Crystal field splitting and correlation effect on the electronic structure of $A_2$IrO$_3$

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The electronic structure of the honeycomb lattice iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$ has been investigated using resonant inelastic x-ray scattering (RIXS). Crystal-field split $d$-$d$ excitations are resolved in the high-resolution RIXS spectra. In particular, the splitting due to non-cubic crystal fields, derived from the splitting of $j_{\text{eff}}$=3/2 states, is much smaller than the typical spin-orbit energy scale in iridates, validating the applicability of $j_{\text{eff}}$ physics in $A_2$IrO$_3$. We also find excitonic enhancement of the particle-hole excitation gap around 0.4 eV, indicating that the nearest-neighbor Coulomb interaction could be large. These findings suggest that both Na$_2$IrO$_3$ and Li$_2$IrO$_3$ can be described as spin-orbit Mott insulators, similar to the square lattice iridate Sr$_2$IrO$_4$.

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The intense interest in iridium oxides, or iridates, arises from a number of competing interactions of similar magnitude. While the on-site Coulomb interaction is the dominant energy scale in 3$d$ transition metal oxides, the spin-orbit coupling (SOC) is largely ignored. On the other hand, for 5$d$ elements such as Ir, the SOC becomes significant, and in fact plays a dominant role. A good example is Sr$_2$IrO$_4$, whose electronic states are well described by $j_{\text{eff}}$=1/2 states arising from the spin-orbit split $t_{2g}$ levels.

One of the most intensely scrutinized families of iridates is the honeycomb lattice family $A_2$IrO$_3$ ($A$=Na,Li). Originally thought of as topological insulators, these materials are now believed to be Mott insulators. A recent calculation suggests that uniaxial strain might still drive the system to topological insulating behavior. Furthermore, these materials could be described with the Kitaev-Heisenberg model, in which bond-dependent Kitaev interaction are realized and support various types of topological phases. The applicability of such intriguing theoretical possibilities to real system crucially depends on the $j_{\text{eff}}$ physics arising from strong SOC. However, the experimental situation seems to be far from clear. In particular, structural refinements find a sizable trigonal distortion of the IrO$_6$ octahedra, which will produce crystal field splittings within the $t_{2g}$ manifold. If the splitting is comparable to the SOC, the $j_{\text{eff}}$=1/2 states will mix with the $j_{\text{eff}}$=3/2 states and the relevant microscopic model becomes quite different from the ideal $j_{\text{eff}}$ physics, preventing the Kitaev-Heisenberg model from being realized. Recent theoretical studies have even suggested that the ground state has a large contribution from the $j_{\text{eff}}$=3/2 state.

Therefore, it is of great importance to elucidate the underlying electronic structure of Na$_2$IrO$_3$ experimentally. In particular, the spectroscopic investigation of excitations between spin-orbit split $j_{\text{eff}}$ states can provide us with direct information regarding the size of the crystal field splitting with respect to the typical SOC energy scale in iridates (0.4-0.5 eV). In the case of Sr$_2$IrO$_4$, such excitations between $j_{\text{eff}}$=3/2 to $j_{\text{eff}}$=1/2 were observed around 0.6-0.8 eV in the resonant inelastic x-ray scattering (RIXS) data, which is accounted for in the quantum chemical calculation by Katukuri et al. The splitting within these “spin-orbit” excitations arises due to non-zero tetragonal crystal fields, and is much smaller (~0.1 eV) than the SOC, justifying the $j_{\text{eff}}$ description of Sr$_2$IrO$_4$.

