

**High-pressure versus isoelectronic doping effect on the honeycomb iridate  $\text{Na}_2\text{IrO}_3$** V. Hermann,<sup>1</sup> J. Ebad-Allah,<sup>1,2</sup> F. Freund,<sup>3</sup> I. M. Pietsch,<sup>3</sup> A. Jesche,<sup>3</sup> A. A. Tsirlin,<sup>3</sup> J. Deisenhofer,<sup>4</sup> M. Hanfland,<sup>5</sup> P. Gegenwart,<sup>3</sup> and C. A. Kuntscher<sup>1,\*</sup><sup>1</sup>*Experimentalphysik II, Augsburg University, 86159 Augsburg, Germany*<sup>2</sup>*Department of Physics, Tanta University, 31527 Tanta, Egypt*<sup>3</sup>*Experimentalphysik VI, Center for Electronic Correlations and Magnetism, Augsburg University, 86159 Augsburg, Germany*<sup>4</sup>*Experimentalphysik V, Center for Electronic Correlations and Magnetism, Augsburg University, 86135 Augsburg, Germany*<sup>5</sup>*European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble, France*

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We study the effect of isoelectronic doping and external pressure in tuning the ground state of the honeycomb iridate  $\text{Na}_2\text{IrO}_3$  by combining optical spectroscopy with synchrotron x-ray diffraction measurements on single crystals. The obtained optical conductivity of  $\text{Na}_2\text{IrO}_3$  is discussed in terms of a Mott-insulating picture versus the formation of quasimolecular orbitals and in terms of Kitaev interactions. With increasing Li content  $x$ ,  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  moves deeper into the Mott-insulating regime, and there are indications that up to a doping level of 24% the compound comes closer to the Kitaev limit. The optical conductivity spectrum of single-crystalline  $\alpha\text{-Li}_2\text{IrO}_3$  does not follow the trends observed for the series up to  $x = 0.24$ . There are strong indications that  $\alpha\text{-Li}_2\text{IrO}_3$  is not as close to the Kitaev limit as  $\text{Na}_2\text{IrO}_3$  and lies closer to the quasimolecular orbital picture instead. Except for the pressure-induced hardening of the phonon modes, the optical properties of  $\text{Na}_2\text{IrO}_3$  seem to be robust against external pressure. Possible explanations of the unexpected evolution of the optical conductivity with isoelectronic doping and the drastic change between  $x = 0.24$  and  $x = 1$  are given by comparing the pressure-induced changes of lattice parameters and the optical conductivity with the corresponding changes induced by doping.

DOI: [10.1103/PhysRevB.96.195137](https://doi.org/10.1103/PhysRevB.96.195137)**I. INTRODUCTION**

The  $5d$  transition-metal compounds show strong spin-orbit coupling (SOC) concurrent with electronic correlations, leading to interesting electronic and magnetic properties. They are discussed in terms of various exotic ground states, like topological insulators [1–3], Mott insulators [4–8], Weyl semimetals [9–11], and spin liquids [12–15]. One important family among the  $5d$  transition-metal compounds is the 213 iridates  $A_2\text{IrO}_3$  (with  $A = \text{Na}, \text{Li}$ ), which have a honeycomb layered structure consisting of  $\text{IrO}_6$  octahedra [16–18].  $\text{Na}_2\text{IrO}_3$  was initially interpreted in terms of a topological insulator [1]; however, experimental and theoretical investigations showed the Mott-insulating nature [19–23] in the vicinity of a Kitaev spin liquid [14,24]. Also a band insulator picture with a quasimolecular orbital (QMO) ground state was suggested as an explanation for its insulating behavior [25,26]. Both  $\text{Na}_2\text{IrO}_3$  and  $\alpha\text{-Li}_2\text{IrO}_3$  order antiferromagnetically below  $T_N \approx 15$  K, excluding the realization of a “pure” Kitaev spin liquid model [27–30], while  $T_N$  systematically decreases by substituting Na atoms by Li [31].

The electronic properties of the iridates are dominated by the  $\text{IrO}_6$  octahedra, where central  $\text{Ir}^{4+}$  ions with five  $5d$  electrons are surrounded by six  $\text{O}^{2-}$  ions. In  $\text{Na}_2\text{IrO}_3$ , the octahedral crystal field (with a small trigonal distortion [32]) will largely split the Ir  $t_{2g}$  and  $e_g$  manifolds, so that all five electrons occupy the  $t_{2g}$  manifold. This  $t_{2g}$  manifold is reconstructed into lower-lying, filled  $j_{\text{eff}} = 3/2$  states and half-filled  $j_{\text{eff}} = 1/2$  states by the strong SOC of the heavy Ir. The Coulomb repulsion  $U$  splits the half-filled  $j_{\text{eff}} = 1/2$  band into an occupied lower Hubbard band and an unoccupied

upper Hubbard band, like in  $\text{Sr}_2\text{IrO}_4$ , leading to the opening of a gap [19–21] with a size of  $\approx 340$  meV, being independent of temperature [20].

The application of external pressure is a very efficient and clean way to tune the ground state of materials without introducing additional scattering centers, in contrast to chemical pressure, which works via atomic substitution. Pressure-dependent resistivity measurements on the perovskite 214 iridate  $\text{Ba}_2\text{IrO}_4$  revealed an insulator-to-metal transition at a critical pressure of 13.4 GPa [33], while the related compound  $\text{Sr}_2\text{IrO}_4$  showed a persistent nonmetallic behavior up to a pressure of 55 GPa [34]. In contrast, most of the pyrochlore iridates  $R_2\text{Ir}_2\text{O}_7$  (with  $R$  being a rare-earth element) are already metallic at ambient conditions with an insulating or semimetallic phase at low temperatures [11,35,36]. Recently, indications for a pressure-induced quantum spin liquid state were observed for  $\alpha\text{-RuCl}_3$  [37,38], which also orders in a honeycomb lattice similar to  $A_2\text{IrO}_3$ .

Here, we study the effect of external pressure and isoelectronic doping on the electro-dynamical and structural properties of the honeycomb iridate  $\text{Na}_2\text{IrO}_3$ . We further juxtapose these effects and discuss which of them is more promising for tuning the system towards the Kitaev limit.

**II. METHODS**

$(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  single crystals (for  $x \leq 0.24$ ) were prepared by a solid-state synthesis as described previously [27,31]. Actual doping levels were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).  $\alpha\text{-Li}_2\text{IrO}_3$  single crystals were grown by vapor transport of separated educts as described in Ref. [39] using elemental lithium and iridium as starting materials. The samples were

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characterized by x-ray diffraction, specific heat, and magnetic susceptibility measurements in order to ensure phase purity and crystal quality. No foreign phases were detected.

