < T < 10 \, K$. Thus the ferro-nematic 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 ferro-nematic 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

$$\chi^{\alpha\beta} = \frac{g^2 \mu_B^2}{3K} (\delta^{\alpha\beta} - n^\alpha n^\beta)$$  \hspace{1cm} (14)

where $n^\alpha$ is the direction of the nematic director (now ferro-aligned at all sites), $g$ is the gyromagnetic ratio, and $\mu_B$ 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 $\sim D$ while the reorientation energy $\sim B^2$ the crossover occurs at a field strength $B_D \sim \sqrt{\frac{D}{\chi}} \sim \sqrt{KD}$.

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 $B_D$ 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 pining 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 ferro-nematic 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 ferro-nematic 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$_2$S$_4$. Another useful experiment that could distinguish the ferro-nematic 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 ferro-nematic state, with a significant increase in the susceptibility when the field exceeds $B_D$. 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.

IV. CONCLUSION

In this paper we have proposed that NiGa$_2$S$_4$ may have a ferro-nematic 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[1]. 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 ferro-nematic order and not the non-collinear 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 paper cond-mat/0605234 appeared which also studies the ferro-nematic state in the J-K spin-1 triangular magnet, and suggests this as a possible ground state in NiGa$_2$S$_4$.

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