In this Letter, we present a comprehensive picture of the low energy electronic structure of Na$_2$IrO$_3$ and Li$_2$IrO$_3$, based on Ir $L_3$-edge RIXS experiments. Our high-resolution RIXS measurements allow us to resolve the crystal field splitting of the $j_{\text{eff}}$=3/2 states due to the trigonal distortion, which is determined to be about 110 meV in both compounds. This energy scale agrees very well with quantum chemical calculations, and is much smaller than the typical value for SOC, validating the $j_{\text{eff}}$ picture in these compounds. We have also studied momentum dependence of the insulating gap; the observed flat dispersion of the insulating gap is consistent with what is expected from a significant Coulomb interaction in both compounds. Taken together, we argue that just as Sr$_2$IrO$_4$, the honeycomb $A_2$IrO$_3$ iridates can
be described as spin-orbit Mott insulators \[2, 14, 17, 20\].

The RIXS experiment was carried out at the Advanced Photon Source using the 30ID MERIX and 9ID RIXS spectrometer. A spherical (1 m radius) diced Si(844) analyzer and Si(844) secondary monochromator were used to obtain overall energy resolution (FWHM) of \(\sim 35\) meV. To minimize the elastic background, most of the measurements were carried out in a horizontal scattering geometry near \(Q = (0 0 6.7)\), for which the scattering angle \(2\theta\) was close to 90°. We use the \(C2/m\) notation for the lattice \[13, 14\]. A single crystal of \(Na_2IrO_3\) and a polycrystalline samples of \(Li_2IrO_3\) were grown by the solid state synthesis method, previously described in detail \[10, 11\]. The \(Na_2IrO_3\) crystal was plate-like with a flat shiny surface, the surface normal was in the (001) direction.

The RIXS process at the \(L_3\)-edge of Ir (or any other d electron system) is a second order process consisting of two dipole transitions (\(2p \rightarrow 5d\) followed by \(5d \rightarrow 2p\)). Therefore, it is especially valuable for detecting excitations between the \(d\)-levels and has been extensively utilized in the study of 3d transition metal compounds \[21–23\]. Recent instrumental advances have made it possible to measure collective magnetic excitations \[21, 22\]. In \(A_2IrO_3\), \(Ir^{4+}\) ions are in the 5d5 configuration in a slightly distorted octahedral environment of oxygen ions, with the edge-sharing \(IrO_6\) octahedra forming a honeycomb net. Due to the octahedral crystal field, there exists a fairly large splitting (10Dq) between the \(t_{2g}\) and \(e_g\) states. Since the 5d orbitals are spatially more extended than the 3d orbitals, the 10Dq value is expected to be much larger. Indeed, in our RIXS investigations of various iridium compounds, well separated \(t_{2g}\) and \(e_g\) states have been observed, with the 10Dq value typically about 3 eV \[24\].

In Fig. 1, a representative high-resolution RIXS spectrum of \(Na_2IrO_3\) is plotted on a wide energy scale. This scan was obtained at room temperature and plotted as a function of energy loss (\(\hbar \omega = E_i - E_f\)). The incident energy, \(E_i = 11.217\) keV, was chosen to maximize the resonant enhancement of the spectral features of interest below 1 eV. A broad and strong feature is observed at 2-4 eV and other sharper features are observed below 1 eV, corresponding to \(d-d\) transitions from occupied \(t_{2g}\) states into the empty \(e_g\) and \(t_{2g}\) levels, respectively. Also plotted in the figure is the room temperature data of polycrystalline \(Li_2IrO_3\). Lack of significant momentum dependence of these \(d-d\) excitations (shown later in Fig. 3) allows one to directly compare the peak positions between the single crystal and powder samples. The spectra were fit to 5 peaks (labeled A-E), as shown by the black dashed lines. The low energy excitations can be fit to three peaks, two Gaussians (B and C) of the same width and one Lorentzian (A) on top of a broad background (Gaussian). Two Lorentzian functions with sloping background were used to fit the higher energy excitations (D and E). The resulting peak positions are listed in Table I.