Room-temperature near-normal incidence reflectance spectra were measured on single crystals (*ab* plane) in the frequency range 200–38 000  $\text{cm}^{-1}$  (0.025–4.7 eV) for  $\text{Na}_2\text{IrO}_3$  and  $\alpha\text{-Li}_2\text{IrO}_3$  and in the range 200–25 000  $\text{cm}^{-1}$  (0.025–3.1 eV) for Li-doped  $\text{Na}_2\text{IrO}_3$ . The  $\text{Na}_2\text{IrO}_3$  and  $\alpha\text{-Li}_2\text{IrO}_3$  single crystals were partially transparent; thus, additional transmission measurements were performed. The reflectance and transmittance measurements were carried out with a Bruker Vertex v80 Fourier transform infrared spectrometer in combination with an infrared microscope (Bruker Hyperion) with a 15 $\times$  Cassegrain objective. The intensity reflected from an Al mirror served as a reference to obtain the absolute reflectance spectra. For the transmittance spectra we measured the intensity  $I_{s,\text{trans}}(\omega)$  of the radiation transmitted through the sample. As a reference the intensity  $I_{\text{ref,trans}}(\omega)$  transmitted through air was used.

In the case of the pure compounds  $\text{Na}_2\text{IrO}_3$  and  $\alpha\text{-Li}_2\text{IrO}_3$ , a Kramers-Kronig analysis of the reflectance was combined with a direct analysis of the reflectance and transmittance ( $R + T$  analysis), following Ref. [40], to obtain the real part of the optical conductivity  $\sigma_1$ . In the partial transparent range,  $\sigma_1$  of the  $R + T$  analysis is used, while in the opaque range the results from a Kramers-Kronig analysis are used [41]. Since the measured single crystals of the doped compounds  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  were opaque in the whole measured frequency range, the optical conductivity was obtained via Kramers-Kronig analysis of the reflectance data. For the high-energy extrapolation [42] we interpolated the frequency range between the measured data and the calculated spectra above 80 000  $\text{cm}^{-1}$  (10 eV) according to a power series in  $1/\omega^s$  with  $s$  up to 4 [43]. The obtained  $\sigma_1$  spectra were fitted with a simple Lorentz-oscillator model.

Pressure-dependent reflectance measurements were carried out on  $\text{Na}_2\text{IrO}_3$  single crystals in the frequency range 200–20 000  $\text{cm}^{-1}$  (0.025–2.5 eV). To obtain the reflectance ratio  $R_{\text{sd}}$  at the sample-diamond interface, the intensity  $I_{s,\text{refl}}(\omega)$  of the radiation reflected from the sample-diamond interface was measured. As the reference, the intensity  $I_{\text{ref,refl}}(\omega)$  of the radiation reflected from the inner diamond-air interface of the empty diamond-anvil cell (DAC) was used. The reflectance ratios were calculated according to  $R_{\text{sd}}(\omega) = R_{\text{dia}} I_{s,\text{refl}}(\omega) / I_{\text{ref,refl}}(\omega)$ , with  $R_{\text{dia}} = 0.167$ , which was assumed to be independent of pressure [44,45]. The reflectance ratios  $R_{\text{sd}}$  were calibrated against the simulated  $R_{\text{sd}}$  obtained from fitting the absolute reflectance outside the cell with the Lorentz model. The calibrated spectra were then fitted with a large number of Lorentz terms (variational dielectric function [46]), using the REFFIT software, to obtain the real part of the optical conductivity at various pressures.

A commercial Diacell CryoDAC-Mega (almax-easylab) DAC was used for generating pressures up to 14 GPa in the far-infrared (FIR) range, while in the midinfrared (MIR), near-infrared (NIR), and visible (VIS) ranges a custom-made Syassen-Holzapfel-type [47] DAC was used for generating pressures up to 24 GPa. Pressure was determined *in situ* by using the ruby-luminescence technique [48]. CsI powder served as quasihydrostatic pressure-transmitting medium.

Since the samples are highly air sensitive [49], they were kept inside an Ar-filled glove box. They were measured quickly after exposing them to air and were stored inside a vacuum desiccator in between measurements. The pressure-dependent spectra were observed from a freshly cleaved sample, which was quickly loaded into the DAC. The typical sample size used for pressure-dependent measurements amounted to  $\approx 120 \mu\text{m} \times 120 \mu\text{m}$  for the FIR range and  $\approx 90 \mu\text{m} \times 90 \mu\text{m}$  for the MIR, NIR, and VIS ranges.

The pressure dependence of the lattice parameters was determined by single-crystal x-ray diffraction (XRD) measurements using synchrotron radiation at beamline ID15B at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The wavelength of the radiation was 0.4114 Å, and more than 300 reflections were used to determine the crystal structure. Diffraction data were analyzed using the CRYSTALISPRO software [50], following the established protocols for the beamline [51].

Phonon frequencies at the  $\Gamma$  point were obtained from density-functional theory (DFT) band-structure calculations using the internal procedure of VASP [52,53] that adopts the finite-displacement method for the calculation of phonons. The Perdew-Burke-Ernzerhof exchange-correlation potential for solids [54] was used along with a  $k$  mesh of up to 64 points in the first Brillouin zone. Given variable magnetic ground states of the honeycomb iridates considered in this work, all calculations were performed for the ferromagnetic spin configuration. We have verified that collinear antiferromagnetic order changes phonon frequencies of  $\text{Na}_2\text{IrO}_3$  by less than 1%, and magnetic order has a negligible effect on lattice dynamics. All calculations were performed on the DFT+ $U$ +SO level because both correlations and spin-orbit (SO) coupling are integral to stabilizing the insulating state of honeycomb iridates [25,26]. The on-site Hubbard repulsion and Hund's exchange parameters of DFT+ $U$ +SO were fixed at  $U_d = 2$  eV and  $J_d = 0.4$  eV [14]. Their variation systematically changes phonon frequencies by a few percent without affecting any of the conclusions presented below.

### III. RESULTS AND DISCUSSION

#### A. Isoelectronic doping

The reflectance and transmittance spectra of the measured  $\text{Na}_2\text{IrO}_3$  crystal are depicted in Fig. 1(a). Consistent with the insulating character of the material [19,20,55–58], the overall reflectivity is low, except for the frequency range 400–600  $\text{cm}^{-1}$  due to strong phonon excitations. The sample is opaque in almost the whole studied frequency range, as given by the transmittance spectrum [see Fig. 1(a)]. For frequencies between 600 and 2000  $\text{cm}^{-1}$  (0.074–0.25 eV) and below 400  $\text{cm}^{-1}$  (50 meV) we obtain a transmittance up to 5%. The corresponding optical conductivity  $\sigma_1$  [Fig. 1(b)] shows a pronounced absorption feature at around 1.5 eV with an absorption onset at  $\sim 340$  meV, confirming earlier experimental reports [19,20]. Above  $\sim 2.5$  eV charge-transfer excitations between the Ir  $5d$  and O  $2p$  orbitals contribute to the optical conductivity spectrum.

