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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_2IrO_3 and Li_2IrO_3.

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In the quest for the materials with novel electronic phases, iridium oxide Na_2IrO_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_2IrO_3 is an insulator with sizable and temperature independent optical gap $\simeq 0.35$ 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}^5 configuration [10]. These facts imply that Na_2IrO_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 λ 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_2IrO_4 [13], $Sr_3Ir_2O_7$ [14], and Na_2IrO_3 [15] made it certain that $\lambda > (E_{JT}, J)$. Thus, low-energy physics of Na_2IrO_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_2IrO_3 undergo antiferromagnetic (AF) order at $T_N \simeq 15$ 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_2IrO_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_2IrO_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):

$$\mathcal{H}_{ij}^{(\gamma)} = 2K\ S_i^\gamma S_j^\gamma + J\ \boldsymbol{S}_i \cdot \boldsymbol{S}_j\ . \qquad (1)$$

Here, $\gamma (= x, y, z)$ labels 3 distinct types of NN bonds of a honeycomb lattice [16] of Ir ions in Na_2IrO_3, and spin axes are oriented along the Ir-O bonds of IrO_6 octahedron. The bond-dependent Ising coupling between the γ 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 φ via $K = A \sin\varphi$ and $J = A \cos\varphi$; the model (1) takes then the following form:

$$\mathcal{H}_{ij}^{(\gamma)} = A\ (2 \sin\varphi\ S_i^\gamma S_j^\gamma + \cos\varphi\ \boldsymbol{S}_i \cdot \boldsymbol{S}_j). \qquad (2)$$

We let the "phase" angle φ to vary from 0 to 2π, 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 $\tilde{\boldsymbol{S}}$, which are obtained from $\boldsymbol{S}$ by changing the sign of its two appropriate components depending on the sublattice index. This transformation results in the $\tilde{\boldsymbol{S}}$-Hamiltonian of the same form as (1), but with effective couplings $\tilde{K} = K + J$ and $\tilde{J} = -J$, revealing a hidden $SU(2)$ symmetry of the

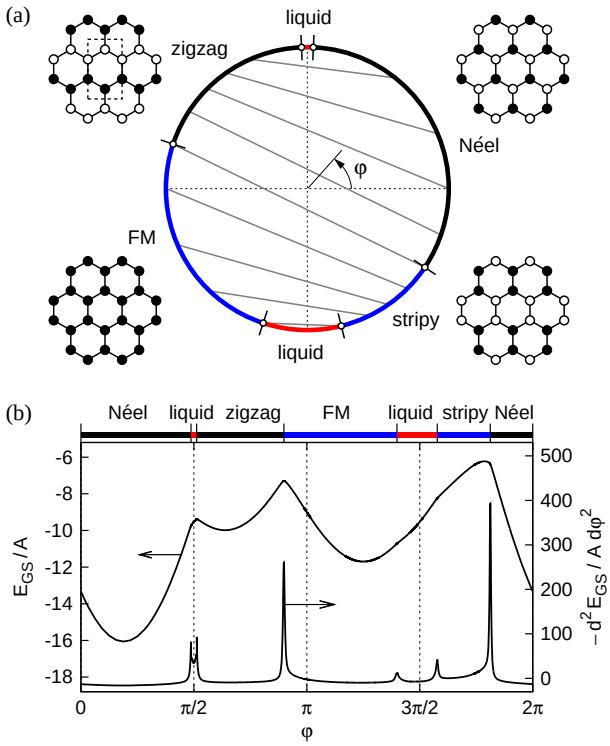

FIG. 1: (color online). (a) Phase diagram of the Kitaev-Heisenberg model containing 2 spin-liquid and 4 spin-ordered phases. The transition points (open dots on φ-circle) are obtained by an exact diagonalization. The gray lines inside the circle connect the points related by the exact mapping (see text). Open/solid circles in the insets indicate up/down spins. The rectangular box in zigzag pattern (top-left) shows the magnetic unit cell. (b) Groundstate energy $E_{\rm GS}$ and its second derivative $-{\rm d}^2E_{\rm GS}/{\rm d}\varphi^2$ revealing the phase transitions.

