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# Magnetic Frustration via Bond-directional Interactions in a Honeycomb Lattice Iridate $\text{Na}_2\text{IrO}_3$

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Traditional approaches to stabilizing quantum spin liquids (QSL) have heavily relied on the geometrical frustration of antiferromagnetically coupled spins on lattices with triangular motifs such as pyrochlore and kagome structures. An alternative route is to exploit anisotropic interactions<sup>1-3</sup>, which are intrinsically bond-directed and hence compete with one another. A prime example is the Kitaev model<sup>4</sup>, which has a QSL as the exact solution but has yet to find a material realization. Here, we show that such bond-directional interactions govern the spin dynamics of the 5d transition-metal oxide  $\text{Na}_2\text{IrO}_3$  and lead to a strong magnetic frustration in a honeycomb lattice. Diffuse magnetic x-ray scattering reveals that spin-rotational symmetry is strongly broken even above the magnetic ordering temperature, with the three spin components exhibiting nano-scale correlations along three different crystallographic directions. This spin-component separation in real space provides direct evidence for dominant bond-directional interactions in  $\text{Na}_2\text{IrO}_3$  and establishes a new route toward frustrated magnetism.

Iridium (IV) ions with pseudospin-1/2 moments form in  $\text{Na}_2\text{IrO}_3$  a quasi-two-dimensional (2D) honeycomb network, which is sandwiched between two layers of oxygen ions that frame edge-shared octahedra around the magnetic ions and mediate superexchange interactions between neighboring pseudospins (Fig. 1a). Owing to the particular spin-orbital structure of the pseudospin<sup>5,6</sup>, the isotropic part of the magnetic interaction is strongly suppressed in the 90° bonding geometry of the edge-shared octahedra<sup>2,3</sup>, thereby allowing otherwise subdominant bond-dependent anisotropic interactions to play the main role and manifest themselves at the forefront of magnetism. This bonding geometry, common to many transition-metal oxides, in combination with the pseudospin that arises from strong spin-orbit coupling gives rise to an entirely new class of magnetism beyond the tra-

ditional paradigm of Heisenberg magnets. On a honeycomb lattice, for instance, the leading anisotropic interactions take the form of the Kitaev model<sup>3</sup>, which is a rare example of exactly solvable models with nontrivial properties such as Majorana fermions and non-abelian statistics, and with potential links to quantum computing<sup>4</sup>.

Realization of the Kitaev model is now being intensively sought out in a growing number of materials<sup>7-13</sup>, including 3D extensions of the honeycomb  $\text{Li}_2\text{IrO}_3$ , dubbed “hyper-honeycomb”<sup>7</sup> and “harmonic-honeycomb”<sup>8</sup>, and 4d transition-metal analogs such as  $\text{RuCl}_3$ <sup>12</sup> and  $\text{Li}_2\text{RhO}_3$ <sup>13</sup>. Although most of these are known to magnetically order at low temperature, they exhibit a rich array of magnetic structures including zig-zag<sup>14-16</sup>, spiral<sup>17</sup>, and other more complex non-coplanar structures<sup>18,19</sup> that are predicted to occur in the vicinity of the Kitaev QSL phase<sup>20-23</sup>, which hosts many degenerate ground states frustrated by three bond-directional Ising-type anisotropies. All of these magnetic orders are captured in an extended version of the Kitaev model written as

$$H = \sum_{\langle ij \rangle \gamma} [K S_i^\gamma S_j^\gamma + J \mathbf{S}_i \cdot \mathbf{S}_j + \Gamma (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha)], \quad (1)$$

which includes, in addition to the Kitaev term  $K$ , the Heisenberg exchange  $J$  that may be incompletely suppressed in the superexchange process and/or arise from a direct exchange process<sup>21</sup>, and the symmetric off-diagonal exchange term  $\Gamma$ , which is symmetry-allowed even in the absence of lattice distortions<sup>23-25</sup>. This “minimal” Hamiltonian couples pseudospins  $\mathbf{S}$  (hereafter referred to as ‘spin’) only on nearest-neighbor bonds  $\langle ij \rangle$ , neglecting further-neighbor couplings, which may be non-negligible. The bond-directional nature of the  $K$  and  $\Gamma$  terms is reflected in the spin components  $[\alpha \neq \beta \neq \gamma \in (x, y, z)]$  which they couple for a given bond ( $\gamma \in x-, y-, z\text{-bonds}$ )(Fig. 1a). For example, the  $K$  term couples only the spin component normal to the  $\text{Ir}_2\text{O}_6$  plaquette containing the particular bond.