Fitting the pronounced absorption feature with the Lorentz model revealed three main contributions: The strongest Lorentz contribution labeled C is located at 1.6 eV, and

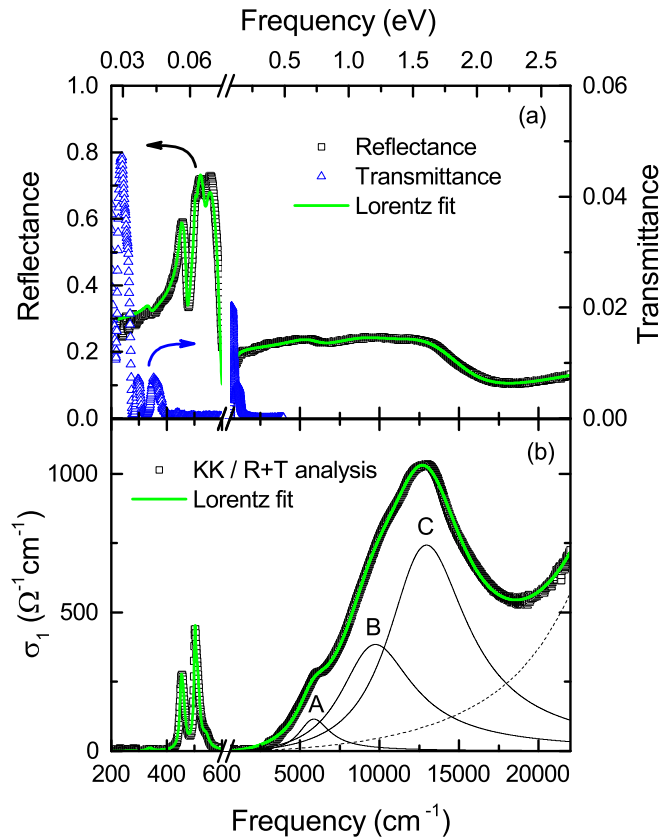


FIG. 1. (a) Reflectance (black squares) and transmittance (blue triangles) spectra of  $\text{Na}_2\text{IrO}_3$  under ambient conditions. The green line is the fit of the reflectance spectrum with Lorentz oscillators. (b) Optical conductivity  $\sigma_1$  using a combined Kramers-Kronig and  $R + T$  analysis, together with the fitting with Lorentz oscillators. The pronounced absorption feature at around 1.5 eV consists of three main contributions labeled A, B, and C. The dashed line indicates the charge-transfer excitations between the Ir  $5d$  and O  $2p$  orbitals.

two weaker contributions, A and B, are at 0.7 and 1.2 eV, respectively. These contributions can be ascribed to Ir  $d-d$  transitions [19,21,25]. Compared to the findings reported by Sohn *et al.* [19], the contributions are slightly shifted in energy, and the two additional Lorentzian peaks at 0.5 and 2.0 eV are not needed to obtain a good fit of our data. Based on recent theoretical calculations, contributions A, B, and C can be ascribed to excitations between the relativistic  $j_{\text{eff}} = 3/2$  ( $j_{3/2}$ ) and  $j_{\text{eff}} = 1/2$  ( $j_{1/2}$ ) orbitals [22,24,25]. Peak C can be ascribed to intersite  $j_{3/2} \rightarrow j_{1/2}$  excitations; peak B can be ascribed to weaker intersite  $j_{1/2} \rightarrow j_{1/2}$  excitations, and peak A can be ascribed to on-site  $j_{3/2} \rightarrow j_{1/2}$  excitations. These on-site excitations are expected to be weaker according to selection rules [24].

The optical conductivity spectrum of  $t_{2g}^5$  systems with a honeycomb lattice structure was theoretically investigated recently [25], starting from a minimal microscopic model, which is able to capture the QMO band-insulating limit as well as the relativistic Mott-insulating regime, taking into account the Coulomb repulsion  $U$ , Hund's coupling  $J_H$ , and SOC  $\lambda$ . Furthermore, Kim *et al.* calculated the hole density  $\bar{n}_{a_{1g}}$  of the  $a_{1g}$  quasimolecular band at the  $\Gamma$  point as an

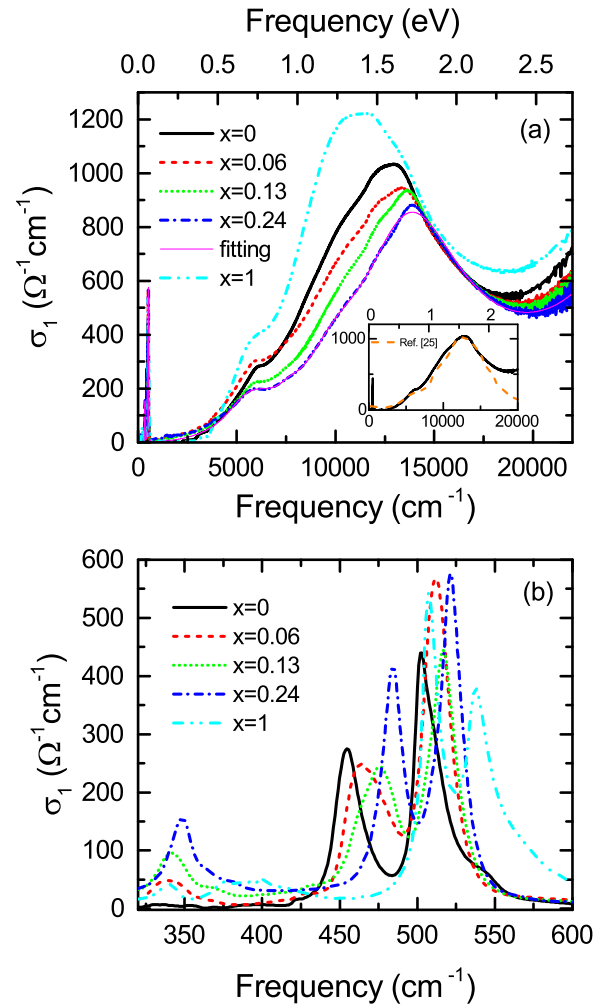


FIG. 2. Optical conductivity  $\sigma_1$  of  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  for various Li contents  $x$  (a) for the complete measured frequency range and (b) for the phonon mode range. The inset in (a) shows a comparison of calculations of Ref. [25] and our result with parameters given in the text.

indication for the QMO character of the material, which should be exactly 1 for the pure QMO state [25]. Comparing the shape of their optical conductivity to their calculated spectra with the Kubo formula and with  $J_H = 1.6t$  ( $t$  is the hopping parameter between adjacent Ir atoms), we find the best match for  $\lambda$  at  $1.6t$  and  $U - 3J_H = 2.0t$ . Setting  $t$  to a reasonable value of  $t = 0.31$  eV, which is slightly higher than  $t \approx 0.27$  eV from various theoretical calculations [26,56,59], we find a three-peak structure matching very well our obtained spectrum, as shown in the inset of Fig. 2(a). In comparison, setting  $t \approx 0.27$  eV as implied by Ref. [25] will make the spectrum with  $U - 3J_H = 3.2t$  fit to our main peak C reasonable well, but peak A is then underestimated too much. The hole density is estimated to be around  $\bar{n}_{a_{1g}} \approx 0.35$ . Thus, our results indicate that  $\text{Na}_2\text{IrO}_3$  is closer to a band-insulating QMO state than the prediction from Kim *et al.* but still within the Mott-insulating regime [25].