To clarify the nature of the excitations revealed by RIXS, we have carried out multiconfiguration self-consistent-field and multireference configuration-interaction (MRCI) calculations \[28\] on clusters consisting of one central \(IrO_6\) octahedron, all adjacent Na or Li ions, and the three nearest-neighbor (NN) \(IrO_6\) octahedra (see Ref. \[19\] and Supplemental Material for details). Local \(d-d\) transitions are computed only for the central \(IrO_6\) octahedron while the NN octahedra are explicitly included in the cluster for providing an accurate description of the nearby charge distribution. Two different lattice configurations are considered, i.e., the \(C2/c\) structure \[10, 20\] and also the \(C2/m\) arrangement proposed more recently \[15, 16, 20\].

Results of spin-orbit MRCI (MRCI+SOC) calculations

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**TABLE I: RIXS and MRCI+SOC excitation energies \((C2/m\) structure) for 213 iridates (eV).**

|      | \(Na213\) RIXS | \(Na213\) MRCI | \(Li213\) RIXS | \(Li213\) MRCI |
|------|----------------|----------------|----------------|----------------|
| Peak A | 0.42(1) | – | 0.45(2) | – |
| Peak B | 0.72(2) | 0.82 | 0.72(2) | 0.80 |
| Peak C | 0.83(2) | 0.89 | 0.83(2) | 0.97 |
| Peak D | 2.4(1) | 2.8–3.4 | 2.6(1) | 3.1–3.7 |
| Peak E | 3.3(1) | 3.8–4.1 | 3.5(1) | 4.1–5.0 |
using the $C2/m$ configuration are listed for Na$_2$IrO$_3$ in the third column of Table I. The MRCl+SOC data fit the experiment reasonably well, with peaks B and C corresponding to $j_{\text{eff}}=3/2$ to $j_{\text{eff}}=1/2$ electronic transitions. Above 2.5 eV, the MRCl+SOC results indicate multiple $t_{2g}$ to $e_g$ excitations displaying a two-peak structure reminiscent of the D and E features in the RIXS spectra. However, MRCl+SOC seems to overestimate somewhat the relative energies of those latter features. Interestingly, for the alternative $C2/c$ structure of Na$_2$IrO$_3$ [10], the splitting between the two doublets originating from the $j_{\text{eff}}=3/2$ quartet in an ideal octahedral environment is much larger and the position of the C peak is overestimated by 0.25 eV in the MRCl+SOC treatment. Since the deviations from the experimental data are in this case larger, the MRCl+SOC results for $C2/c$ symmetry are not listed in Table I. The $t_{2g}$ splittings in calculations with no SOC are in fact as large as 0.6 eV for the $C2/c$ structure of Na$_2$IrO$_3$, which gives rise to a highly uneven admixture of $t_{2g}$ components in the spin-orbit calculations. In contrast, for the $C2/m$ configuration, the $t_{2g}$ splittings are about 0.1 eV and the three different $t_{2g}$ hole configurations contribute with similar weight to the spin-orbit ground-state wave function (see Table II).

For Li$_2$IrO$_3$, the calculations correctly reproduce the shift to higher energies of the $t_{2g}$ to $e_g$ transitions relative to those in Na$_2$IrO$_3$. The discrepancy between the experimental values and the MRCl+SOC results (e.g., peak C) could be caused by the uncertainty in the structural model used for this calculation ($C2/m$ from Ref. [29]). Since local structural disorder is not easily captured in the regular diffraction data, local structure probes such as pair-distribution function (PDF) measurements can sometimes be useful for clarifying the structural details. We have carried out X-ray PDF studies on Li$_2$IrO$_3$ and Na$_2$IrO$_3$ powder samples. Details of these measurements and the comparison of the two structures are reported in the Supplemental Material. Except for the overall lattice contraction, the Li$_2$IrO$_3$ PDF seems to be well described by the $C2/m$ symmetry, eliminating the local structural disorder as a possible explanation. Most likely cause of the structural uncertainty is the oxygen position, since x-ray structural probes are not particularly sensitive to light elements like oxygen [29, 30]. We note that the latest refinements using both powder neutron and single crystal x-ray data on Na$_2$IrO$_3$ do show important differences compared to earlier x-ray powder diffraction data and the MRCl+SOC results are very different for the two structures. Better structural refinements using neutron diffraction would reduce the oxygen position uncertainty in Li$_2$IrO$_3$ and could improve the agreement between our MRCl+SOC calculation and the experiment.

