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Zigzag Magnetic Order in the Iridium Oxide Na$_2$IrO$_3$

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We explore the phase diagram of spin-orbit Mott insulators on a honeycomb lattice, within the Kitaev-Heisenberg model extended to its full parameter space. Zigzag-type magnetic order is found to occupy a large part of the phase diagram of the model, and its physical origin is explained as due to interorbital $t_{2g} - e_g$ hopping. Magnetic susceptibility, spin wave spectra, and zigzag order parameter are calculated and compared to the experimental data, obtaining thereby the spin coupling constants in Na$_2$IrO$_3$ and Li$_2$IrO$_3$.

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In the quest for the materials with novel electronic phases, iridium oxide Na$_2$IrO$_3$ came into focus recently [1–7] due to theoretical predictions [8, 9] that this system may host Kitaev model physics and quantum spin Hall effect.

Na$_2$IrO$_3$ is an insulator with sizable and temperature independent optical gap $\gtrsim 0.35$ eV [7], and shows Curie-Weiss type susceptibility [1, 6] with moments corresponding to effective spin one-half of Ir$^{4+}$ ion with $t_{2g}^2$ configuration [10]. These facts imply that Na$_2$IrO$_3$ is a Mott insulator with well localized Ir-moments.

Collective behavior of local moments in Mott insulators is governed by three distinct and often competing forces: (i) orbital-lattice (Jahn-Teller) coupling, (ii) virtual hopping of electrons across the Mott gap resulting in exchange interactions, and (iii) relativistic spin-orbit coupling (see Ref. [11] for extensive discussions). The corresponding energy scales $E_{JT}$, $J$, and $\lambda$ vary broadly depending on the type of magnetic ions and chemical bonding [12]. When $\lambda > (E_{JT}, J)$, as often realized for Co, Rh, Ir ions in octahedral environment, local moments acquire a large orbital component which may result in a strong departure from spin-only Heisenberg models [8, 11]. The direct observation of large spin-orbit splitting $3\lambda / 2 \sim 0.6 - 0.7$ eV in insulating iridates Sr$_2$IrO$_4$ [13], Sr$_3$Ir$_2$O$_7$ [14], and Na$_2$IrO$_3$ [15] made it certain that $\lambda > (E_{JT}, J)$. Thus, low-energy physics of Na$_2$IrO$_3$ is governed by interactions among the spin-orbit entangled Kramers doublets of Ir-ions.

It is also established now [3–5] that Ir-moments in Na$_2$IrO$_3$ undergo antiferromagnetic (AF) order at $T_N \approx 15$ K. The fact that $T_N$ is much smaller than paramagnetic Curie temperature (−125 K) [6] and spin-wave energies [4] implies that the underlying interactions are strongly frustrated. This is natural in so-called Kitaev-Heisenberg (KH) model [16] where long range order is suppressed by the proximity to the Kitaev spin-liquid (SL) state. However, the observed “zigzag” magnetic pattern [ferromagnetic (FM) zigzag chains, AF-coupled to each other] came as a surprising challenge to this simple and attractive model. To resolve the “zigzag puzzle”, a number of proposals, ranging from various modifications of the KH model [4, 6, 17–19] to a complete denial [20] of a local moment picture in Na$_2$IrO$_3$, have been put forward.

In this Letter, we show that the zigzag order is in fact a natural ground state (GS) of the KH model, in a previously overlooked parameter range. Next, we identify the exchange process that supports a zigzag-phase regime. Further, we calculate spin-wave spectra, the ordered moment, and magnetic susceptibility of the model in zigzag phase, and find a nice agreement with experiments. This lends strong support to the KH model as a dominant interaction in Na$_2$IrO$_3$ and related oxides.

The model.— Nearest-neighbor (NN) interaction between isospin one-half Kramers doublets of Ir$^{4+}$ ions, coupled via 90°-exchange bonds, reads as follows (the exchange processes are described later):

$$H^{(\gamma)}_{ij} = 2K S_i^\gamma S_j^\gamma + J S_i \cdot S_j.$$  \hspace{1cm} (1)

Here, $\gamma(=x,y,z)$ labels 3 distinct types of NN bonds of a honeycomb lattice [16] of Ir ions in Na$_2$IrO$_3$, and spin axes are oriented along the Ir-O bonds of IrO$_6$ octahedron. The bond-dependent Ising coupling between the $\gamma$ components of spins is nothing but Kitaev model [21], and the second term stands for the Heisenberg exchange.