The effect of Li doping on the optical conductivity of  $\text{Na}_2\text{IrO}_3$  in the frequency range of the Ir  $d-d$  transitions and the phonon modes is illustrated in Figs. 2(a) and 2(b), respectively.

Applying a simple Lorentz model with three contributions similar to those for  $\text{Na}_2\text{IrO}_3$ , we find that the main peak C shifts to higher energies with increasing Li content  $x$  up to  $x = 0.24$  ( $\sim 0.1$  eV for  $x = 0.24$ ), which is the highest doping level achieved in our samples, whereas the lowest-energy contribution A is stable regarding Li substitution, with only a slight tendency towards lower energy. The overall spectral weight of the  $d$ - $d$  excitation band decreases with increasing doping level. One further notices a small spectral weight contribution below  $\sim 340$  meV for the Li-doped samples compared to pure  $\text{Na}_2\text{IrO}_3$ . According to the calculations of Kim *et al.* [25], the decrease in the spectral weight along with a shift of the main excitation C to higher energies can refer to an increase of the  $(U - 3J_H)/t$  value, thereby going more into the Mott-insulating regime, which is quite surprising and will be discussed in Sec. III C.

For pure  $\alpha$ - $\text{Li}_2\text{IrO}_3$  we find a charge gap very similar in size ( $\sim 340$  meV) to that for  $\text{Na}_2\text{IrO}_3$ , consistent with theoretical predictions [22,24]. However, the optical conductivity spectrum does not follow the above-described trends for the Ir  $d$ - $d$  transitions, which we observe for the Li-doped  $\text{Na}_2\text{IrO}_3$  compounds. Compared to  $\text{Na}_2\text{IrO}_3$ , the overall spectral weight of the  $d$ - $d$  excitations is increased, with the main contribution centered at around 1.4 eV, i.e., at considerably lower energy than in  $\text{Na}_2\text{IrO}_3$ . An increase in spectral weight between 0.7 and 1.5 eV was theoretically predicted for  $\alpha$ - $\text{Li}_2\text{IrO}_3$  [22,24]. In particular, in contrast to  $\text{Na}_2\text{IrO}_3$  the direct metal-metal hopping was shown to be significant in the case of  $\alpha$ - $\text{Li}_2\text{IrO}_3$ , which leads to additional spectral weight of  $j_{1/2} \rightarrow j_{1/2}$  excitations located at around 1.1 eV. This is in accordance with the calculations of Kim *et al.* [25] for  $\text{Na}_2\text{IrO}_3$ . The increase in the spectral weight along with a shift of the main peak to lower energies is a signal for a reduction in the  $(U - 3J_H)/t$  value, simply explained by an increase in the hopping parameter  $t$  due to the decrease in lattice parameters. This brings  $\alpha$ - $\text{Li}_2\text{IrO}_3$  closer to the QMO limit than  $\text{Na}_2\text{IrO}_3$ .

Furthermore, the honeycomb lattices of  $A_2\text{IrO}_3$  are discussed in terms of Kitaev interactions [14,28,60–63]. According to Li *et al.* [24], the Kitaev limit will be most closely approached by the  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  compound with the lowest spectral weight near  $\omega \approx 1.1$  eV, where the spectral weight is contributed by intersite  $j_{1/2} \rightarrow j_{1/2}$  excitations. They furthermore claim that the values of the corresponding direct metal-metal hopping integrals are directly related to the magnetic interactions and that the Kitaev limit will be obtained only when the direct metal-metal hopping is small in comparison to the oxygen-assisted intersite hopping. Following this interpretation would identify the 24% doped  $(\text{Na}_{0.76}\text{Li}_{0.24})_2\text{IrO}_3$  as the closest of the measured materials to the Kitaev limit signaled by the decrease in contribution B, while the enhanced direct metal-metal hopping signals that  $\alpha$ - $\text{Li}_2\text{IrO}_3$  should be less close to the Kitaev limit compared to  $\text{Na}_2\text{IrO}_3$  [14,24]. The proposed shift toward the Kitaev limit upon Li substitution is consistent with the reduction in  $T_N$  from 15 K at  $x = 0$  to 6 K at  $x = 0.24$ . On the other hand, at  $x = 1$  the  $T_N$  of about 15 K is recovered [31].

Next we focus on the analysis of the phonon mode spectrum of  $\text{Na}_2\text{IrO}_3$  and its changes with Li doping. Experimentally, we observe up to six phonon modes which are listed in Table I and whose frequencies are plotted in Fig. 6(c) as a function of

TABLE I. Experimentally observed phonon frequencies (in  $\text{cm}^{-1}$ ) for  $\text{Na}_2\text{IrO}_3$ ,  $(\text{Na}_{0.76}\text{Li}_{0.24})_2\text{IrO}_3$ , and  $\alpha$ - $\text{Li}_2\text{IrO}_3$  at ambient pressure.

Mode	$\text{Na}_2\text{IrO}_3$	$(\text{Na}_{0.76}\text{Li}_{0.24})_2\text{IrO}_3$	$\alpha$ - $\text{Li}_2\text{IrO}_3$
1		347	387
2	452	475	506
3	460	484	512
4	502	510	537
5	511	522	540
6	542		566

Li doping level  $x$ . With increasing Li content  $x$  all observed phonon modes harden [see also Fig. 2(b)]. The fit of the phonon mode spectrum with Lorentz oscillators is depicted in Fig. 3(a) for the Li concentration  $x = 0.13$  as an example, together with the labeling of the five phonon modes. Phonon mode 1 is observed only in samples containing Li (note that for the pure Li compound, phonon mode 1 is present but the absolute value of the optical conductivity could not be determined due to technical reasons, namely, very low intensity of the transmission for the  $R + T$  analysis). An additional mode 6 is observed only in the pure compounds  $\text{Na}_2\text{IrO}_3$  and  $\alpha$ - $\text{Li}_2\text{IrO}_3$  and not in the doped compounds.