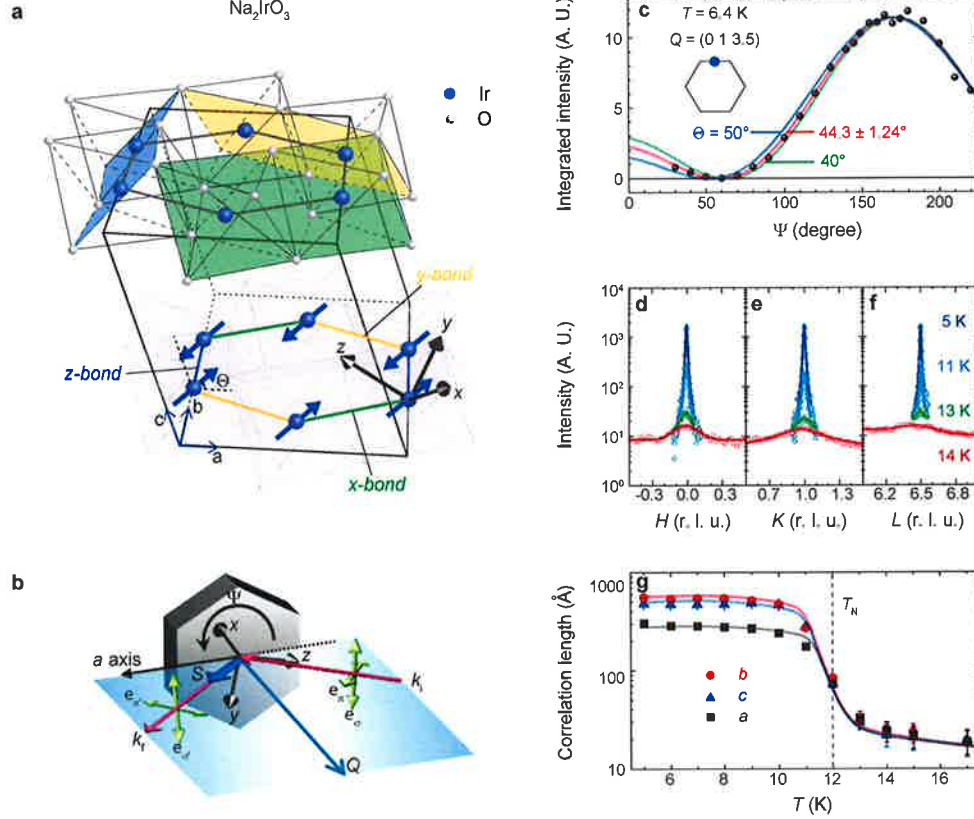


FIG. 1. **Magnetic easy axis and temperature dependence of the zig-zag order.** (a) Honeycomb layers of  $\text{Ir}^{4+}$  in the monoclinic Bravais lattice. Green, yellow, and blue planes show  $\text{Ir}_2\text{O}_6$  plaquettes normal to local  $x$ ,  $y$ , and  $z$  axes (black arrows), respectively, which point along three nearest neighbor Ir-O bonds in an octahedron. Ir-Ir bonds are labeled following the plaquettes they belong to.  $\text{Na}^+$  is not shown for clarity. Blue arrows show the spins in the static zig-zag order propagating along the  $b$  direction. Spins are antiparallel between the layers (not shown). (b) Illustration of the scattering geometry. Shown in blue is the scattering plane defined by the incident ( $\mathbf{k}_i$ ) and outgoing ( $\mathbf{k}_f$ ) wavevector (red arrows). Green arrows show the x-ray polarizations. The azimuth  $\Psi$  is defined as the angle between the  $a$  axis and the scattering plane. (c)  $\Psi$ -dependence of the magnetic Bragg peak (blue filled circle) intensity at  $(0\ 1\ 3.5)$  measured in the  $\sigma$ - $\pi'$  channel. Black hexagon is the Brillouin zone of the honeycomb net. Red solid line shows the best fitting result to the data with  $\Theta = 44.3^\circ$ . Green and blue lines show the calculated  $\Psi$  dependence for  $\Theta = 40^\circ$  and  $50^\circ$ , respectively. (d-f)  $H$ ,  $K$ , and  $L$  scans of the magnetic Bragg peak at  $(0\ 1\ 6.5)$  for selected temperatures. (g) Temperature dependence of the correlation lengths along the  $a$ ,  $b$ , and  $c$  axes from Gaussian fitting to the scans. Error bars represent the standard deviation in the fitting procedure. The solid lines are guides to eye.

Despite these extra terms that may account for finite-temperature magnetic orders in the candidate materials, the fact that the Kitaev QSL phase has a finite window of stability against these perturbations<sup>20,25</sup> calls for investigation of competing phases and a vigorous search for the Kitaev QSL phase.