Let us introduce the energy scale $A = \sqrt{K^2 + J^2}$ and the angle $\varphi$ via $K = A \sin \varphi$ and $J = A \cos \varphi$; the model (1) takes then the following form:

$$H^{(\gamma)}_{ij} = A (2 \sin \varphi S_i^\gamma S_j^\gamma + \cos \varphi S_i \cdot S_j).$$  \hspace{1cm} (2)

We let the “phase” angle $\varphi$ to vary from 0 to $2\pi$, uncovering thereby additional phases of the model that escaped attention previously [16], including its zigzag ordered state which is of a particular interest here.

It is instructive to introduce, following Refs. [11, 16], 4 sublattices with the fictitious spins $\mathbf{S}$, which are obtained from $\mathbf{S}$ by changing the sign of its two appropriate components depending on the sublattice index. This transformation results in the $\mathbf{S}$-Hamiltonian of the same form as (1), but with effective couplings $K = K + J$ and $J = -J$, revealing a hidden $SU(2)$ symmetry of the
model at $K = -J$ (where the Kitaev term $\tilde{K}$ vanishes).

For the angles, the mapping reads as $\tan \tilde{\varphi} = -\tan \varphi - 1$.

**Phase diagram.**— In its full parameter space, the KH model accommodates 6 different phases, best visualized using the phase-angle $\varphi$ as in Fig. 1(a). In addition to the previously discussed [16, 22, 23] Néel-AF, stripy-AF, and SL states near $\varphi = 0, -\frac{\pi}{4}$, and $-\frac{3\pi}{4}$, respectively, we observe 3 more states. First one is “AF” ($K > 0$) Kitaev spin-liquid near $\varphi = \frac{\pi}{4}$. Second, FM phase broadly extending over the third quadrant of the $\varphi$-circle. The FM and stripy-AF states are connected [see Fig. 1(a)] by the 4-sublattice transformation, which implies their identical dynamics. Finally, near $\varphi = \frac{3\pi}{4}$, the most wanted phase, zigzag-AF, appears occupying almost a quarter of the phase space. Thanks to the above mapping, it is understood that the zigzag and Néel states are isomorphic, too. In particular, the $\varphi = \frac{3\pi}{4}$ zigzag is identical to Heisenberg-AF of the fictitious spins [24].

To obtain the phase boundaries, we have diagonalized the model numerically, using a hexagonal 24-site cluster with periodic boundary conditions. The cluster is compatible with the above 4-sublattice transformation and $\varphi \leftrightarrow \tilde{\varphi}$ mapping. As seen in Fig. 1(b), the second derivative of the GS energy $E_{\text{GS}}$ with respect to $\varphi$ well detects the phase transitions. Three pairs of linked transition points are found: $\approx (88^\circ, 92^\circ)$ and $(−76^\circ, −108^\circ)$ for the spin liquid/order transitions around $±\frac{\pi}{4}$, and $(162^\circ, −34^\circ)$ for the transitions between ordered phases.

The transitions from zigzag-AF to FM, and from stripy-AF to Néel-AF are expected to be of first order by symmetry; the corresponding peaks in Fig. 1(b) are indeed very sharp. The spin liquid/order transitions near $\varphi = ±\frac{\pi}{4}$ lead to wider and much less pronounced peaks, suggesting a second (or weakly first) order transition [16]. On the contrary, liquid/order transitions around $\varphi = \frac{\pi}{2}$ show up as very narrow peaks; on the finite cluster studied, they correspond to real level crossings. Nature of these phase transitions remains to be clarified [25].

While at $J = 0$ (i.e. $\varphi = ±\frac{\pi}{4}$) the sign of $K$ is irrelevant [21], the stability of the AF- and FM-type Kitaev spin-liquids against $J$-perturbation is very different: the SL phase near $\frac{\pi}{4}$ ($-\frac{\pi}{4}$) is less (more) robust. This phase behavior is related to a different nature of the competing ordered phases: for the $\frac{\pi}{4}$ SL, these are highly quantum zigzag and Néel states, while the SL near $-\frac{\pi}{4}$ is sandwiched by more classical (FM and “fluctuation free” stripy [16]) states which are energetically less favorable than quantum SL state.

**Exchange interactions in $\text{Na}_2\text{IrO}_3$.**— Having fixed the parameter space ($K > 0, J < 0$) for zigzag phase, we turn now to the physical processes behind the model (1). Exchange interactions in Mott insulators arise due to vir-
tual hoppings of electrons. This may happen in many different ways, depending sensitively on chemical bonding, intra-ionic electron structure, etc. The case of present interest (i.e., strong spin-orbit coupling, $t_{2g}^2$ configuration, and 90°-bonding geometry) has been addressed in several papers [8, 11, 16, 26]. There are following four physical processes that contribute to $K$ and $J$ couplings.

