Chiral spin-order in some purported Kitaev spin-liquid compounds

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Abstract

We examine recent magnetic torque measurements in two compounds, γ-Li$_2$IrO$_3$ and RuCl$_3$, which have been discussed as possible realizations of the Kitaev model. The analysis of the reported discontinuity in torque, as an external magnetic field is rotated across the c-axis in both crystals, suggests that they have a translationally-invariant chiral spin-order of the from $\langle S_i (S_j \times S_k) \rangle \neq 0$ in the ground state and persisting over a very wide range of magnetic field and temperature. An extra-ordinary $|B|B^2$ dependence of the torque for small fields, beside the usual $B^2$ part, is predicted due to the chiral spin-order, and found to be consistent with experiments upon further analysis of the data. Other experiments such as inelastic scattering and thermal Hall effect and several questions raised by the discovery of chiral spin-order, including its topological consequences are discussed.

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INTRODUCTION

In the last few decades, there has been much discussion of the possibility of insulators with magnetic ions which do not order down to the lowest temperatures due to quantum fluctuations [1]. Such states have been given the name spin-liquids. The interest in such problems is high in view of their possible connection to emergent quantum numbers, fractionalization of excitations, etc. The theory, calculations and experimental realizations have been clear in one dimension. In two dimensions, Kitaev [2] has provided exact results on some models, while there have been many approximate discussions on several related models. The models are rather special and not easily realizable although impressive crystal symmetry analysis [3] has led to the search for materials with the requisite anisotropic exchange. The fact that a variety of such compounds show no customary magnetic order down to temperatures an order of magnitude or more below their magnetic interaction energies, and are not spin-glasses, speaks for quantum fluctuations in a general way. But specific experimental signatures have been murky.

We analyze clear and anomalous results from magnetic torque measurements in two compounds, $\gamma$-Li$_2$IrO$_3$ [5] and RuCl$_3$, which due to their structure and quantum-chemistry may host Kitaev-like exchange anisotropy between effective $S = 1/2$ ions on hexagonal networks [3] together with additional interactions. These compounds exhibit antiferromagnetic (AFM) order [6, 7] at low temperatures and small applied magnetic fields. But inelastic neutron scattering experiments [9], Raman spectroscopy [10], and thermal transport [8] suggest unusual properties in and outside of the AFM region that are not to be expected in AFMs. Suggestions have been made that these properties are characteristic of Kitaev spin-liquids [10–13]. We show here that the experimental results are consistent with a specific local order parameter, which does however have topological properties.

MAGNETIC TORQUE

A torque $\tau$ is generated when a magnetic field $\mathbf{B}$ is applied to an anisotropic magnetic crystal in a direction which is not one of the principal axes for the magnetic susceptibility
\( \tau = \mathbf{M}(B) \times \mathbf{B}. \) 

(1)

\( M_i = \chi_{ij} B_j. \) 

(2)

\( M_i \) is the uniform magnetization in the \( i-th \) direction. In the linear regime, the torque in a magnetic material with orthorhombic or hexagonal symmetry normally follows the angle dependence

\[ \tau_\alpha(\theta) = \frac{1}{2}(\chi_p - \chi_c) \sin(2\theta)B^2, \] 

(3)

where \( \theta \) is measured from the \( a-b \) plane. \( \chi_c \) and \( \chi_p \) are the susceptibilities with field in the \( c- \)axis and in one of the symmetry axes orthogonal to it, respectively. The above is true in a paramagnet or in an ordered AFM compound, however complicated the order may be, provided the AFM order preserves the principal axes invoked above.

The results for the torque measurements as a function of angle for various applied fields are shown in Fig (1) for both compounds [15]. At small enough fields, the results are dominated by the angle dependence of Eq. [3] [4]. At larger fields \( B \gtrsim B^*(\theta,T) \), the dominant term in the angle-dependent torque has the anomalous angle dependence

\[ \frac{\tau_\alpha(\theta)}{|B|} = |\mathbf{N}(B)| \sin \theta \, \text{sign}(\cos \theta). \] 

(4)