Although the notion of magnetic frustration induced by competing bond-directional interactions is compelling, it remains a theoretical construct without an existential proof for such interactions in a real-world material. Moreover, theories for iridium compounds based on itinerant electrons suggest alternative pictures<sup>26–28</sup>. In principle, measurement of the dynamical structure factor through inelastic neutron scattering (INS) or resonant in-

elastic x-ray scattering (RIXS) provides the most direct access to the Hamiltonian describing the magnetic interactions. However, a fully momentum and energy resolved dynamical structure factor thus far remains elusive for any of the candidate materials; RIXS suffers from insufficient energy resolution<sup>29</sup> and INS is currently limited by unavailability of large-volume single crystals<sup>15</sup>. In this Letter, we take a new approach using diffuse magnetic x-ray scattering to provide direct evidence for predominant bond-directional interactions in  $\text{Na}_2\text{IrO}_3$  via the measurement of equal-time correlations of spin components above the ordering temperature ( $T_N = 12\text{--}15\text{ K}$ , See Fig. S1).

We start from establishing the spin orientation in the

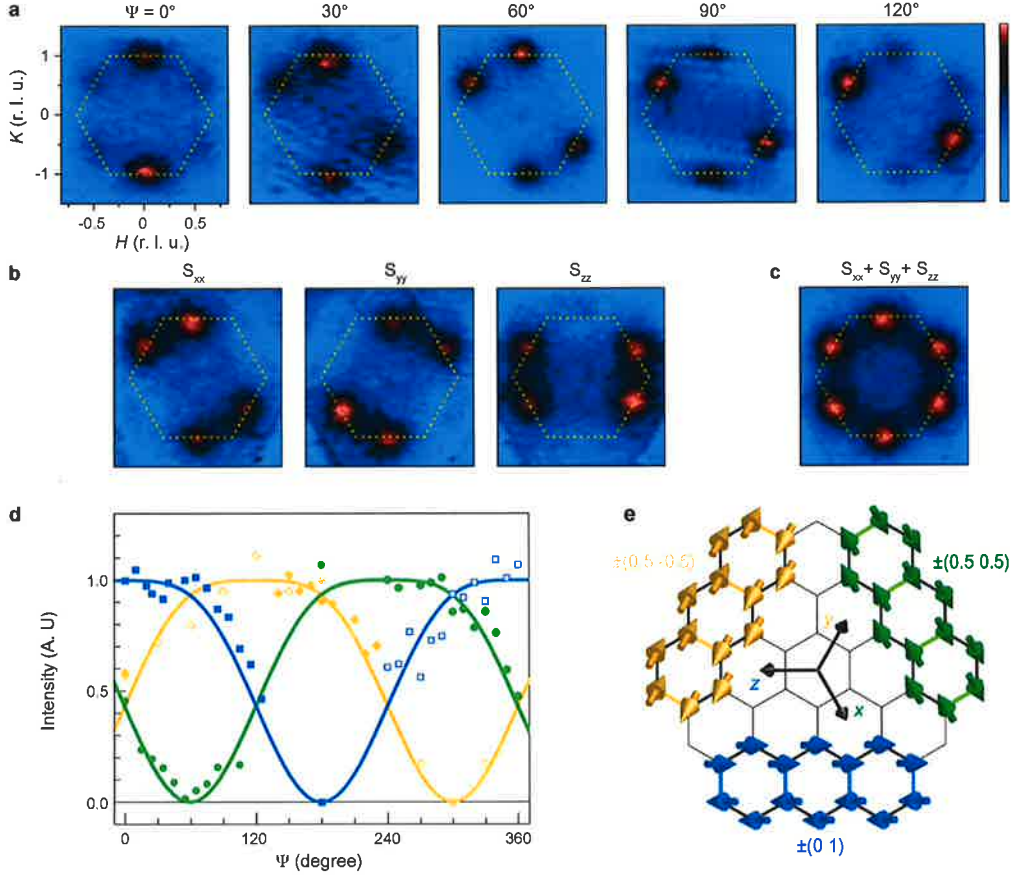


FIG. 2. Diffuse magnetic x-ray scattering intensities above  $T_N$ . (a) Intensity plots in the HK plane measured at  $T = 17$  K for selected azimuth angles summing  $\pi$ - $\sigma'$  and  $\pi$ - $\pi'$  channels, sensitive to spin components parallel to  $\mathbf{k}_i$  and perpendicular to the scattering plane, respectively. For example,  $\Psi = 0^\circ$  measures sum of correlations  $S_{xx}$  and  $S_{yy}$ . The dashed hexagon indicates the first Brillouin zone of the honeycomb net. (b) Spin-component-resolved equal-time correlations extracted from (a). (c) Spin-component-integrated equal-time correlations extracted from (a). Peaks are located at  $\mathbf{Q} = \pm(0, 1)$ ,  $\pm(0.5, 0.5)$ , and  $\pm(0.5, -0.5)$ . (d)  $\Psi$ -dependence of the diffuse peak intensities for Sample #1 (open symbol) and #2 (closed symbol). Solid lines show the calculated  $\Psi$ -dependence for  $x$ -,  $y$ -, and  $z$ -zig-zag states shown in (e) for the  $\pi$ - $\sigma'$  and  $\pi$ - $\pi'$  polarization channels summed. (e) Zig-zag orders propagating along three equivalent directions. Blue zig-zag is the static structure, and green and yellow zig-zags are generated by  $120^\circ$  rotation of the blue zig-zag.