DFT+ $U$ +SO calculations provide microscopic insight into  $\Gamma$ -point phonons probed in the optical measurements. The

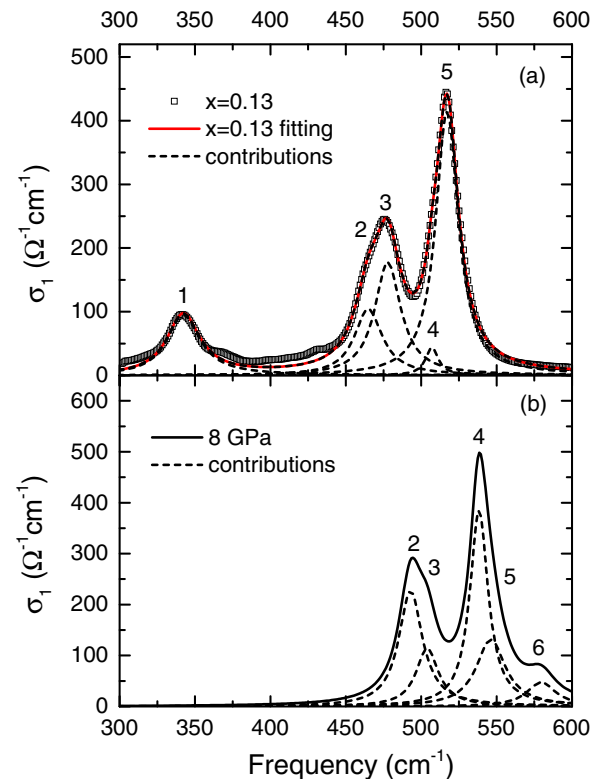


FIG. 3. Optical conductivity  $\sigma_1$  of  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  in the phonon mode range: (a) For  $x = 0.13$  at ambient pressure together with the fitting with the Lorentz model and Lorentzian contributions 1 to 5. (b) For  $x = 0$  at a pressure of 8 GPa together with Lorentzian contributions 2 to 6.

TABLE II. Calculated  $\Gamma$ -point phonon frequencies (in  $\text{cm}^{-1}$ ) for  $\text{Na}_2\text{IrO}_3$  ( $x = 0$ ) at ambient pressure, compressed  $\text{Na}_2\text{IrO}_3$  (comp.; with lattice parameters of the  $x = 0.24$  sample but no Li substitution),  $\text{Na}_{1.5}\text{Li}_{0.5}\text{IrO}_3$  ( $x = 0.25$ , with lattice parameters of the  $x = 0.24$  sample and placing Li atoms into the center of the Ir hexagons) at ambient pressure, and  $\alpha\text{-Li}_2\text{IrO}_3$  ( $x = 1.0$ ) at ambient pressure. For each mode, the atoms with largest displacements are listed.

Mode	$\text{Na}_2\text{IrO}_3$						
	$\text{Na}_2\text{IrO}_3$	Atoms	comp.	$x = 0.25$	Atoms	$\alpha\text{-Li}_2\text{IrO}_3$	
c1	$A_u$	544	O	567	570	O	579
c2	$A_u$	503	Ir-O	525	532	Ir-O-Li	528
c3	$B_u$	502	Ir-O	518	535	Ir-O-Li	542
c4	$B_u$	497	Ir-O	515	525	Ir-O-Li	527
c5	$A_u$	454	Ir-O	506	485	Ir-O-Li	501
c6	$B_u$	453	Ir-O	507	484	Ir-O-Li	503
c7	$B_u$	425	Na-O	469	369	Li	406
c8	$A_u$	413	Na-O	463	361	Li	385
c9	$B_u$	379	Na-O	453	346	Li	392
c10	$B_u$	288	Na	299	344	Li	331
c11	$A_u$	269	Na	289	336	Li	337
c12	$B_u$	267	Na	283	310	Li	314

$C2/m$  symmetry of the crystal structure allows 18 infrared-active modes that are split into 7 modes of the  $A_u$  symmetry and 11 modes of the  $B_u$  symmetry. Their frequencies and natures are listed in Table II, where we restrict ourselves to modes above  $250 \text{ cm}^{-1}$  because low-energy modes are less characteristic and were not probed in our experiment.

In  $\text{Na}_2\text{IrO}_3$ , only the high-frequency mode c1 at  $544 \text{ cm}^{-1}$  [mode 6 in Fig. 6(c) below] is a purely oxygen based vibration. Five modes, c2–c6, found between  $453$  and  $503 \text{ cm}^{-1}$  entail significant contributions of Ir and can be seen as collective vibrations of the Ir-O framework. Experimentally, we resolve only four modes in this frequency range [modes 2–5 in Fig. 6(c) below] because some of the modes are nearly degenerate. Three further modes, c7–c9, found between  $379$  and  $425 \text{ cm}^{-1}$  and not observed experimentally, presumably due to their low oscillator strengths, are Na-O vibrations, whereas further infrared-active modes positioned below  $288 \text{ cm}^{-1}$  are dominated by Na atoms.

We explored the effect of Li doping by using lattice parameters of the  $x = 0.24$  sample and placing Li atoms into the center of the Ir hexagons (see phonon modes in Table II, column  $x = 0.25$ ). The high-energy mode c1 preserves its oxygen-based nature. However, modes c2, c5, and c6, which previously did not involve Na atoms, now feature comparable contributions of Ir and Li. The spectrum at lower energies changes entirely. No equivalent of modes c7–c9 can be found, and instead, Li-based vibrations dominate the spectrum below  $369 \text{ cm}^{-1}$ . This elucidates the origin of mode 1, which was observed in the Li-doped samples but not in the pure  $\text{Na}_2\text{IrO}_3$ . Moreover, the phonon spectrum at  $x = 0.25$  bears strong similarities to that of  $\alpha\text{-Li}_2\text{IrO}_3$  in terms of the nature of phonon modes because both Li and Ir atoms contribute to modes c2–c6. No infrared-active modes are seen in  $\alpha\text{-Li}_2\text{IrO}_3$  between  $406$  and  $501 \text{ cm}^{-1}$ , whereas below  $406 \text{ cm}^{-1}$  multiple Li-based vibrations occur.

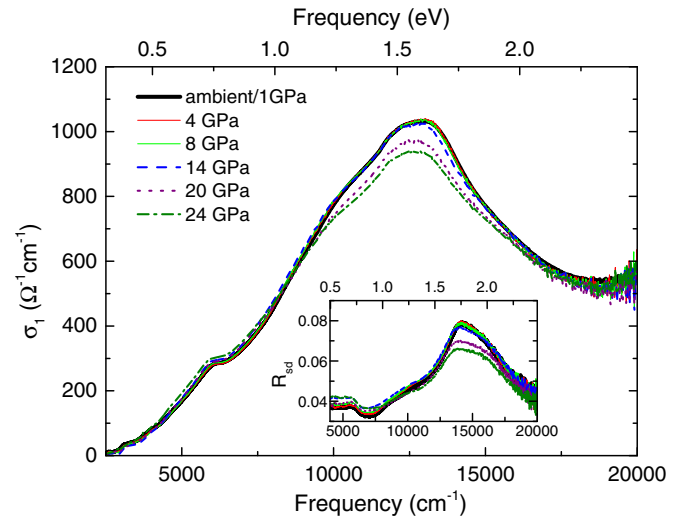


FIG. 4. Pressure-dependent optical conductivity spectra in the frequency range of the  $d$ - $d$  excitations of  $\text{Na}_2\text{IrO}_3$  up to 24 GPa. The inset shows the corresponding pressure-dependent reflectivity spectra  $R_{sd}$ .