\( \tau(\theta)/|B| \) jumps from its maximum positive value at \( \theta \approx (\pi/2)^- \) to its maximum negative value at \( \theta \approx (\pi/2)^+ \) [5]. \( \tau_\alpha \) remains the same for \( B \to -B \). Fig. (1) shows that \( \mathbf{N} \) has a similar magnitude as \( \mathbf{M} \); both are extensive. \( \mathbf{N}(B) \) reaches a maximum at about 30 Tesla at \( T = 4 \) K in \( \gamma\text{-Li}_2\text{IrO}_3 \) and then slowly decreases with increasing field (Figure 1). This slow decrease is consistent with the exchange interaction energy scale \( J \), determined by the deviation from the Curie law at 200 K [4]. In fact, as further discussed below, closer examination reveals that data at low fields is consistent with a torque which is the sum of the two terms with angular dependence of the form (3) and (4). This behavior continues at temperatures and magnetic fields well beyond the AFM state [5].

In RuCl\(_3\) [15], the discontinuity occurs as magnetic field crosses the direction perpendicular to the honeycomb plane, suggesting that \( \mathbf{N}(B) \) in Eq. (4) lies within the honeycomb plane. Furthermore, the discontinuity appears consistent with a six-fold modulation as the rotation plane of the magnetic field changes with the azimuthal angle \( \phi \) [16]. In \( \gamma\text{-Li}_2\text{IrO}_3\),
Figure 1: Magnetic field evolution of the angle-dependent torque at low temperatures in (a) $\gamma$-Li$_2$IrO$_3$ and (b) RuCl$_3$. A discontinuity in $\tau/B$ as magnetic field crosses the $c$-axis in a plane going through it is observed up to the highest measured fields in both compounds. More comprehensive results in RuCl$_3$, including for the discontinuity at near $\theta = \pi/2$, have been obtained recently, through measurements of the magnetotropic coefficient [16, 24].

there are two inequivalent honeycomb planes which share the $c$–direction and are oriented azimuthally at $\sim \pm 35^\circ$ from the $b$–axis. In this system, the discontinuity in torque also occurs as magnetic field crosses the $c$–axis, which reflects the discontinuous behavior of the total $N(B) = N_1(B) + N_2(B)$, where $N_1(B)$ and $N_2(B)$ refer to the two inequivalent honeycomb planes.

More comprehensive results in RuCl$_3$ have been obtained recently in the magnetotropic coefficient [16, 24], which measures the angular derivative of torque. The discontinuity observed in torque measurements manifests itself as a sharp peak in the magnetotropic coefficient. Upon continual rotation of the sample in a magnetic field, the sharp peak is observed when field is aligned perpendicular to the honeycomb planes, confirming the discontinuity as magnetic field crosses the c-axis.

As noted above, the angular dependence in (4) preserves the point-group symmetries of the crystal. It is the singularity when the field is aligned close to the $c$-axis which is anomalous. One might think that $N(B)$ is an ordinary magnetization-vector which at high fields lies purely in the hexagonal planes and jumps as the angle of the field is changed across
the c-axis. However, we have not found any spin-reorientation free-energy for a collinear or a non-collinear magnetic order parameter characterized by a vector at zero or non-zero \( Q \) or any two-dimensional magnetic tensor order parameter which gives the observed jump. Actually, a much stronger argument that something much more interesting is afoot is given by the behavior of \( N(B) \) at small \( B \) which is discussed below.

**A HYPOTHESIS AND ITS TEST**

The simplest state which gives the observed properties is a state with a finite thermodynamic average of the solid-angle

\[
\Omega \equiv \frac{1}{2N} \sum_{(i,i',i'')} \langle S_i \Delta (S_{i'}, \Delta \times S_{i''}, \Delta) \rangle.
\]  

\( \Delta \) labels the two triangular sub-lattices of a hexagonal unit-cell, labelled by \( i \); for a given \( \Delta \), \( (i,i',i'') \) label the three sites in the sub-lattice in a unit-cell \textit{in an ordered way}, say clockwise with respect to the axis perpendicular to the hexagon. \( N \) is the number of unit-cells, and 2 is the number of sub-lattices. We need consider only the case that \( \Delta = 1,2 \) contribute equally to \( \Omega \). So, henceforth we will drop the subscript \( \Delta \) as well as the factor \( 1/2 \), with the understanding that \( (i,i',i'') \) refer to sites in the same sub-lattice in a unit-cell. (5) can be easily generalized to more than one hexagonal plaquette per unit-cell. The order parameter \( \Omega \) is odd under time-reversal and all reflections - it is chiral. The product of time-reversal and chirality is preserved, as is translation by lattice vectors. Note that individual spins and pairs fluctuate so that \( < S_i > = 0 \) and \( < S_{i'} \times S_{i''} > = 0 \), while the thermodynamic average \( \Omega \) maintains its fixed value. Such an order cannot be discovered by polarized neutron scattering. Other methods which may show consistency with such an order are discussed below.