Process 1: Direct hopping $t'$ between NN $t_{2g}$ orbitals. Since no oxygen orbital is involved, 90°-bonding is irrelevant; the resulting Hamiltonian is $H_1 = I_1 S_i S_j$, with $I_1 \approx \frac{\Omega}{2} t'/U$ [16]. Here, $U$ is Coulomb repulsion between $t_{2g}$ electrons. Typically, one has $t'/t < 1$, when compared to the indirect hopping $t$ of $t_{2g}$ orbitals via oxygen ions.

Process 2: Interorbital NN $t_{2g} - e_g$ hopping $\tilde{t}$. This is the dominant pathway in 90°-bonding geometry since it involves strong $t_{pd\sigma}$ overlap between oxygen-2$p$ and $e_g$ orbitals; typically, $\tilde{t}/t \sim 2$. The corresponding Hamiltonian is [11]:

$$H_2^{(\gamma)} = I_2 (2S_i^\gamma S_j^\gamma - S_i S_j).$$

This is nothing but the model (1) with $K = -J = I_2 > 0$, i.e., at its SU(2) symmetric point $\varphi = \frac{\pi}{2}$ inside the zigzag phase, see Fig. 2. For the Mott-insulating iridates (as opposed to charge-transfer cobaltates [11]), we estimate $I_2 \approx \frac{\Omega}{2} (t'/U)^2 J_H$, where $U$ is (optically active) excitation energy associated with $t_{2g} - e_g$ hopping, and $J_H$ is Hund’s interaction between $t_{2g}$ and $e_g$ orbitals. The physics behind this expression is clear: $(\tilde{t}/U)^2$ measures the amount of $t_{2g}$ spin which is transferred to NN $e_g$ orbital; once arrived, it encounters the “host” $t_{2g}$ spin and has to obey the Hund’s rule.

For its remarkable properties, the Hamiltonian $H_2$ (3) deserves a few more words. On a triangular lattice, it shows a nontrivial spin vortex ground state [11, 27]; however, the elementary excitations are simple SU(2) magnons of a conventional Heisenberg-AF. When regarded as “$J$”-part of a doped $t$–$J$ model, it leads to an exotic pairing [11, 28].

Process 3: Indirect hopping $t$ between NN $t_{2g}$ orbitals via oxygen ions. This gives rise to the Kitaev model $H_3^{(\gamma)} = -I_3 S_i^\gamma S_j^\gamma$, with $I_3 \approx \frac{\Omega}{2} (t^2/U)(J_H/U)$ [8] where $J_H$ is Hund’s coupling between $t_{2g}$ electrons. This process supports $\varphi = -\frac{\pi}{2}$ SL state, see Fig. 2.

Process 4: Mechanisms involving pd charge-transfer excitations with energy $\Delta_{pd}$. Two holes may meet at an oxygen and experience Coulomb $U_p$ and Hund’s $J'_H$ interactions, or cycle around a Ir$_2$O$_2$ plaquette (Fig. 2). The resulting Hamiltonian $H_4$ has the form of $H_2$ (3). The coupling constant $I_4 \approx \frac{\Omega}{2} (t_{pd}^2 - t_{pd} - \frac{1}{a_0})$ is negative [29], supporting stripy-AF not observed in Na$_2$IrO$_3$.

Putting things together, we observe that it is the interorbital $t_{2g} - e_g$ hopping $H_2$ process that uniquely supports zigzag order in Na$_2$IrO$_3$. This implies in general that multiorbital Hubbard-type models, when applied to iridates with 90°-bonding geometry, must include $e_g$ states as well, even though the moments reside predominantly in the $t_{2g}$ shell.

Up to this point, we neglected trigonal field splitting $\Delta$ of the $t_{2g}$ level due to the $c$-axis compression present in Na$_2$IrO$_3$. This approximation is valid as long as $\Delta$ is much smaller than spin-orbit coupling $\lambda \approx 0.4$ eV [13, 15, 30] and seems to be justified, since the recent *ab-initio* calculations [20] suggest that $\Delta \approx 75$ meV only [31].

We have also examined the longer-range couplings, using the hopping matrix of Ref. [20], and found that second-NN interaction has the form of (3) (as previously noticed [32, 33]), while third-NN coupling is of AF-Heisenberg type [the corresponding coupling constants are $\frac{1}{3}(t_{2g3}/U)$]. The second (third)-NN interaction would oppose (support) zigzag order; however, we believe that these couplings are not significant in Na$_2$IrO$_3$ because the hoppings $t_2$ and $t_3$ are small [34].