Replacing atoms in a solid by isoelectronic atoms with a smaller covalent radius is expected to lead to a chemical pressure effect without any charge doping. Applying this general rule to  $\text{Na}_2\text{IrO}_3$ , one would expect a significant reduction in the lattice parameters of  $\text{Na}_2\text{IrO}_3$  by substituting Na with smaller Li atoms. It has been shown that the changes in the lattice parameters in  $\text{Na}_2\text{IrO}_3$  induced by Li doping are specific [31]: While the lattice parameters  $a$  and  $b$  are strongly decreased at the same rate by increasing Li content  $x$  (leading to an almost undistorted honeycomb Ir structure up to  $x \leq 0.25$ ), the lattice parameter  $c$  remains almost unchanged. Hence, the  $ca$  lattice parameter ratio increases with increasing doping  $x$ . This experimental finding was explained by the fact that Li atoms preferentially occupy the Na sites within the Ir honeycomb layers for  $x \leq 0.25$ , consistent with theoretical calculations [31]. The Na layers between the honeycomb layers remain basically unaffected for such low doping concentrations, and hence, no effective pressure is applied along the  $c$  axis. The effect of external, hydrostatic pressure on the physical properties of  $\text{Na}_2\text{IrO}_3$  is expected to be quite different, and hence, a direct comparison with the effect of Li doping on the physical properties like crystal structure and optical response is appealing. Therefore, we studied the optical properties and crystal structure of  $\text{Na}_2\text{IrO}_3$  single crystals as a function of external pressure.

## B. External pressure

The pressure-dependent optical conductivity spectra of  $\text{Na}_2\text{IrO}_3$  are shown in Fig. 4 in the range of the  $d$ - $d$  excitations and in Fig. 5(b) for the phonon energy range for some selected pressures. The reflectance ratios  $R_{sd}$  are included in the corresponding figures. In the range of the  $d$ - $d$  excitations we do not observe a significant change in the optical conductivity up to 8 GPa. For pressures above 8 GPa we observe a significant loss of spectral weight for the main excitation along with a slight shift of the three main peaks to lower energy. An

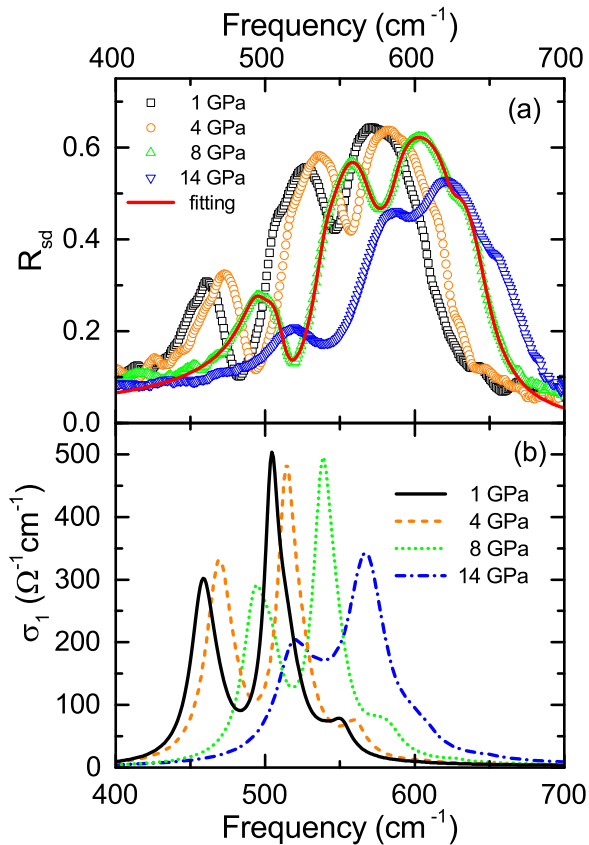


FIG. 5. (a) Pressure-dependent reflectivity spectra  $R_{sd}$  of  $\text{Na}_2\text{IrO}_3$  in the phonon mode range for selected pressures. As an example, the fitting of the reflectivity spectrum at 8 GPa with the Lorentz model is shown. (b) The corresponding real part of the optical conductivity. With increasing pressure all phonon modes harden and show a damping above 8 GPa.

additional contribution appears at around 2.0 eV, consistent with earlier studies [19], which is more clearly observed for the higher pressures. Overall, the optical excitations in  $\text{Na}_2\text{IrO}_3$  are quite robust regarding external pressure. These findings suggest that the  $(U - 3J_H)/t$  value is not significantly affected for pressures up to 8 GPa and is only slightly decreased for higher pressures.

In Fig. 5(b) the reflectivity spectra of  $\text{Na}_2\text{IrO}_3$  are depicted in the phonon mode range for selected pressures. In order to obtain the phonon frequencies as a function of pressure, we performed a fitting with Lorentz functions, taking into account the sample-diamond interface and the fitting of the ambient-pressure data as an extrapolation [64]. As an example, the fitting of the reflectance spectrum at 8 GPa is shown in Fig. 5(a). The so-obtained optical conductivity spectra in the phonon mode range are depicted in Fig. 5(b). We find five major phonon modes in the range 400–600  $\text{cm}^{-1}$ , labeled 2–6 according to Fig. 3(b), consistent with the ambient-pressure data. Similar to the free-standing measurements, phonon mode 1 has an extremely small oscillator strength and is accessible only by  $R + T$  analysis. Since the oscillator strength of this mode is not increased with pressure, we will not discuss it further. Like in the ambient-pressure data, we obtain two double-peak structures, with a small contribution of mode 6. There is

an additional very weak contribution in the high-energy range of the phonon mode region, which is not considered in the following due to its extremely small oscillator strength.

The pressure-dependent phonon frequencies are plotted in Fig. 6(c). We observe a monotonic hardening of all five phonon modes with increasing pressure, in agreement with the DFT results (Table II). Additionally, a broadening of the modes occurs for pressures above 8 GPa (see Fig. 5). Generally, the damping of phonon modes indicates an increasing metallic character of a material which is, however, not revealed by the pressure dependence of the overall reflectivity spectrum. In other words, it is a signal for only a small decrease of the  $(U - 3J_H)/t$  value, consistent with the results from the  $d-d$  excitations.

Next we discuss the effect of external pressure on the crystal structure of  $\text{Na}_2\text{IrO}_3$  based on pressure-dependent XRD measurements carried out on single crystals. In Figs. 6(a) and 6(b) we show the evolution of the lattice parameters  $a$ ,  $b' := b/\sqrt{3}$ ,  $c$ ,  $\beta$ , unit-cell volume  $V$ , and  $c/a$  ratio of  $\text{Na}_2\text{IrO}_3$  as a function of external pressure in comparison to the evolution with Li doping level  $x$ , as extracted from Ref. [31]. The parameter  $b'$  allows a more direct comparison between the lattice parameters  $a$  and  $b$  regarding the pressure evolution. The pressure scale is adjusted to the doping level  $x$  for  $x \leq 0.24$  samples using  $a$  and  $b'$ , and extended to  $x = 1$ . The full Li substitution corresponds to an external pressure of 29 GPa.