static zig-zag order<sup>14–16</sup> below  $T_N$ , as shown in Fig. 1a, using standard resonant magnetic x-ray diffraction. In this measurement, the x-ray polarization projects out a certain spin component; the intensity depends on the spin orientation via the relation  $I \propto |\mathbf{k}_f \cdot \mathbf{S}|^2$  for the  $\sigma$ - $\pi'$  channel measured, where  $\mathbf{k}_f$  is the scattered x-ray wave vector (Fig. 1b). Figure 1c shows the intensity variation as the sample is rotated about the ordering wave vector  $\mathbf{Q} = (0, 1, 3.5)$  by an azimuth angle  $\Psi$ , which causes  $\mathbf{S}$  to precess around  $\mathbf{Q}$ . Earlier studies<sup>14,16</sup> have established that  $\mathbf{S}$  is constrained to lie in the  $ac$  plane, so this measurement of  $I(\Psi)$  determines the spin orientation by resolving the tilting angle  $\Theta$  of  $\mathbf{S}$  with respect to the  $a$  axis. The best fitting result with  $\Theta = 44.3^\circ$  indicates that the magnetic easy axis is approximately half way in between the cubic  $x$  and  $y$  axes (Fig. 1a). This static spin orientation is a compromise among all anisotropic interactions present in the system, and is strongly tied to the magnetic struc-

ture because of their bond-directional nature. To see this point, consider, for example, the  $K$  term: in the zig-zag structure propagating along  $b$  direction, where the spins are antiferromagnetically aligned on the  $z$ -bond and ferromagnetically aligned on the  $x$ -bond and  $y$ -bond, a ferromagnetic (antiferromagnetic)  $K$  favors spins pointing perpendicular to (along) the  $z$ -axis for a pair of spins on the  $z$ -bond, and along (perpendicular to) the  $x$ -axis and  $y$ -axis for the pairs on the  $x$ -bond and  $y$ -bond, respectively.

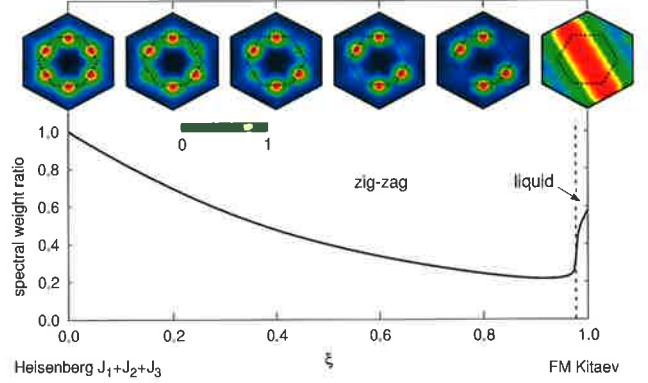
The zig-zag order is one of the many magnetic states (including the aforementioned spiral and non-coplanar structures) that are classically degenerate in the pure Kitaev limit<sup>30</sup> and comprise the micro-states in the QSL phase. Away from the pure Kitaev limit, depending on their energy separations, signatures of other magnetic states and their associated magnetic anisotropies may become observable in the paramagnetic phase through



diffuse magnetic scattering. In particular, zig-zag orders propagating in two other directions,  $\pm 120^\circ$  rotated from the static one, are expected for a honeycomb net with  $C_3$  symmetry. [The actual 3D crystal structure has only an approximate  $C_3$  symmetry because of a monoclinic distortion, which singles out one propagation direction for the long-range ordered state (along  $b$  direction) out of the three possible under the ideal  $C_3$  symmetry<sup>15</sup>.]

With other magnetic correlations possibly emerging at high temperature in mind, we follow the temperature evolution of the zig-zag order. Figures 1d-f show  $H$ ,  $K$ , and  $L$  scans, respectively, of the magnetic Bragg peak at  $\mathbf{Q} = (0\ 1\ 6.5)$  for selected temperatures. Figure 1g shows the correlation lengths along the  $a$ ,  $b$ , and  $c$  axes as a function of temperature. As the temperature increases above  $T_N$ , the zig-zag correlations diminish rather isotropically despite dominant 2D couplings in the honeycomb net. This 3D characteristic of the magnetic correlations contrasts with that of the quasi-2D Heisenberg antiferromagnet  $\text{Sr}_2\text{IrO}_4$ , which displays 2D long-range correlations well above  $T_N$ <sup>31</sup>, and implies that the critical temperature in  $\text{Na}_2\text{IrO}_3$  is limited by the anisotropic interactions rather than the interlayer coupling; the Mermin-Wagner theorem requires either the symmetry to be lower than  $\text{SU}(2)$  or the dimension to be higher than 2D for a finite temperature phase transition. The zig-zag correlations survive on the length scale of several nanometers (approximately 3 unit cells wide) above  $T_N$ , but the peak intensities drop by two orders of magnitude. To isolate such small signals from the background, we used an experimental setup that maximizes the signal-to-noise ratio as described in the Methods section.

