Honeycomb lattice Na$_2$IrO$_3$ at high pressures: A robust spin-orbit Mott insulator

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The honeycomb iridate Na$_2$IrO$_3$ has received much attention as a candidate to realize a quantum spin liquid state, but the nature of its insulating state remains controversial. We found that the material exhibits structural transitions at 3 and 10 GPa. The former is accompanied by 166-meV suppression of the activation gap, but the energies for the low-lying interband transitions change by less than 10 meV. This can be reconciled in a picture in which the application of high pressure barely shifts the electronic bands, but rather merely broadens them. First-principles calculations uncover a strong correlation between the band gap and the $\beta$ angle of the monoclinic structure, indicating non-negligible interlayer coupling. These results offer clear evidence for a spin-orbit Mott insulating state in Na$_2$IrO$_3$ and are inconsistent with the quasimolecular orbital model.

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The insulating state in iridium oxides came as a surprise. With greater spatial extent of the 5$d$ electron orbitals than in 3$d$ transition metal oxides, the iridates were speculated to have large bandwidth $W$ and small Coulomb interaction $U$, disobeying the $U > W$ Mott criterion [1]. The importance of spin-orbit coupling (SOC) in this class of materials was only recognized in the past decade, culminating in the notion of spin-orbit coupling (SOC) in this class of materials. The interplay of SOC and electron correlation is expected to generate exotic ground states [6–11], including the quantum spin Hall effect [12], quantum spin liquid [13,14], and a topological insulating phase [15,16]. While Sr$_2$IrO$_4$ is now generally accepted as a spin-orbit Mott insulator [2–4], the nature of the ground state of other iridates such as Na$_2$IrO$_3$ is yet to be clarified.

Na$_2$IrO$_3$ has received much attention due to the possibility of a novel quantum spin liquid state [13,14,17–34], described in the Kitaev model [35], but the nature of its insulating state remains controversial. Because a gap of ~340 meV [36] is already open far above the zigzag antiferromagnetic [18,21,23] ordering temperature, the Slater-type mechanism was ruled out. As a close cousin of Sr$_2$IrO$_4$, initially Na$_2$IrO$_3$ was also considered a spin-orbit Mott insulator. Early angle-resolved photoemission spectroscopy [36], optics [36], and resonant inelastic x-ray scattering [37] data were interpreted in this picture. Noting that Na$_2$IrO$_3$ has edge-sharing IrO$_6$ octahedra forming a honeycomb lattice [Fig. 1(b)] and the nearest-neighbor oxygen-assisted hopping is highly anisotropic, Mazin et al. proposed that the electron hopping is mainly confined within one honeycomb, forming nearly dispersionless quasimolecular orbitals (QMOs) [38,39]. New optics data were thought to support this model [40,41]. These two scenarios appear contradictory, featuring localized and itinerant electronic states, respectively. However, they were recently unified in a theoretical framework, demonstrating a crossover between the two tuned by either SOC or $U$ [42]. Based on the magnitude of $\lambda$ and $U$ in Na$_2$IrO$_3$, it was argued that a spin-orbit Mott insulator should be stabilized [42], which still awaits experimental confirmation. Establishing Na$_2$IrO$_3$ as a spin-orbit Mott insulator is a prerequisite for realizing the Kitaev quantum spin liquid state in this material.

In this paper, we investigate the insulating state in Na$_2$IrO$_3$ using a combination of high-pressure experiments and first-principles calculations. The in-plane resistance drops precipitously by more than one order of magnitude across a structural transition near 3 GPa [43], while the energies of the low-lying interband transitions do not experience a significant change. This can be well accounted for by the spin-orbit Mott insulating state, in which the application of high pressure...
barely shifts the energy bands (because they are mainly determined by the pressure-independent SOC and $U$) but merely broadens them, diminishing the activation gap and rendering the material less insulating [see an illustration in Fig. 1(a)]. Calculations further reveal that the band gap is sensitively controlled by the $\beta$ angle that dictates the interlayer stacking offset, suggesting a route for bandwidth control via interlayer hybridization. Our comprehensive study provides a coherent picture for $\text{Na}_2\text{IrO}_3$ as a robust spin-orbit Mott insulator, paving the way for exploring novel physics in this intriguing material.