Long ago, Herring [17] derived that \( i S_i (S_j \times S_k) \) appears in the permutation operator or the ring-exchange Hamiltonian for three-spins at sites \((i,j,k)\) in a magnetic insulator. A variational ground state wave-function proposed by Kalmeyer and Laughlin [18] (see also [19]) for spins in an insulator on a triangular lattice, as an alternative possibility to AFM order, has the symmetries of the order parameter \( \Omega \). Wen, Wilczek and Zee [20] discussed the order parameter \( \Omega \) in the context of their description of anyonic excitations. Such an order parameter, which is equivalent to spin-currents within each unit-cell in the lattice may
be derived to be locally stable in a mean-field theory from physically relevant interaction terms in the Hamiltonian analogously to the loop charge-currents in Ref. (21, 22).

Note that an operator of the form $S_i (S_{i'} \times S_{i''})$ is hermitian and can belong in a Hamiltonian. Given an order parameter $\Omega$, it follows that, since a magnetic field $B$ has the same symmetries as $S$, the lowest order in $B$ term found in the Hamiltonian (beside the Zeeman term) is

$$H' = \gamma B \sum_{(i'\,i'')} < S_{i'} \times S_{i''} > (B)$$  \hspace{1cm} (6)$$

$\gamma$ is a coefficient with dimension of the Bohr magneton and formally includes in it the product of the eigenvalues of the parity and time-reversal operators with the product remaining invariant. $(i',i'')$ are also ordered in a specific way following the definition after Eq. (5). The observed behavior in Eq. (4) can be understood if

$$N(B) = \gamma \sum_{(i'\,i'')} < S_{i'} \times S_{i''} > (B).$$  \hspace{1cm} (7)$$

$N(B)$ is even under time-reversal and odd under parity, and $N(0) = 0$, as stated above. It may be called a *quantum screw vector* because it is characterized by its helicity and magnitude. In considering the contribution of (6) to the ground state energy, we take $N(B)$ to lie in the hexagonal planes for all $B$’s under consideration. Then beside the angle-dependence between the vectors $B$ and $N$, we must also take into account that the helicity of $N$ is picked by the projection of $B$ on $N$. This is because for $\Omega$ to have a fixed value while $\langle S_i \rangle = \langle S_{i'} \times S_{i''} \rangle = 0$, the direction of $(S_{i'} \times S_{i''})$ must flip on flipping the projection of $S_i$ on $(S_{i'} \times S_{i''})$. The direction of $S_i$ is itself determined by the direction of $B$. Therefore the change of the ground state energy on applying a field $B$ has a contribution,

$$\delta E_a(B) = -\gamma |B||N(B)|| \cos \theta |f(\phi).$$  \hspace{1cm} (8)$$

$f(\phi)$ is the dependence on the azimuthal angle of the magnetic field. It should respect the reflection symmetry of the planes passing through the c-axis. Details of the $f(\phi)$ depend on the quantization axis for the spins, which are determined by the microscopic Hamiltonian and are in general different for different sites. We cannot say more about this without knowledge of the microscopic Hamiltonian.
Figure 2: (a) The coefficients $A$ and $A_2$, determined by fitting the angle-dependence of the $\tau/B$ in Figure (1a) and more such data at fixed temperature to $A \sign(\cos \theta) \sin \theta + A_2 \sin 2\theta$, as a function of magnetic field. (b) The low-field dependence of $A$ and $A_2$. $A$ is multiplied by 10 for viewing on the $A_2$ scale. $A$ plotted against $B^2$ (inset) displays the $B^3$ dependence of the anomalous component of the torque at low fields. The shaded region in the first figure shows the region in which AFM is found below $B < B^*(\theta)$, the latter varies from 3 tesla for field in the hexagonal planes to 18 tesla for field normal to them Ref. ([4]).