One of our main findings is that the splitting of the strong RIXS peak located at 0.7-0.8 eV is due to the trigonal distortion which is well corroborated with our MRCl+SOC calculations. The fact that this splitting (110 meV) is much smaller than a SOC of 0.4-0.5 eV strongly supports that these excitations are transitions from crystal-field-split $j_{\text{eff}}=3/2$ to $j_{\text{eff}}=1/2$ states (labeled spin-orbit exciton in Ref. [8]). Given that the optical gap in this material is about 350 meV [20] and that there is no such excitation in the MRCl+SOC calculations which only look at on-site $d$-$d$ excitations, it is reasonable to associate feature A at low energy as arising from the excitation of a particle and hole pair across the charge gap. Additional periodic density functional theory (DFT) calculations shows that a moderate size $U$ and SOC can indeed open a (Mott) gap of 300-400 meV, in accordance with the experimental observation (see Supplemental Material).

The nature of the charge excitation gap can be further revealed by its momentum dependence. In Fig. 2, we plot the momentum dependence of the low energy peaks (A-C) in Na$_2$IrO$_3$. In the honeycomb plane, the magnetic ordering doubles the unit cell [31], and correspondingly the first Brillouin zone (BZ) becomes smaller. Two different BZ schemes are illustrated in the inset of Fig. 2 (a) to aid the comparison. We will use the rectangular BZ notation. Note that the two high symmetry directions of interest, the $q=(0 0)$ and $q=(0 K)$ in rectangular notation, correspond to the $Γ−M$ and $Γ−K$ directions in the honeycomb plane, respectively. One can see that the overall momentum dependence of the peak positions is very small, except for peak A. To investigate the behavior of peak A in detail, the low energy portion of the spectra was fit to a Lorentzian peak. Since the peak seems to disappear at $q=(1 0)$, we have used the spectrum at this $q$ as an empirical background. The fitting results for peak positions, widths, and intensities are shown in Fig. 2(b)-(c). The width and peak position remains almost unchanged ($≈ 10$ meV dispersion), but the intensity is strongly peaked around the BZ center. This can be clearly seen in the pseudocolor plot of the spectra shown in Fig. 2(d), in which a strong peak around $q=(0 0)$ and 0.42 eV is contrasted with the $q$-independent features B+C. In addition, one can see that the spectral weight changes abruptly around 0.4 eV, confirming that this is the particle-hole continuum boundary. Based on our RIXS results, the electronic excitations in A$_2$IrO$_3$ can be summarized as shown in Fig. 2(e).

It is clear from this observation that the insulating
FIG. 2: (Color online) (a) Momentum dependence of the low energy RIXS spectra of Na$_2$IrO$_3$ obtained at $T = 9$ K. The inset shows a schematic diagram of the (H K 0) reciprocal space plane. The Brillouin zones (BZ) corresponding to the monoclinic unit cell are blue rectangles. For comparison, we also plot the BZ of the honeycomb net in black. The circles are the points where RIXS spectra are taken. The low energy peaks denoted with red triangles are fit to a Lorentzian, and the momentum dependence of (b) the peak position and width, and (c) the peak intensity are shown. (d) Same data are plotted in false color scale. (e) Schematics of electronic excitations in $A_2$IrO$_3$ determined from our RIXS measurements.

The observed spectra are powder averaged. We associate the excitations below 1 eV and a broad two-peak feature at 2-5 eV. These two energy scales are very similar in Sr$_2$IrO$_4$, but the large separation in Na$_2$IrO$_3$ allows one to investigate these two types of excitations separately.