Figure 2a maps the diffuse scattering intensity over a region in momentum space encompassing a full Brillouin zone of the honeycomb net, at several different  $\Psi$  angles to resolve the spin-components (see Fig. S2). These maps integrate the dynamic structure factor over the range  $0 \leq \omega \leq 100$  meV, covering the entire range of magnetic excitations (see Fig. 4), and serve as an excellent approximation for the equal-time correlation  $S_{\alpha\alpha} = \langle S_{\mathbf{Q}}^\alpha S_{-\mathbf{Q}}^\alpha \rangle$  ( $\alpha = x, y, z$ ). When averaged over the three spin components, the intensity map (Fig. 2c) indeed shows three zig-zag correlations above  $T_N$  with peaks at  $\mathbf{Q} = \pm(0\ 1)$ ,  $\pm(0.5\ 0.5)$ , and  $\pm(0.5\ -0.5)$  of equal intensities, confirming the near-ideal  $C_3$  symmetry. However, the spin-component resolved maps, shown in Fig. 2b, manifestly break the  $C_3$  symmetry. The system is left invariant only when  $C_3$  rotation is performed simultaneously in the real space and in the spin space, i.e. cyclic permutation of spin indices. This ‘global’  $C_3$  symmetry implies a strong entanglement between the real space and the spin space. Specifically, the full azimuth dependence of each zig-zag state, shown in Fig. 2d, follows well the curves simulated for spin orientation fixed relative to the propagation direction, as depicted in Fig. 2e. In other words, specifying a spin component amounts to fixing the momentum direction and vice versa. This one-to-one correspondence



**FIG. 3. Simulation of diffuse scattering using exact diagonalization.** The Kitaev-Heisenberg model including up to third nearest-neighbor Heisenberg interactions was considered.  $\xi$  interpolates between the pure Heisenberg model and the pure Kitaev model via  $J_1=J_2=J_3=1-\xi$  and  $K=-\xi$ . A ferromagnetic  $K$  with finite  $J_1, J_2$ , and  $J_3$  stabilizes the zig-zag state for most values of  $\xi$ . The black curve shows the spectral asymmetry defined as the ratio of spectral weight at  $\mathbf{Q}=(0.5, 0.5)$  to that at  $\mathbf{Q}=(0\ 1)$ . Images show equal-time correlations  $\langle S_{\mathbf{Q}}^\alpha S_{-\mathbf{Q}}^\alpha \rangle$  obtained by exact diagonalization using a 24-site cluster and plotted in the extended Brillouin zone for selected  $\xi$ . The correlations for  $y$  and  $z$  components (not shown) can be generated by  $\pm 120^\circ$  rotations of the images shown.

between the spin space and the real space is a direct consequence of the bond-dependent nature of the anisotropic exchange terms.

Qualitatively, it is immediately seen that the anisotropic interactions dominate over the isotropic interactions and the system is very far away from the pure Heisenberg limit, in which case the spatial correlations must be spin-component independent with three zig-zag peaks having equal intensities by symmetry (as in the spin-averaged correlation shown in Fig. 2c preserving  $C_3$  symmetry). A measure of how close the system is to either the Heisenberg or the Kitaev limits is provided by the intensity ratio of the weakest peak to the two bright ones in the spin-component-resolved correlations (Fig. 2b). To quantify this measure, represented by a variable linearly interpolating between these two limits,  $\xi$ , requires specifying the minimal Hamiltonian, which is not precisely known. For an estimation at a semi-quantitative level, we adopt a simple Hamiltonian that neglects all anisotropic terms beyond the  $K$  term. (This in turn requires including further neighbor Heisenberg couplings  $J_2$  and  $J_3$  to stabilize the zig-zag order<sup>32</sup>, which we take to be equal to  $J_1$  for simplicity.) Figure 3 shows the simulated patterns for selected  $\xi$ . It is clear that the observed diffuse pattern is consistent with the simulated one for the large  $\xi$  limit. In fact, the observed intensity ratio of  $\approx 0.2$  is even smaller than calculated (Fig. 3) for the largest  $\xi$  in the zig-zag phase, which confirms the predominant anisotropic interactions.