The anomalous contribution to the torque $\tau_a(B)$ derived from the ground state energy $\delta E_a(B)$ is,

$$\tau_a(B) = \frac{d \delta E_a(B)}{d\theta}.$$  

$\tau_a(B)$ has precisely the form (4) with which experiments have been fitted; it changes sign across $\cos(\theta) = 0$ and its magnitude is proportional to $\sin(\theta)$. It is invariant under $B \rightarrow -B$, because the chiral spin-order state is not only odd under time-reversal but also under parity with the product preserved. It also preserves all the point group symmetries as in the experiments.

There can be no linear (or odd power) dependence of $|N|(B)$ on $B$. A prediction which follows is that the leading dependence of $|N(B)| \propto B^2$, i.e. $\tau_a$ proportional to $|B|B^2$. As discussed above, this follows from the symmetries of the chiral spin-order and the fact that it involves three spin-operators, each of which is tuned by $B$. More specifically, given the
spin-structure of $N$, $\tau_\alpha(\theta, \phi)$ depends on the product of the two orthogonal components of the field in the hexagonal planes with direction determined by the appropriate quantization axes, and of the component perpendicular to the plane which is a natural quantization axis. One may therefore also understand the observed discontinuity in the torque as follows: When the component of the field perpendicular to the plane and one of the components in the plane is held fixed and the other component in the plane changes sign, the torque must also change sign. This obviously happens when $\theta$ is turned across $\pi/2$.

Detailed experiments probing the $\phi$-dependence of the torque are not available. For $\phi$ in a symmetry direction, the predicted field dependence of the anomalous torque at low fields has been tested by a detailed analysis of the data which is given in Fig. (1a) of Ref. [4]. This shows $\tau/|B|$ continuously as a function of $B$ at multiple field orientation angles. More than a hundred field slices are taken from this data and the angle dependence at these fixed fields is then fit to the sum of the two terms (3) and (4) with denser field slices at low field to ascertain the dependence on magnetic field. The results are shown in Fig. (2). $A_2(B)$ is the coefficient of the term proportional to $\sin(2\theta)$, i.e. the normal term proportional to the anisotropy of the magnetic susceptibility. $A(B)$ is the coefficient of the term $\sin(\theta)\text{sign}(|\cos(\theta)|)$, i.e. it is proportional to $|N(B)|$. The low field results are shown in an expanded form in Fig. (2-b), and show the predicted $B^2$ dependence up to 3 tesla. This is the maximum field where the low-field angle dependence can be fit without crossing the angle-dependent AFM phase boundary. The high-field behaviour of $A(B)$ and $A_2(B)$ can only be extracted above 18 tesla, outside of the shaded region in figure (2-a). A magnetoresistive contribution inherent to the torque detection method is removed by anti-symmetrization of the data. A zero-field offset due to the bridge circuit used in the torque measurement is removed such that torque is zero at zero field. However, whether these systematic effects are removed or not, the qualitative behavior of the $A$’s remains the same. We also note that in the low-field limit, $A_2$ dominates the total torque signal and we suggest direct measurements of $M(B)$ to support that the leading order correction goes as $B^2$.

In the experiments $|N(B)|$ has a broad peak at an intermediate field and then decreases very slowly. The slow decrease of this component at larger $B$ indicates decay of the chiral order parameter at an energy scale of the large bare magnetic couplings in the compound indicated by the Weiss-constant.

If $|N(B)|/B^2 \neq 0$, it follows that the order parameter $\Omega \neq 0$ in zero applied field. It
co-exists with the AFM order parameter $M(Q)$, and continues at temperatures and fields beyond where $M(Q) = 0$. We have found that there is a steep rise in the coefficient $A$ near $B = B^*(\theta)$ where the AFM order and the coefficient $A_2$ begins to sharply decrease. This suggests the allowed coupling of the form proportional to $u|M(Q)|^2|\Omega|^2$, where $u$ is the repulsive coupling energy.