$\text{Na}_2\text{IrO}_3$ single crystals were synthesized from off-stoichiometric quantities of $\text{IrO}_2$ and $\text{Na}_2\text{CO}_3$ using a self-flux method [23]. Freshly cleaved platelets were used in the infrared spectroscopy and resistance measurements, while fine powder ground from the crystals was used in x-ray powder diffraction (XRD). All high-pressure experiments employed the diamond-anvil cell technique. Infrared spectroscopy and XRD were performed at Beamlines U2A and X17C, respectively, of the National Synchrotron Light Source, Brookhaven National Laboratory (see details in Ref. [44]). Four-probe resistance measurements were performed using a CuBe cell with Au electrodes, as described elsewhere [45].

We first investigated the stability of the crystal structure under pressure. $\text{Na}_2\text{IrO}_3$ is a layered material with the monoclinic space group $C2/m$ [21,23]. In the $ab$ plane, edge-sharing $\text{IrO}_2$ octahedra form a honeycomb lattice. The layers stack along the $c$ axis with $\beta = 109.037^\circ$ and are separated by sodium atoms [Fig. 1(b)]. XRD data up to 14.8 GPa can be fit well based on this known crystal structure [47], yielding the pressure dependence of the lattice parameters shown in Figs. 1(c) and 1(d). A smooth contraction is seen along all three axes. Interestingly, the $\beta$ angle goes through a minimum near 4 GPa, where it decreases slightly by 0.3° from the ambient-pressure value. This is in contrast to the monotonic increases up to 25 GPa reported in Ref. [48], calling for further investigations to resolve the discrepancy.

The structural anomaly signified by the $\beta$ angle is further corroborated by infrared spectroscopy of phonons. Figure 1(f) shows the near-ambient absorbance as the blue line, acquired by polarizing the electric field in the $ab$ plane. Four phonon modes are clearly identified at 139, 219, 283, and 333 cm$^{-1}$. Modes above 400 cm$^{-1}$ absorb light more strongly and saturate the absorbance [47]. Upon increasing pressure, the 333 cm$^{-1}$ mode evolves into three, with itself exhibiting a kink in the pressure dependence of the frequency at 3 GPa [see Fig. 1(e) and [47]]. At 10 GPa, the 219 cm$^{-1}$ mode splits into two. Combined with anomalous pressure dependence in the linewidth and oscillator strength of these phonon modes [47], we deduce pressure-induced structural transitions near 3 and 10 GPa. The smooth compression of the unit-cell volume [Fig. 1(c)] suggests second-order nature of these transitions. The phonon data shown here set constraints on possible structures at high pressure predicted by theory [49].

We next focus on pressure effects on the electronic structure. In $\text{Na}_2\text{IrO}_3$, the low-lying interband transitions fall in the midinfrared, with typical absorbance spectra shown in Fig. 2(a). Apart from a pronounced phonon mode below 0.1 eV, the absorbance is dominated by two broad peaks with significant overlap. These peaks were also seen in Ref. [40], but overlooked in Refs. [36,48]. They can be understood as due to the interband transitions from the two valence bands