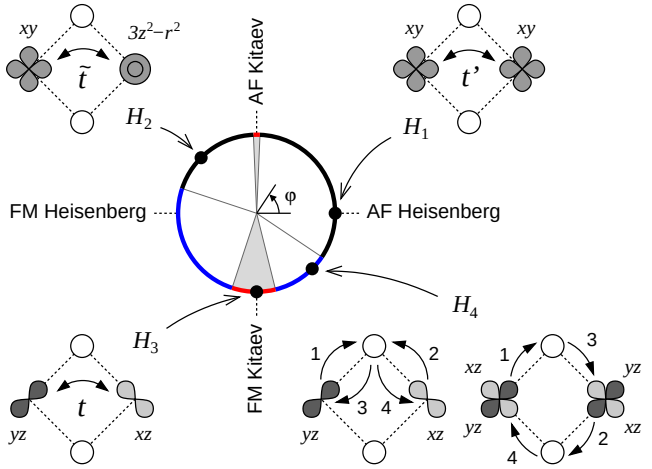

FIG. 2: (color online). Schematics of 4 different exchange processes (see text for details), arranged around the φ-phase diagram of Fig. 1(a). Taken separately, the Hamiltonians H_1, H_2, H_3, and H_4 would favor "pure" Néel-AF, zigzag-AF, Kitaev-SL, and stripy-AF states, respectively, as indicated by arrows connecting H_i with the dots on φ-circle. The circle is divided into the phase-sectors by gray lines; SL phases are shaded.

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 φ 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 $-\frac{\pi}{2}$, respectively, we observe 3 more states. First one is "AF" ($K>0$) Kitaev spin-liquid near $\varphi=\frac{\pi}{2}$. Second, FM phase broadly extending over the third quadrant of the φ-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 $\varphi=\frac{3}{4}\pi$, 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 $\varphi=\frac{3}{4}\pi$ 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 $E_{\rm GS}$ with respect to φ well detects the phase transitions. Three pairs of linked transition points are found: $\simeq(88^\circ,92^\circ)$ and $(-76^\circ,-108^\circ)$ for the spin liquid/order transitions around $\pm\frac{\pi}{2}$, 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 $\varphi=-\frac{\pi}{2}$ 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. $\varphi=\pm\frac{\pi}{2}$) 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 $\frac{\pi}{2}$ ($-\frac{\pi}{2}$) is less (more) robust. This phase behavior is related to a different nature of the competing ordered phases: for the $\frac{\pi}{2}$ SL, these are highly quantum zigzag and Néel states, while the SL near $-\frac{\pi}{2}$ is sandwiched by more classical (FM and "fluctuation free" stripy [16]) states which are energetically less favorable than quantum SL state.

Exchange interactions in Na_2IrO_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}^5 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 $H_1 = I_1\ \boldsymbol{S}_i \cdot \boldsymbol{S}_j$ with $I_1 \simeq (\frac{2}{3}t')^2/U$ [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-2p and e_g orbitals; typically, $\tilde{t}/t \sim 2$. The corresponding Hamiltonian is [11]:

$$H_2^{(\gamma)} = I_2\ (2S_i^\gamma S_j^\gamma - \boldsymbol{S}_i \cdot \boldsymbol{S}_j). \qquad (3)$$

This is nothing but the model (1) with $K = -J = I_2 > 0$, i.e., at its SU(2) symmetric point $\varphi = \frac{3}{4}\pi$ inside the zigzag phase, see Fig. 2. For the Mott-insulating iridates (as opposed to charge-transfer cobaltates [11]), we estimate $I_2 \simeq \frac{4}{9}(\tilde{t}/\tilde{U})^2 \tilde{J}_H$, where $\tilde{U}$ is (optically active) excitation energy associated with $t_{2g} - e_g$ hopping, and $\tilde{J}_H$ is Hund's interaction between t_{2g} and e_g orbitals. The physics behind this expression is clear: $(\tilde{t}/\tilde{U})^2$ 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 $I_3 \simeq \frac{8}{3}(t^2/U)(J_H/U)$ [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 Δ_{pd}. Two holes may meet at an oxygen and experience Coulomb U_p and Hund's J_H^p interactions, or cycle around a Ir_2O_2 plaquette (Fig. 2). The resulting Hamiltonian H_4 has the form of H_2 (3). The coupling constant $I_4 \simeq \frac{8}{9}t^2(\frac{2}{2\Delta_{pd}+U_p-J_H^p} - \frac{1}{\Delta_{pd}})$ is negative [29], supporting stripy-AF not observed in Na_2IrO_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_2IrO_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.

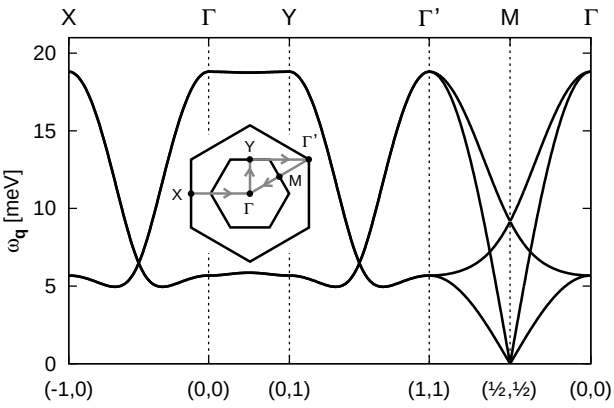

FIG. 3: Magnon spectra in the zigzag phase calculated using Eq. (4) with $(J, K) = (-4.0, 10.5)$ meV. The inset shows the path along the symmetry directions in the reciprocal space; notations of Ref. [4] are used.