To summarize, we have carried out a resonant inelastic x-ray scattering investigations of electronic excitations in Na$_2$IrO$_3$ and Li$_2$IrO$_3$. We observe three well-defined features below 1 eV and a broad two peak feature at 2-5 eV. By comparing our observation with quantum chemical calculations, we associate these features with $d$-$d$ transitions. Specifically, the high energy excitations are from $t_{2g}$ to $e_g$ excitations, while the low energy excitations around 0.7-0.8 eV are excitations from $j_{eff}=3/2$ to $j_{eff}=1/2$ states. The splitting of the latter feature arising from the trigonal crystal field is about 110 meV, much smaller than the spin-orbit coupling energy scale of Ir compounds, which validates the applicability of $j_{eff}$ physics in $A_2$IrO$_3$. In addition, we observe a lower energy excitation around 0.4 eV, which shows very little momentum dependence and is associated with the particle-hole excitation across the Mott gap; the "excitonic" behavior of this peak suggests the nearest-neighbor Coulomb interaction $V$ is sizable. We conclude that the electronic structures of both Na$_2$IrO$_3$ and Li$_2$IrO$_3$ are similar and these systems can be described as spin-orbit Mott insulators.
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S1. First principle electronic structure calculations

In order to understand the origin of the low energy excitations around 0.4 eV, we have carried out periodic density functional theory (DFT) electronic-structure calculations. We have used the DFT code OpenMX [S1] based on the linear combination of pseudo-atomic orbital (LCPAO) formalism [S2], the Perdew-Burke-Ernzerhof GGA-functional, 8 × 8 k-points grids within the Brillouin zone, and 300 Ry for the real-space grid. The SOC is treated via a fully-relativistic j-dependent pseudopotential in the non-collinear DFT formalism [S4, S5, S6]. We applied the C2/m monoclinic crystal structure reported in Ref. [S7] and the zigzag-type magnetic order suggested in Ref. [S8] for Na2IrO3. For Li2IrO3, we used the same magnetic structure as for Na2IrO3 and structural data from Refs. [S9].

Densities of states (DOS) from GGA and GGA+U [S2] calculations are plotted in Fig. S1. The solid line is the total DOS and the filled shaded area represents partial d-orbitals DOS. From top to bottom, the calculations were done with no SOC or U, with SOC, and with both SOC and U. As expected the 5d states are dominant near the Fermi level, although there exists some modest amount of hybridization between Ir 5d and O 2p states. A moderate size U can open a (Mott) gap of 300–400 meV, in accordance with the experimental observation. Compared to Na2IrO3, the bandwidths in Li2IrO3 are a little bit larger but the nature of the gap is essentially the same.

S2. Quantum chemical calculations

To investigate in detail the electronic structure and the essential interactions in the A2IrO3 iridates, we further performed correlated quantum chemical calculations. In the quantum-chemical study, we employed multiconfiguration self-consistent-field and multireference configuration-interaction (MRCl) methods [S10] as implemented in the MOLPRO package [S11]. The calcu-
Na$_2$IrO$_3$ and Li$_2$IrO$_3$ upon inclusion of spin-orbit coupling and on-site correlation. The solid line is the total DOS and the filled shaded area represents partial d-orbital DOS.

Calculations were performed on fragments consisting of one central IrO$_6$ octahedron for which the local d–d transitions are explicitly computed plus all nearest-neighbor (NN) octahedra, three in A$_2$IrO$_5$, and adjacent Na or Li ions. To simplify the analysis of the wave functions, the NN Ir$^{4+}$ ions were modeled as closed-shell Pt$^{4+}$ species S12, S13. The remaining part of the crystal is represented as an array of point charges that reproduce the Madelung field in the cluster region. Effective core potentials and basis sets as described in earlier investigations on Sr$_2$IrO$_4$, Ba$_2$IrO$_4$, and CaIrO$_3$ were used S12, S13.