We do not attempt here to evaluate the parameters involved in $H_1$–$H_4$; *ab-initio* calculations as in Ref. [35] might be more useful in this regard. Instead, having obtained a zigzag order in our model (1) and identified the physical process driving this order, we turn now to the experimental data. The $J$ and $K$ values in Na$_2$IrO$_3$ and Li$_2$IrO$_3$ will be extracted below from analysis of the neutron scattering and magnetic susceptibility data.

**Spin-waves in the zigzag phase.** Consider a single domain zigzag state, e.g., with FM chains running perpendicular to $z$-type bonds. Following Ref. [4], we introduce a rectangular $a \times b$ magnetic unit cell $\sqrt{3}a_0 \times 3a_0$ in terms of hexagon-edge $a_0$, see Fig. 1(a), and define the $ab$-plane wave vector $\mathbf{q}$ in units of $(h, k)$ as $\mathbf{q} = (\frac{2\pi}{a} h, \frac{2\pi}{b} k)$. Standard spin-wave theory gives four dispersive branches:

$$\omega^2_{1,2}(h, k) = [K^2 + (K + J)^2] c_h^2 - K J (1 - s_h s_k)$$
$$\pm |(K + J)c_h| \sqrt{(2K - J)^2 - (2K s_h - J s_k)^2},$$

FIG. 3: Magnon spectra in the zigzag phase calculated using Eq. (4) with $(J, K) = (-4.0, 10.5)$ meV. The inset shows the path along the symmetry directions in the reciprocal space; notations of Ref. [4] are used.
The parameters are varied such that consistent with the neutron data \[4\] while possible quantifying the Kitaev term mapping out entire magnon spectra is highly desirable to \[\chi\] form magnetic susceptibility \[\text{magnon spectra for Na}\text{IrO}_3\] as neutron scattering data \[4\]. With this, we predict \[T\] \(\sim 100\) K where the finite-size effects become significant.

and \(\omega_{3,4}(h,k) = \omega_{1,2}(-h,k)\), with \(c_h = \cos \pi h\), \(s_h = \sin \pi h\), and \(s_k = \sin \pi k\). If \(K = -J\), i.e. at \(\varphi = \frac{\pi}{2}\) point of hidden SU(2) symmetry, two branches are degenerate \((\omega_1 = \omega_2)\) and become true Goldstone modes. Away from this special point, small magnon gap is expected to open by quantum effects not considered here. For \(q\) with \(h = k\), the dispersions \((4)\) simplify to \(\omega_1(h,h) = \sqrt{2K(2K + J)} |c_h|\) and \(\omega_2(h,h) = \sqrt{2Jg_{\text{ch}}}|\), revealing two different energy scales in magnon spectra set by \(K\) and \(J\) couplings.

While the bandwidth of the lowest dispersive mode (set by \(J\)) is already known to be about \(5-6\) meV \[4\], we are not aware of the high energy magnon data to estimate \(K\) in \(\text{Na}_2\text{IrO}_3\). We have therefore examined (see below) the magnetic susceptibility data \[1, 6\], and obtained \((J,K) \approx (-4.0, 10.5)\) meV that well fit the susceptibility as well as neutron scattering data \[4\]. With this, we predict magnon spectra for \(\text{Na}_2\text{IrO}_3\) shown in Fig. 3. The lowest dispersive \((J)\) mode is as observed \[4\], indeed. However, mapping out entire magnon spectra is highly desirable to quantify the Kitaev term \(K\) directly.

**Magnetic susceptibility.** We have calculated the uniform magnetic susceptibility \(\chi(T)\) of the model \((1)\) on 8- and 14-site clusters by exact diagonalization, and on 24-site cluster using finite-temperature Lanczos method \[36, 37\]. The parameters are varied such that \(J = A \cos \varphi\) is consistent with the neutron data \[4\] while \(\varphi\) stays within the zigzag sector of Fig. 1(a); this strongly narrows the possible \(K\)-window. For the data fits, we let \(g\)-factor of Ir\(^{4+}\) ion to deviate from 2 (due to the covalency effects \[10\]), and include \(T\)-independent Van Vleck term \(\chi_0\). The result for \(J = -4.0\) meV, \(K = 10.5\) meV, \(g = 1.78\), \(\chi_0 = 0.16 \times 10^{-3}\) cm\(^3\)/mol fits the \(\text{Na}_2\text{IrO}_3\) data nicely (Fig. 4); deviations occur at low temperatures only, when correlation length exceeds the size of the cluster used. The fit is quite robust: similar results can be found for small only variations, locating \(\text{Na}_2\text{IrO}_3\) near \(\varphi = 111 \pm 2^\circ\) of the model phase diagram Fig.1(a). The spin couplings obtained are reasonable for the 90\(^\circ\)-exchange bonds (as expected \[8, 11\], they are much smaller than in 180\(^\circ\)-bond perovskites \[13, 14\]).