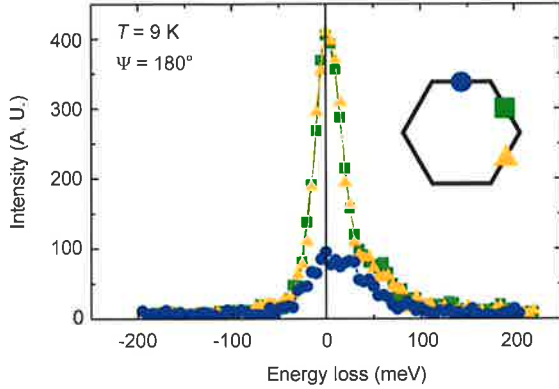


FIG. 4. **Resonant inelastic x-ray scattering spectra below  $T_N$ .** RIXS spectra recorded at  $T=9$  K and  $\Psi=180^\circ$ .  $\mathbf{Q} = (0\ 1)$ ,  $(0.5\ 0.5)$ , and  $(0.5\ -0.5)$ , shown as blue, green, and yellow filled symbols, respectively, marked on the Brillouin zone of the honeycomb net and color-coded with the spectra. At this  $\Psi$  angle,  $\mathbf{S}$  lies approximately along  $\mathbf{k}_f$  and  $\pi$ - $\sigma'$  and  $\pi$ - $\pi'$  channels measure the two spin components transverse to  $\mathbf{S}$ .

Interpreted within this model, our calculations would imply that the system is very close to the Kitaev limit. However, it is becoming increasingly evident that other anisotropic terms beyond the Kitaev interaction do play a role<sup>22,23</sup>. This is, in fact, evident from the static spin not pointing along one of the cubic axes favored by the  $K$  term; all other anisotropic terms conspire to rotate the spin away from the principal axes. This in turn suggests that the zig-zag structure is further stabilized by other anisotropic terms. The zig-zag correlations survive at least up to  $\sim 70$  K (see Fig. S3), which is in accord with the observation that coherent spin-waves<sup>15</sup> disperse up to  $\approx 5$  meV. This energy scale coincides with the temperature scale ( $\approx 100$  K) below which the magnetic susceptibility deviates from the Curie-Weiss behavior<sup>33</sup>. This

energy scale is, however, still far too small in comparison to the energy ( $\approx 100$  meV) spanned by the magnetic excitations (Fig. 4), suggesting that the zig-zag order is an emergent phenomenon. Despite that the macroscopic degeneracy in the Kitaev QSL phase is reduced down to three zig-zags, the high-energy Kitaev interactions leave their signature in the low-energy sector: the three spin components, each carrying its own zig-zag, compete and melt the long-range order at a temperature much lower than that suggested by the Weiss temperature ( $\Theta_W$ ), leading to a large frustration parameter<sup>33</sup> ( $\equiv \Theta_W/T_N$ ) of  $\approx 8$ .

Beneath a rather mundane static collinear antiferromagnetic structure, the spins on the honeycomb lattice undergo fluctuations of a peculiar type that suppress the tendency to order. To reveal their full dynamics remains a challenge, but RIXS allows a glimpse into their unconventional nature. Figure 4 shows the excitation spectra recorded in the ordered phase, in the scattering geometry that probes two spin components transverse to the static moment. The soft excitations ( $\omega \approx 0$ ) are observed at  $\mathbf{Q} = \pm(0.5\ 0.5)$  and  $\mathbf{Q} = \pm(0.5\ -0.5)$ , away from the Bragg peak at  $\mathbf{Q} = (0\ \pm 1)$ . This is a notable exception to the universality held in conventional magnets that spin waves emanate from Bragg peaks by virtue of the Goldstone theorem, and magnetic anisotropy is manifested as a spin-wave gap, even in systems with extremely large magnetic anisotropy<sup>34</sup>. By contrast, the spin gap in our system is small (unresolved in our spectra and estimated to be smaller than 2 meV from INS data<sup>15</sup>) compared to the overall energy scale of the system, despite the fact that the magnetism is dominated by the anisotropic terms. Rather, the anisotropy is manifested as the separation of the long-wavelength spin waves from the Bragg peaks, which is a natural consequence of each spin component displaying its own real-space correlations. Our results reveal the key fingerprint of the Kitaev model in  $\text{Na}_2\text{IrO}_3$ , and paves a new path for frustrated magnetism via the bond-directional magnetic couplings.

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**Author contribution** B.J.K. conceived the project. S.H.C., J.W.K., J.K., and B.J.K. performed the experiment with support from Y.C., T.G., A.A., M.M.S., and M.K. H.Z. and K.M. grew the single crystals; C.S., C.M., and K.M. characterized the samples under supervision of J.F.M. and Y.S. S.H.C., J.W.K., and B.J.K. analyzed the data. J.C. performed the numerical calculations; J.C., G.J., and G.K. developed the theoretical model. All authors discussed the results. B.J.K. led the manuscript preparation with contributions from all authors.