**S3. Additional momentum dependence**

In many layered systems, such as the cuprates S14, momentum dependence along the L-direction is expected to be small. However, recent DFT calculations have shown dispersion of the optical gap along the L-direction S15. In order to investigate this we measured the momentum dependence along the Q = (0 0 L) direction in Na$_2$IrO$_3$ at T = 9 K. These spectra were taken with the same high-resolution setup as the one in Fig. 3 (a). The RIXS spectra in Fig. S2 show no observable dispersion, supporting the 2D nature of Na$_2$IrO$_3$. We have also measured the momentum dependence of the high energy excitation (labelled D and E in Fig. 1). These spectra were taken with an overall resolution of ~150 meV. Fig. S3 show RIXS spectra taken along the Q = (-H -H 6.9) direction in Na$_2$IrO$_3$ at T = 9 K. No observable changes were seen.

**S4. X-Ray Atomic Pair Distribution Function (PDF) Measurements**

Atomic PDF measurements were performed at 300 K at the 6-ID-D beamline of the Advanced Photon Source at Argonne National Laboratory, utilizing a General Electric amorphous silicon image plate (IP) detector. A monochromatic incident x-ray beam 0.5mm × 0.5mm in size was used, conditioned to have energy of 74.353 keV (λ=0.1668 Å). Finely pulverized Li$_2$IrO$_3$ and Na$_2$IrO$_3$ samples were packed in cylindrical polyimide capillaries 1.0 mm in diameter and sealed at both ends. The IP detector was mounted orthogonally to the beam path with a

![FIG. S1](image1.png)

**FIG. S1:** (color online) The evolution of the DOS for both Na$_2$IrO$_3$ and Li$_2$IrO$_3$ upon inclusion of spin-orbit coupling and on-site correlation. The solid line is the total DOS and the filled shaded area represents partial d-orbital DOS.

![FIG. S2](image2.png)

**FIG. S2:** Momentum dependence of the low energy RIXS spectra in Na$_2$IrO$_3$ along the Q = (0 0 L) direction. All data sets collected at T = 9 K.

![FIG. S3](image3.png)

**FIG. S3:** Momentum dependence of the high energy RIXS spectra in Na$_2$IrO$_3$ along the Q = (H H 6.9) direction. All data sets collected at T = 9 K with a resolution of ~150 meV (FWHM).
FIG. S4: (color online) Atomic PDF of Li$_2$IrO$_3$ and Na$_2$IrO$_3$ at 300 K. (a) Li$_2$IrO$_3$ data (gray open symbols) and refined $C2/m$ model (red solid line), with the difference curve (green solid line) that is offset for clarity. (b) The same as (a) but for Na$_2$IrO$_3$. (c) Direct comparison of Li$_2$IrO$_3$ and Na$_2$IrO$_3$ experimental PDF data at 300 K, scaled such that the intensities of the first PDF peaks overlap. Dashed vertical lines in (a) and (b) correspond to the first two sharp PDF peaks in Li$_2$IrO$_3$. Arrows denote specific PDF features discussed in the text.

The PDF data of Li$_2$IrO$_3$ could be explained over a broad $r$-range within the $C2/m$ model with all crystallographic sites fully occupied, with no indication of local structural distortions being present, as evident in Fig. S4 (a). Structural parameters, as refined over a 1.25-20.0 Å range, can be summarized as follows: $a=5.172(1)$ Å, $b=8.926(2)$ Å, $c=5.122(2)$ Å, $\beta = 109.91(4)^\circ$, with Ir at 4g (0.5, 0.167(1), 0), Li1 at 2a (0,0,0), Li2 at 2d (0.5, 0, 0.5), Li3 at 4h (0.5, 0.31(6), 0.5), O1 at 8j (0.752(5), 0.173(2), 0.709(4)), and O2 at 4i (0.707(8), 0, 0.260(7)) atomic positions. The Ir-O distances and Ir-O-Ir bond angles range from 2.01 to 2.04 Å and 93.6 to 94.8° respectively, while Ir-Ir nearest neighbor distances are in the range from 2.984 to 2.992 Å.