FIG. 1. (a) Schematic for the formation of a spin-orbit Mott insulator. The $J_{ab} = 1/2$ and $3/2$ bands form due to SOC with strength $\lambda$. Coulomb repulsion $U$ splits the $J_{ab} = 1/2$ band into an upper Hubbard band (UHB) and a lower Hubbard band (LHB), resulting in a band gap $E_g$ at the Fermi level $E_F$. The dotted lines depict bandwidth broadening. (b) Crystal structure of $\text{Na}_2\text{IrO}_3$ [46]. (c) Pressure dependence of the lattice parameters shown in Fig. 2(a). Apart from a pronounced phonon mode below 0.1 eV, the absorbance is dominated by two broad peaks with significant overlap. These peaks were also seen in Ref. [40], but overlooked in Refs. [36,48]. They can be understood as due to the interband transitions from the two valence bands...
closest to the Fermi level to the lowest-lying conduction band, regardless of the physical origin of these bands [47]. Under pressure, the overall spectral weight experiences a nonmonotonic change [47]. Figure 2(b) shows the integrated area under absorbance from 0.34 to 0.94 eV as a function of pressure. Kinks are observed near 3 and 10 GPa, consistent with the pressures for the structural transitions. A small hump at ∼0.4 eV gradually develops above 10 GPa [highlighted by the arrow in Fig. 2(a)], possibly due to changes of the electronic structure associated with the second structural transition.

Figure 2(a) (inset) shows a fit of the absorbance at 0.3 GPa. A summation of two Lorentzian functions with a third Lorentzian background (to account for higher-energy transitions [40]) fits the data well, yielding the peak energies $E_A$ and $E_B$ obtained by fitting analysis of the absorbance. The shaded regions represent the expected amount of pressure-induced increase in the QMO picture.

Boltzmann constant. An example fit at 15.8 GPa is shown in Fig. 3(a) (inset). The pressure dependence of $E_g$ is shown as open squares in Fig. 3(b). At ambient pressure, $E_g \approx 250$ meV. Increasing pressure induces a drastic decline of $E_g$ starting at 4 GPa, nearly coinciding with that for the first structural transition. Above 16 GPa, $E_g$ levels off to approximately 70 meV. We extract the resistance at different pressures for selected temperature points above 100 K. Figure 3(b) shows that its pressure dependence is similar to that of $E_g$, confirming that the electrical transport above 150 K is dominated by thermally activated conduction.

Remarkably, the activation gap diminishes by $\Delta E_g = 166$ meV up to near 10 GPa, while the low-lying interband transition energies change by less than 10 meV in the same pressure range. This implies that the application of high pressure barely shifts the electronic bands but broadens them due to enhanced electron hopping, resulting in reduced $E_g$. These results hold important clues about whether the spin-orbit Mott insulator or the QMO picture fits Na$_2$IrO$_3$.

In the former picture, peak A (B) is assigned as due to the optical transition from the lower Hubbard band ($J_{\text{eff}} = 3/2$ band) to the upper Hubbard band, hence $E_A = U$ and $E_B = (U + 3\lambda)/2$ [see Fig. 1(a)]. Since both $U$ and $\lambda$ are dominated by ionic atomic properties and therefore insensitive to pressure, both $E_A$ and $E_B$ are expected to be stable under pressure. This is highly consistent with our data shown in Fig. 2, offering clear evidence for a spin-orbit Mott insulating state in Na$_2$IrO$_3$. Quantitatively, we estimate $U = E_A = 0.52$ eV and $\lambda$ the activation gap.
The optical conductivity that correspond to the transitions 2 and 5.

\[ \lambda = (2E_B - E_A)/3 = 0.32 \text{ eV}, \] consistent with the expected values for 5d electrons, \( U \sim 0.4\text{–}2 \text{ eV} \) and \( \lambda \sim 0.1\text{–}1 \text{ eV} \) [11].

In the QMO model, considering only the oxygen-assisted nearest-neighbor hopping \( t \), an \( A_{1g} \) singlet and an \( E_{2u} \) doublet constitute the lowest-lying bands near the Fermi level, with eigenenergies of \( 2t \) and \( t \), respectively [38]. Inclusion of SOC splits the \( E_{2u} \) doublet [42]. Peaks A and B are therefore assigned as due to the optical transitions from the split \( E_{2u} \) to the \( A_{1g} \) QMOs. In the limit of small SOC, as assumed by the QMO model, the transition energies are \( E_A = t - \lambda/2 \) and \( E_B = t + \lambda/2 \). Since \( t \) is determined by the orbital overlap and hence the unit-cell volume, it is expected that pressure-induced volume contraction should shift both peaks to higher energies, with an amount denoted as \( \Delta t \). One can estimate \( \Delta t \) by noting \( W \sim 4t \) [51] and \( \Delta W \sim \Delta E_A \), yielding \( \Delta t \sim 42 \text{ meV} \), well within our spectral resolution. This amount of shift for peaks A and B is shown as shaded regions in Fig. 2(c), in stark contrast to the small changes observed in our experiment.