With increasing pressure, the lattice parameters  $a$ ,  $b'$ , and  $c$  decrease monotonically, with the strongest effect observed for the lattice parameter  $c$  perpendicular to the Ir honeycomb layers. The effect of pressure on the lattice parameter  $c$  is approximately doubled compared to the  $a$  and  $b'$  parameters. Hence, the highest compressibility of  $\text{Na}_2\text{IrO}_3$  is found along the  $c$  axis, which is illustrated by the  $c/a$  ratio that decreases from 1.04 to 0.99 [see Fig. 6(b)]. This effect can be ascribed to the two-dimensional nature of the Ir-O framework. The two in-plane lattice parameters  $a$  and  $b'$  are affected in a very similar manner, which excludes any pressure-induced distortion of the Ir hexagons. The angle  $\beta$  increases monotonically with increasing pressure [see Fig. 6(b)]. Furthermore, there is no sign of a pressure-induced structural phase transition within the measured pressure range.

In Fig. 6(a), the unit-cell volume  $V$  is plotted as a function of pressure  $p$ , as calculated from the pressure-dependent lattice parameters, together with the fit according to the Murnaghan equation of state [65],

$$V(p) = V_0[(B'_0/B_0)p + 1]^{-1/B'_0}, \quad (1)$$

with the bulk modulus  $B_0 = -dp/d \ln V$  and its first derivative  $B'_0$  at ambient pressure. From the fitting we obtained  $B_0 = 89.9 \pm 1.2$  GPa and  $B'_0 = 5.0 \pm 0.2$ . In comparison, for pyrochlore iridates like  $\text{Eu}_2\text{Ir}_2\text{O}_7$  and similar compounds like  $\text{Eu}_2\text{Sn}_2\text{O}_7$ , bulk moduli  $B_0$  in the range 166 to 285 GPa and  $B'_0$  in the range 3.8 to 28 are reported [66–69]. For the perovskite iridate  $\text{Sr}_2\text{IrO}_4$ ,  $B_0 = 174 \pm 5$  GPa and  $B'_0 = 4.0 \pm 0.7$  are found [70], while for the stripy-honeycomb  $\gamma$ - $\text{Li}_2\text{IrO}_3$ ,  $B_0$  around 130 GPa was reported recently [71]. Therefore, the bulk modulus for the honeycomb iridate  $\text{Na}_2\text{IrO}_3$  is smaller than for pyrochlore, perovskite, and stripy-honeycomb iridates; that is,  $\text{Na}_2\text{IrO}_3$  is more compressible. This effect can be attributed to the two-dimensional, layered character of its

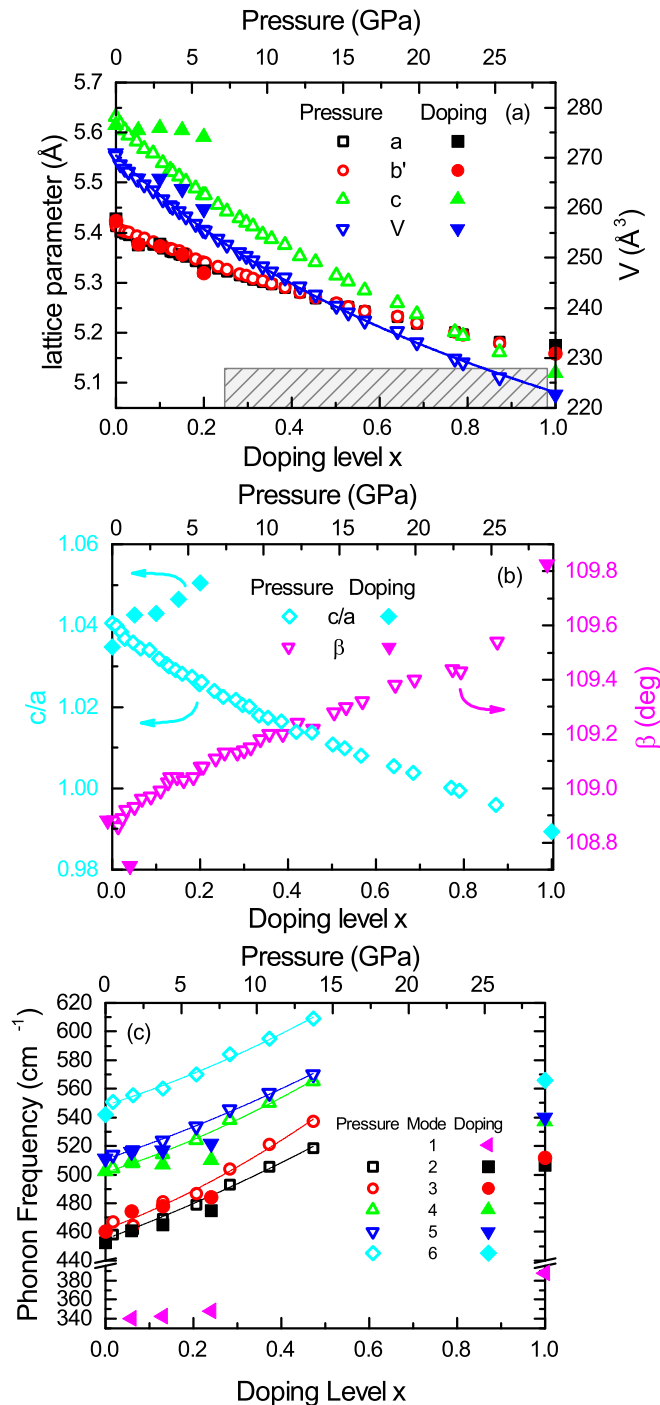


FIG. 6. (a) and (b) Lattice parameters  $a$ ,  $b' := b/\sqrt{3}$ ,  $c$ ,  $\beta$ , unit-cell volume  $V$ , and  $c/a$  ratio of Na<sub>2</sub>IrO<sub>3</sub> as a function of external pressure (open symbols) and Li doping level  $x$  (solid symbols). The results for doping levels  $x = 0.05$ – $0.2$  and  $x = 1$  are extracted from Refs. [31,39], respectively. The pressure scale is adjusted to the doping level  $x$  according to the evolution of the lattice parameters  $a$  and  $b$ . The volume  $V$  is fitted by the Murnaghan equation of state as discussed in the text. The hatched area in (a) marks the miscibility gap for doping levels  $0.25 < x < 1$  [31]. (c) Phonon mode frequencies as a function of external pressure and Li doping level  $x$ , keeping the pressure scaling as adjusted for the lattice parameters in (a) and (b). The solid lines are parabolic fits to the pressure-dependent mode frequencies.

crystal structure, which can be relatively easily compressed along the  $c$  axis, as illustrated by the pressure dependence of the lattice parameter  $c$  [see Figs. 6(a) and 6(b)]. This anisotropic compressibility is in line with the hierarchy of phonon modes. The Na-O bonds responsible for the compression along  $c$  are softer than their Ir-O counterparts, which determine the compressibility in the  $ab$  plane (Table II). Comparing the bulk modulus of Na<sub>2</sub>IrO<sub>3</sub> with typical layered compounds like Bi<sub>2</sub>Te<sub>3</sub> ( $B_0 = 22$ – $28$  GPa and  $B'_0 = 13.8$ – $17.1$  for low pressures and  $B_0 = 36$ – $38$  GPa and  $B'_0 = 4.6$ – $5.5$  for higher pressures) [72–74] or graphite ( $B_0 = 33.8$ – $39$  GPa and  $B'_0 = 8.9$ – $10$ ) [75–78], however, reveals that Na<sub>2</sub>IrO<sub>3</sub> is much less compressible.