**Relation to Kitaev states**

The ground state of the Kitaev model preserves time-reversal invariance unlike $\Omega \neq 0$. An external magnetic field has no effect on the ground state (or the excitations) in the Kitaev model to order $B$ or $B^2$. For a magnetic field coupling as $\sum_{\alpha=x,y,z} B_\alpha S_\alpha$, a state with $\Omega$ is generated to $O(B_x B_y B_z/J^3)$, where $J$ are the three couplings in the model assumed equal \[2\]. In effect at this order the flux $w(p) = \prod_{i\in p} S_i$ around the hexagonal plaquettes $p$ in the Kitaev model, which has a finite expectation value in the ground state in the absence of the field, breaks up into a product of a pair of expectation values of $\Omega$ due to the breaking of time-reversal. In the Kitaev model, an anomalous torque related to $N(B)$ is also expected with a discontinuity near $\theta = \pi/2$, but such a torque would be proportional to $B^6$ at low fields as opposed to $O(B^3)$ observed in the experiments discussed above.

**SOME PROPERTIES OF THE CHIRAL SPIN-ORDERED STATE**

Since $\Omega$ breaks time-reversal, an internal magnetic field is generated. It may be observed by Kerr effect and by muon resonance. Similarly, breaking of chirality should be visible in second harmonic generation and in optical polarimetry.

There have been several inelastic scattering experiments - neutron scattering \[9\] and Raman \[10\] seeing a continuum of excitations carrying angular momenta of $\pm 1$. Continua of excitations are not to be expected in any spin-wave theory for conventional ordered states, especially at long wavelengths. In a state with a ground state expectation value $\Omega$, the simplest excitations (if they exist, see below) for a given total momentum $q$ are expected to form a continuum. This is because the simplest low-energy excitation, formed from linear combinations of local $\pm 1$ excitations of $S_i$ must be accompanied by excitations of $(S_j \times S_k)$ to correspond to the lowest local change in $\Omega$. As discussed below, one should also expect
topological excitations. The nature of the excitations in the chiral order parameter which has $Z_2 \times Z_2$ symmetry determines whether, despite a local order parameter, a conventional phase transition exists. None associated with $\Omega$ has been reported in the temperature range investigated, which however is less than the estimates of the Weiss constant.

Given the expectation value $\Omega$, thermal Hall conductivity $\kappa_{xy}$ is to be expected because of chiral surface states accompanying such an order parameter. Kitaev predicts a quantized value for this quantity in a (large) field due to field induced chiral spin-order when the bulk ground state has a gap [2]. In RuCl$_3$, there is indeed good evidence for a finite $\kappa_{xy}$ [8]. Its value is even quantized to the predicted value but only in an intermediate field regime. The field dependence both at lower and at higher fields is complicated [25, 26] and further theory and experiments are required to understand it. Such measurements in $\gamma$-Li$_2$IrO$_3$ are suggested as are torque measurements in other samples in which spin-liquids (Kitaev or not) are suggested.

A state with $\Omega \neq 0$ is expected to have a quantized spin-Hall effect. This was verified by Haldane and Arovas [23] by explicit calculation of the Chern number 2 (representing semion excitations) in a model of a hexagonal lattice with a effective Hamiltonian including the hermitian operator $S_i (S_j \times S_k)$ supplemented with a Heisenberg Hamiltonian. A quantized spin-Hall effect on applying gradient of a magnetic field is then expected. This can happen only when the (degenerate) ground state is separated from the excitations with a gap. The connection to a quantized thermal Hall effect follows, but not if there are gapless excitations which are observed in RuCl$_3$. With gapless excitations un-quantized thermal Hall effect is to be expected.

It should be noted that while RuCl$_3$ may be considered two dimensional to a good approximation, $\gamma$-Li$_2$IrO$_3$, is three dimensional. While the two kinds of hexagonal planes (mentioned earlier) do not share any ions, we see no reason of symmetry that there is zero interactions between the magnetic ions in them.

Further theoretical work suggested is investigations of the effective Hamiltonians relevant for these compounds for the order parameter $\Omega$, conditions for it to have gap-less or gapped excitations, with and without an applied magnetic field, and the Chern class. Detailed investigations of torque as a function of temperature and other techniques in the samples discussed above and those without the nuisance of an AFM order parameter are also suggested. The azimuthal angle dependence of the torque has information on the
microscopic Hamiltonian and should be carefully measured. The chiral order parameter may also be around in other candidate ”spin-liquids”. It seem to us that torque measurements may be the most direct way to reveal them.

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