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## Supplementary Information

### A. Methods

#### A.1 Single crystal growth & characterization

Single crystals of  $\text{Na}_2\text{IrO}_3$  were grown following two different recipes using  $\text{Na}_2\text{CO}_3$  flux (Sample #1) and self-flux (Sample #2). For Sample #1, a mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{IrO}_2$  with a molar ratio of 50 : 1 was melted at  $1050^\circ\text{C}$  for 6 hours followed by fast cooling at a rate of  $100^\circ\text{C}/\text{hour}$  down to  $1000^\circ\text{C}$ , slow cooling at a rate of  $1^\circ\text{C}/\text{hour}$  down to  $800^\circ\text{C}$  and furnace-cooling to room temperature in a sequence. Hexagonal pillar-shaped crystals with typical dimension of  $0.2\text{ mm} \times 0.2\text{ mm} \times 0.4\text{ mm}$  were obtained after dissolving  $\text{Na}_2\text{CO}_3$  flux in acetone and water. For Sample #2, powders of  $\text{Na}_2\text{CO}_3$  were mixed with 10-20% excess  $\text{IrO}_2$  and were calcined at  $700^\circ\text{C}$  for 24 hours. Single crystals were grown on top of a powder matrix in a subsequent heating at  $1050^\circ\text{C}$ . Plate-like crystals with typical dimension of  $5\text{ mm} \times 5\text{ mm} \times 0.1\text{ mm}$  were physically extracted.

The powder x-ray diffraction patterns of both Sample #1 and #2 were consistent with the crystal structure in

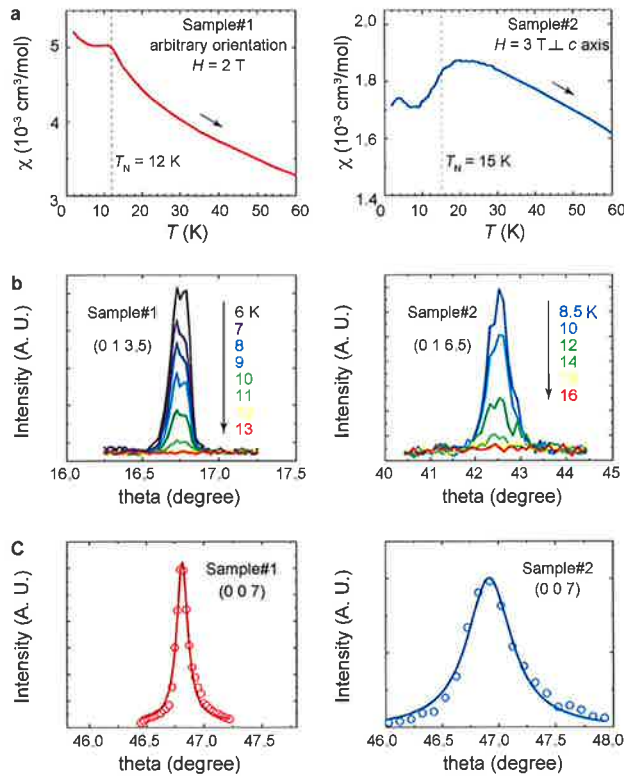


FIG. S1. **Characterization of Sample #1 and Sample #2** (a) Temperature dependence of magnetic susceptibility. Dotted lines indicate  $T_N$ . Black arrows indicate that the data were measured while warming after zero-field cooling. (b) Temperature dependence of the magnetic Bragg peaks. (c) Sample mosaicity.

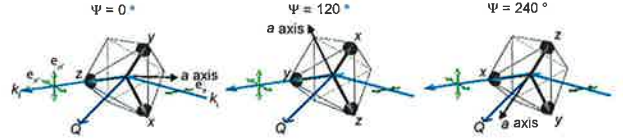


FIG. S2. **Scattering configurations.** (a)  $\Psi = 0^\circ$ , (b)  $\Psi = 120^\circ$ , and (c)  $\Psi = 240^\circ$ . The azimuth  $\Psi$  is the angle between the  $a$  axis and the scattering plane. Thick black arrows denote the local  $x$ ,  $y$ , and  $z$  axes in the  $\text{IrO}_6$  octahedron.  $a$  axis is indicated by a thin black arrow. Cyan arrows are the incident and scattered x-rays with the wave vectors  $\mathbf{k}_i$  and  $\mathbf{k}_f$ , respectively. Green arrows indicate the x-ray polarizations.  $\mathbf{Q}$  (dark blue arrow) is the momentum transfer.

the  $\text{C2}/m$  space group as previously reported<sup>15</sup>. Sample #1 had a slightly lower  $T_N = 12\text{ K}$  compared to Sample #2 with  $T_N = 15\text{ K}$ , as measured by SQUID magnetometry (Fig. S1a) and by resonant x-ray diffraction through the magnetic Bragg peaks at  $Q = (0\ 1\ n + \frac{1}{2})$  ( $n$ : integer) (Fig. S1b). Sample #1 was found to be of multi domains but had a superior crystallinity with  $0.1^\circ$  mosaicity (as compared to  $0.5^\circ$  mosaicity of Sample #2) (Fig. S1c), and thus was used for the resonant diffraction experiment (polarization analysis and measurement of the magnetic correlation length.) Sample #2 was found to be of a single domain and was used for the RIXS measurement. Both Sample #1 and #2 were used for the diffuse scattering measurement and gave identical results.