Up to this point, we neglected trigonal field splitting Δ of the t_{2g} level due to the c-axis compression present in Na_2IrO_3. This approximation is valid as long as Δ is much smaller than spin-orbit coupling $\lambda \simeq 0.4$ eV [13, 15, 30] and seems to be justified, since the recent *ab-initio* calculations [20] suggest that $\Delta \simeq 75$ 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 $\frac{4}{9}(t_{2,3}^2/U)$]. The second (third)-NN interaction would oppose (support) zigzag order; however, we believe that these couplings are not significant in Na_2IrO_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_2IrO_3 and Li_2IrO_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:

$$\omega_{1,2}^2(h,k) = \left[K^2 + (K+J)^2\right] c_h^2 - KJ(1 - s_h s_k) \\ \pm |(K+J)c_h| \sqrt{(2K-J)^2 - (2Ks_h - Js_k)^2}\ , \quad (4)$$

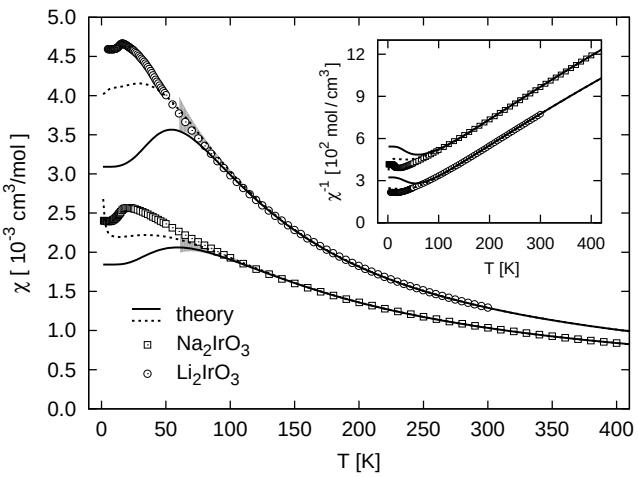

FIG. 4: Experimental magnetic susceptibilities $\chi(T)$ for Na_2IrO_3 [1, 6] (squares) and Li_2IrO_3 [6] (circles) fitted by the theoretical calculations. Exact χ of the 8-site (14-site) cluster is shown as solid (dashed) lines. Lanczos results for the 24-site cluster are indicated by shading [37]. Their comparison suggests that the calculated χ gives the thermodynamic limit down to $T \approx 100$ 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 $\varphi = \frac{3}{4}\pi$ 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 $\mathbf{q}$ with $h = k$, the dispersions (4) simplify to $\omega_1(h,h) = \sqrt{2K(2K+J)}\ |c_h|$ and $\omega_2(h,h) = \sqrt{2}|Jc_h|$, 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 Na_2IrO_3. We have therefore examined (see below) the magnetic susceptibility data [1, 6], and obtained $(J,K) \simeq (-4.0, 10.5)$ meV that well fit the susceptibility as well as neutron scattering data [4]. With this, we predict magnon spectra for Na_2IrO_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 φ 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 χ_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 Na_2IrO_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 Na_2IrO_3 near $\varphi = 111 \pm 2°$ of the model phase diagram Fig.1(a). The spin couplings obtained are reasonable for the 90°-exchange bonds (as expected [8, 11], they are much smaller than in 180°-bond perovskites [13, 14]). The magnitude of Van Vleck term also agrees with our estimate $\chi_0 \simeq \frac{8}{3\lambda}\mu_B^2 N_A \simeq 0.2 \times 10^{-3}$ cm^3/mol for Ir^{4+} ion, considering spin-orbit coupling $\lambda \simeq 0.4$ eV [13, 15, 30].

Dominance of the Kitaev term ($2K/J \sim 5$ in Na_2IrO_3) implies strong frustration hence enhanced quantum fluctuations; this explains the reduced ordered moment $m \simeq 0.22\,\mu_B$ [5]. With the J, K, and g values above, we calculated the leading order spin-wave correction to m and obtained $m \simeq 0.33\,\mu_B$ [38].

For the sake of curiosity, we have also fitted $\chi(T)$ data of Li_2IrO_3 [6], a sister compound of Na_2IrO_3. Acceptable results have been found for the angle window $\varphi = 124 \pm 6°$; 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 $T_N \simeq 15$ K, despite very different high temperature susceptibilities.

To conclude, we have clarified the origin of zigzag magnetic order in Na_2IrO_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°-exchange bonding geometry, including triangular, honeycomb, hyperkagome lattice iridates.

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