On the other hand, while the fit of the $C2/m$ crystallographic model to the PDF data of Na$_2$IrO$_3$ is consistent with the low-$r$ PDF features, significant discrepancies are observed beginning at around 6 Å, as can be seen in Fig. S4 (b), and no convergence could be achieved in broad $r$-range fits irrespective of refinement strategies attempted. The $C2/m$ model is inadequate in describing the intermediate structure of Na$_2$IrO$_3$ and the actual symmetry of the intermediate range structure is lower. This PDF is consistent with there being an appreciable amount of disorder in the Na$_2$IrO$_3$ sample compared to Li$_2$IrO$_3$. To qualitatively illustrate this, it is useful to directly compare the experimental PDFs of the two $A_2IrO_3$ systems, Fig. S4 (c). Local structural features are compared first. The first sharp PDF feature containing nearest neighbor Ir-O distance in Na$_2$IrO$_3$ occurs at around 2 Å, and coincides with that of Li$_2$IrO$_3$. The next sharp PDF feature, which includes the Ir-Ir near neighbor peak, in Na$_2$IrO$_3$ occurs at an observably larger distance in Na$_2$IrO$_3$ (3.105 Å) than in Li$_2$IrO$_3$ (2.985 Å), indicating that the Ir-rings of the honeycomb network are appreciably larger, and reflecting the lattice expansion on going from smaller Li to larger Na. Despite the shift in peak positions, the relative intensities of these short range PDF features are comparable for the two samples, and have comparable peak widths, suggesting that the underlying local environments are very similar in the two systems.

We now consider the intermediate lengthscale in PDFs shown in Fig. S4 (c). What is immediately apparent is that starting from about 5-5.5 Å the PDF features of Na$_2$IrO$_3$ are visibly broader than those in Li$_2$IrO$_3$ indicative of disorder in the former. Notably, while the $C2/m$ model explains the features in the PDF of Li$_2$IrO$_3$ in 6-7 Å range (marked by black arrows in Fig. S4 (a)), the same model fails to explain the corresponding features in the Na$_2$IrO$_3$ data. The two features marked by arrows in Li$_2$IrO$_3$ PDF are both sharp and of approximately equal intensity. In contrast, the corresponding PDF peaks in Na$_2$IrO$_3$ PDF (marked by black arrows in Fig. S4(b)) have very different intensities. The PDF feature at around 6 Å in Na$_2$IrO$_3$ is rather broad, with extra intensity appearing at the low-$r$ side of the peak (indicated by red arrow in Fig. S4 (b)), and is clearly multicomponent. This is precisely the region where the broad $r$-range fits first fail to explain the PDF of Na$_2$IrO$_3$, as these features are not incorporated into the $C2/m$ structural model. Although extracting the details of the actual intermediate structure of Na$_2$IrO$_3$ from the present 300 K data is a difficult task, further hampered by the thermal broadening that lowers the PDF resolution and requiring elaborate analysis of the low-temperature PDF data for full characterization, it is tempting to speculate about the origin of the observed features. Considerations of the crystallographic model reveal that in the 6 Å range there are contributions from the third Ir-Ir neighbors in the honeycomb, as well as contributions involving Ir-Ir pairs belonging to two successive honeycomb sheets. It is plausible that the observed discrepancies originate...
from stacking faults suggested in reference [S7], where appreciable rods of diffuse scattering were observed in the single crystal scattering experiments. However, if we assume that stacking faults occur randomly at the < 10% level, a sharp signal in PDF such as that seen in the difference curve shown in Fig. S4 (b) is difficult to explain. Considering that the PDF feature around 5.3 Å in Na₂IrO₃, containing the next near neighbor Ir-Ir distance of the honeycomb, is already broad compared to its Li₂IrO₃ counterpart, we cannot rule out the possibility that in addition to the distortions generated by stacking faults there are also in-plane distortions of the honeycomb lattice of Na₂IrO₃ involving correlations beyond that of the Ir-Ir near neighbor.

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