#### A.2 Resonant x-ray scattering

Incident x-ray was tuned to Ir  $L_3$  edge (11.2145 keV). The resonant x-ray diffraction was carried out at 6 ID-B beamline of the Advanced Photon Source. The polarization analysis was performed in the vertical scattering geometry using a pyrolytic graphite analyzer probing  $\sigma$ - $\pi'$  channel. The RIXS was performed at ID20 of the European Synchrotron Radiation Facility. The total instrumental energy resolution of 24 meV was achieved with a monochromator and a diced spherical analyzer made from Si (844) and a position-sensitive area detector placed on a Rowland circle with 2m radius. The diffuse magnetic scattering was performed using the RIXS spectrometers at 9 ID, 27 ID, and 30 ID (MERIX) beamlines of the Advanced Photon Source where a monochromator of 90 meV bandwidth was used for an order of magnitude higher incident photon flux than that from the Si (844) monochromator. In these experiments, horizontal scattering geometry was used with the  $\pi$ -incident x-ray polarization measuring the sum of  $\pi$ - $\sigma'$  and  $\pi$ - $\pi'$  channels. The in-plane momentum resolution of the RIXS spectrometer was  $\pm 0.048\text{ \AA}^{-1}$ . The use of the RIXS spectrometers rejecting all inelastically scattered x-rays outside of the 100 meV energy window centered at the elastic line led to a significant improvement in the signal-to-noise ratio. A typical counting time of 2 hours was required for a map shown in Fig. 2.



### B. Extraction of the spin-component resolved equal-time correlators

The x-ray scattering intensity measured without using a polarization analyzer contains contributions from both  $\pi$ - $\sigma'$  and  $\pi$ - $\pi'$  channels, probing spin components along  $\mathbf{k}_i$  and perpendicular to the horizontal scattering plane, respectively. In other words, two spin components perpendicular to  $\mathbf{k}_f$  are measured in the  $90^\circ$  horizontal scattering geometry used. For example, when  $\Psi=0^\circ$ , the  $z$  local cubic axis points approximately along  $\mathbf{k}_f$  (Fig. S2), and thus the scattering intensity measures the correlation  $S_{xx}+S_{yy}$ . Likewise,  $\Psi=120^\circ$  ( $\Psi=240^\circ$ ) measures  $S_{xx}+S_{zz}$  ( $S_{yy}+S_{zz}$ ). Then,  $S_{xx}$ ,  $S_{yy}$ , and  $S_{zz}$  can be extracted by solving a set of linear equations.

### C. Temperature dependence of the diffuse magnetic peak

The short-range zig-zag order is observable at least up to  $T \approx 70$  K (Fig. S3a). The magnetic correlation length (1.6-1.8 nm) along the  $a$  axis does not vary significantly in the measured temperature region. Fig. S3b plots the diffuse map at  $\Psi=0^\circ$  at  $T=50$  K, which is similar to the diffuse map recorded at  $T=17$  K (shown in Fig. 2a)

apart from thermal broadenings.

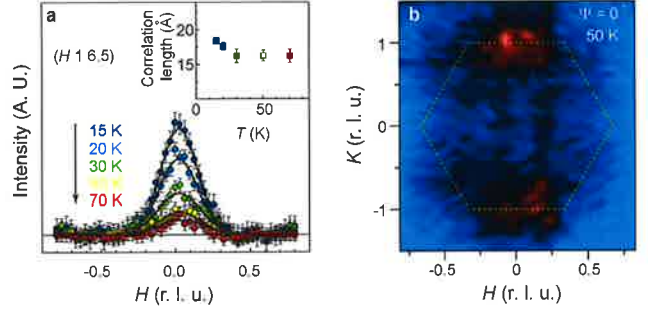


FIG. S3. Diffuse magnetic x-ray scattering intensities above  $T_N$ . (a)  $H$  profiles of the diffuse peak at  $Q = (0\ 1)$ . Shown in the inset is the magnetic correlation length along the  $a$  axis derived from Gaussian fitting (solid curves) of the data for Sample #1. (b) Diffuse map at  $\Psi=0^\circ$  at  $T=50$  K. The dashed hexagon indicates the first Brillouin zone of the honeycomb net.