The magnitude of Van Vleck term also agrees with our estimate \(\chi_0 \approx \frac{8}{3} \nu_B^2 N_A \approx 0.2 \times 10^{-3}\) cm\(^3\)/mol for Ir\(^{4+}\) ion, considering spin-orbit coupling \(\lambda \approx 0.4\) eV \[13, 15, 30\].

Dominance of the Kitaev term \((2K/J \approx 5\) in \(\text{Na}_2\text{IrO}_3\)) implies strong frustration hence enhanced quantum fluctuations; this explains the reduced ordered moment \(m \approx 0.22 \mu_B\) \[5\]. With the \(J, K\), and \(g\) values above, we calculated the leading order spin-wave correction to \(m\) and obtained \(m \approx 0.33 \mu_B\) \[38\].

For the sake of curiosity, we have also fitted \(\chi(T)\) data of \(\text{Li}_2\text{IrO}_3\) \[6\], a sister compound of \(\text{Na}_2\text{IrO}_3\). Acceptable results have been found for the angle window \(\varphi = 124 \pm 6^\circ\): a representative plot for \(J = -5.3\) meV, \(K = 7.9\) meV, \(g = 1.94\), \(\chi_0 = 0.14 \times 10^{-3}\) cm\(^3\)/mol is shown in Fig. 4. It is worth noticing that the value of \(J\), which controls the bandwidth of the softest spin-wave mode (see Fig. 3), appears to be similar in both compounds. This may explain why they undergo magnetic transition at similar \(T_N \approx 15\) K, despite very different high temperature susceptibilities.

To conclude, we have clarified the origin of zigzag magnetic order in \(\text{Na}_2\text{IrO}_3\) in terms of nearest-neighbor Kitaev-Heisenberg model for localized Ir-moments. The model well agrees with the low-energy magnon and high temperature magnetic susceptibility data. A general implication of this work is that the interactions considered here should hold a key for understanding the magnetism of a broad class of spin-orbit Mott insulators with 90\(^\circ\)-exchange bonding geometry, including triangular, honeycomb, hyperkagome lattice iridates.

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[24] After initial submission of this work, we became aware of the recent derivation [Y. Yu, L. Liang, Q. Niu, and S. Qin, arXiv:1202.1610] of the KH model and zigzag phase from a single band Hubbard model with the spin- and link-dependent NN-hoppings. However, such hoppings are not present in the hexagonal iridates $A_2IrO_3$ [8, 9].


[29] The results for $I_4$ of Refs. [8, 11, 26] were incomplete.


[31] Typically, “noncubic” corrections to the interactions between Kramers doublets scale as $(\frac{\lambda}{\Delta})^2$ which is about 0.01 if $\Delta = 75$ meV. $\theta$ is about 0.01 if $\Delta = 75$ meV. $(\frac{\lambda}{\Delta})^2$. The case of $\Delta > \lambda$ can be excluded also on the grounds that, in this limit, the interactions become bond-independent and support either Ising-FM or bond-independent $\lambda$ (28) which is about 0.01 if $\Delta = 75$ meV. $\theta$ is given by tan $\theta = 2\sqrt{2}/(\lambda + 2\Delta)$. The case of $\Delta > \lambda$ can be excluded also on the grounds that, in this limit, the interactions become bond-independent and support either Ising-FM or Oxy-AF states [11], instead of zigzag order observed.


[34] The second-NN hopping $t_2 \approx 75$ meV is about 4 times less than NN hopping $t$ via oxygen, and $t_2 \approx 30$ meV [20].


[37] We used $M = 10^6$ Lanczos steps and $N_{st} = 1024$ random sampling vectors. The values of $\chi$ and their statistical error are presented in Fig. 4 in the form of $3\sigma$-intervals estimated by taking many sets of the sampling vectors.

[38] Hybridization of the Ir-5$d$ and O-2$p$ orbitals on antiferromagnetic bonds [5], as well as the higher order quantum corrections may further reduce $m$. 