To further gain insight into the effects of pressure on the electronic structure, we performed local spin density approximation (LSDA) + \( U \) calculations including SOC, using the pressure-dependent lattice parameters. The methods are described in [47]. The structural transitions were neglected because of the lack of high-pressure structural details. Due to the antiferromagnetic order inherent in the theoretical model, the number of bands doubles. The optical conductivity therefore exhibits more interband transition peaks than observed experimentally. Figure 4(c) shows the dominant in-plane component of the optical conductivity tensor \( \sigma_{xx} \) at selected pressures. We track the pressure evolution of two peaks, i.e., 2 and 5, each associated with one group of bands just below the Fermi level. The maximum change of the peak energy is 33 and 24 meV, respectively [Fig. 4(d)], slightly higher than the amount obtained experimentally. This suggests that the band energies are robust even in the presence of structural transitions, supporting the spin-orbit Mott insulator scenario.

Our calculations further reveal a striking correlation between the band gap and the \( \beta \) angle under pressure, albeit the subtle change for the latter [Fig. 1(d)]. Increasing \( \beta \) from 90° results in enhanced offset of the atomic positions between the \( \text{IrO}_2 \) honeycomb layers [see Fig. 1(b)]. Interlayer hybridization via oxygen and sodium orbitals is suppressed accordingly, leading to bandwidth reduction and band gap increase. Tuning \( \beta \) away from 90° therefore effectively drives the system from three-dimensional-like toward two-dimensional, reminiscent of the dimensionality-controlled insulator-metal transition in \( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \) [3]. Although the correlation between the band gap and \( \beta \) was not observed experimentally due to the complications from structural transitions, it implies the importance of interlayer coupling in \( \text{Na}_2\text{IrO}_3 \), inconsistent with the QMO model that assumes purely intralayer electron hopping.

We lastly discuss the role of trigonal distortion. The \( J_{\text{eff}} \) description for the spin-orbit Mott insulators assumes regular \( \text{IrO}_6 \) octahedra, but structural studies found trigonal distortion in \( \text{Na}_2\text{IrO}_3 \) [21,23], whose role was emphasized by some authors [15,40,52] but considered minimal by others [37,38]. Large trigonal distortion has been shown to mix the \( \text{singlet} \) and an \( \text{u-g doublet} \) [42]. Peaks A and B are therefore assigned as due to the optical transitions from the split \( E_{2u} \) to the \( A_{1g} \) QMOs. In the limit of small SOC, as assumed by the QMO model, the transition energies are \( E_A = t - \lambda/2 \) and \( E_B = t + \lambda/2 \). Since \( t \) is determined by the orbital overlap and hence the unit-cell volume, it is expected that pressure-induced volume contraction should shift both peaks to higher energies, with an amount denoted as \( \Delta t \). One can estimate \( \Delta t \) by noting \( W \sim 4t \) [51] and \( \Delta W \sim \Delta E_A \), yielding \( \Delta t \sim 42 \text{ meV} \), well within our spectral resolution. This amount of shift for peaks A and B is shown as shaded regions in Fig. 2(c), in stark contrast to the small changes observed in our experiment.

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[51] $W \sim 4t$ is assumed in Ref. [38]. First-principles and tight-binding calculations for Na$_2$IrO$_3$ actually suggest $W < 2t$ for the low-lying bands (see, e.g., Ref [15]), which sets a lower bound for $\Delta t > 0.5\Delta E_g = 83$ meV.