### C. Comparison between isoelectronic doping and external pressure

The optical conductivity identifies qualitative differences between the effects of partial Li substitution ( $x \leq 0.24$ ), full Li substitution (pure  $\alpha$ -Li<sub>2</sub>IrO<sub>3</sub>), and external pressure. With both increasing Li content (up to  $x = 0.24$ ) and increasing pressure above 8 GPa, the spectral weight in the range of the  $d$ - $d$  excitations decreases. In the case of doping, this decrease is stronger, and also a shift of the main excitation to higher energies is observed. On the contrary, full substitution with Li leads to an increase in the spectral weight along with a shift of the main excitations towards lower energies. We interpret these differences in terms of the Mott vs QMO picture and in terms of the proximity to the Kitaev limit. The partial Li substitution turns out to be most promising for approaching the Kitaev limit and, concurrently, enhances the Mott-insulating character. Full Li substitution goes in exactly the opposite direction by taking the system farther away from the Kitaev limit and toward the QMO state. The effect of external pressure is relatively mild. At pressures below 8–10 GPa, which are feasible for low-temperature magnetism studies, no visible changes in the optical conductivity occur.

These dissimilar trends are not immediately obvious from the structural perspective. Indeed, the physics of the hexagonal iridates is largely confined to the Ir-O layers, and the compression in the  $ab$  plane is about the same in all three cases [Fig. 6(a)]. Moreover,  $\alpha$ -Li<sub>2</sub>IrO<sub>3</sub> may even be viewed as Na<sub>2</sub>IrO<sub>3</sub> compressed to approximately 29 GPa, when all three lattice parameters are considered. On the other hand, it seems crucial that partial Li substitution leaves the  $c$  parameter nearly unchanged, in stark contrast to the effects of external pressure and full Li substitution. Given that oxygen-assisted Ir-O-Ir hopping plays a central role in the physics of Na<sub>2</sub>IrO<sub>3</sub> [24], we believe that not only the compression in the  $ab$  plane but also a change in the relative positions of Ir and O are of importance. Indeed, oxygen-mediated hoppings largely depend on the Ir-O-Ir angle, which, in turn, should be affected by the  $c$  parameter.

The difference between the fully substituted  $\alpha$ -Li<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> compressed to 29 GPa is subtler and cannot be explained by the evolution of lattice parameters, but it becomes clearer when we consider the evolution of phonon modes. In general, one expects that compression of the structure caused by external pressure or isoelectronic doping with smaller Li atoms increases the phonon frequencies because atoms get

closer to each other and individual bonds harden. In the case of Li doping, the introduction of lighter Li atoms is a concurrent effect that should increase phonon frequencies too. Indeed, Fig. 6(c) demonstrates a steady increase in the experimental phonon frequencies, whereas the computed frequencies for  $c1-c6$  increase as well (compare different columns in Table II). This trend no longer holds for modes  $c7-c9$ , which shift to higher frequencies upon compression of  $\text{Na}_2\text{IrO}_3$  (see column  $\text{Na}_2\text{IrO}_3$  comp. in Table II) but to lower frequencies upon partial or full Li substitution in pure  $\alpha\text{-Li}_2\text{IrO}_3$  (columns  $x = 0.25$  and  $\alpha\text{-Li}_2\text{IrO}_3$  in Table II). It becomes even more counterintuitive when the nature of these phonon modes is considered. With heavier Na atoms replaced by lighter Li, one would hardly expect the softening of  $c7-c9$  that occurs in  $\alpha\text{-Li}_2\text{IrO}_3$ . This shows that, despite similar lattice dimensions,  $\alpha\text{-Li}_2\text{IrO}_3$  cannot be viewed as an ambient-pressure analog of  $\text{Na}_2\text{IrO}_3$  compressed to 29 GPa.

Altogether, we see that the three effects considered in this study (partial and full Li substitution and external pressure) are all dissimilar, and among them partial Li substitution looks most promising for enhancing the Kitaev interaction term.

#### IV. CONCLUSION

In summary, from investigating  $(\text{Na}_{1-x}\text{Li}_x)_2\text{IrO}_3$  single crystals for doping levels  $x \leq 0.24$  and  $x = 1$  by optical spectroscopy at ambient conditions we found that all measured compounds are relativistic Mott insulators despite being close to the quasimolecular orbital regime. Isoelectronic doping of  $\text{Na}_2\text{IrO}_3$  by Li up to the doping level of  $x = 0.24$  brings the material closer to the Kitaev limit and more into the Mott-insulating regime. From an experimental point of view all observed phonon modes harden with increasing Li content  $x$  due to the chemical pressure effect, while our DFT+ $U$ +SO calculations show that the nature of individual modes is changed even for low doping. Full substitution of Na by Li atoms does not follow the above trends: in  $\alpha\text{-Li}_2\text{IrO}_3$ ,

the intersite  $j_{1/2} \rightarrow j_{1/2}$  excitations appear to be enhanced according to the optical conductivity spectrum. Furthermore, our data suggest that  $\alpha\text{-Li}_2\text{IrO}_3$  is less close to the Kitaev limit and lies closer to the quasimolecular orbital regime than the Li-doped samples.

Pressure-dependent optical and x-ray diffraction measurements on  $\text{Na}_2\text{IrO}_3$  single crystals enabled a comparison of the effect of Li doping with external pressure. With increasing pressure, the lattice parameters of  $\text{Na}_2\text{IrO}_3$  decrease monotonically, with the largest effect found for parameter  $c$ , which is perpendicular to the honeycomb layers. The lattice parameters of  $\alpha\text{-Li}_2\text{IrO}_3$  are consistent with the pressure-induced changes in the lattice parameters of  $\text{Na}_2\text{IrO}_3$  at 29 GPa, whereas for doping levels  $x \leq 0.24$  the  $c$  lattice parameter remains unchanged. With increasing pressure all phonon modes harden, but their nature remains nearly unchanged, in contrast to the effect of Li doping. The effect of pressure on the Ir  $d-d$  excitations is much less pronounced compared to Li substitution, and we found out that partial Li substitution is most promising for tuning the system towards the Kitaev limit.

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