In recent years, layered honeycomb 4$d$ and 5$d$ metal oxides, such as Na$_2$IrO$_3$, α-Li$_2$IrO$_3$, and α-RuCl$_3$, have been intensively scrutinized as Kitaev physics candidates due to the presence of sizable nearest-neighbor bond-dependent spin-orbital 1/2 Ising interactions. However, instead of the expected $Z_2$ spin liquid groundstate, as shown by Kitaev, these materials order magnetically either in a zig-zag structure (Na$_2$IrO$_3$, α-RuCl$_3$) or an incommensurate spiral structure (α-Li$_2$IrO$_3$). This magnetic long-range order has been suggested to originate from further non-Kitaev interactions and a present debate is whether the magnetic excitations in these materials nevertheless retain some of the non-trivial features of the Kitaev model, such as fractionalization. It might be expected that one route to enhance Kitaev interactions would be by applying pressure or by doping. However, the physics of this structural family is much richer and there are many more instabilities that interfere with the Kitaev interactions, in particular under pressure. Indeed, Li$_2$RuO$_3$ is nonmagnetic and strongly dimerized at ambient pressure, while SrRu$_2$O$_4$ is an ultra-high-temperature antiferromagnet, despite having the same planar geometry, and shows no bond disproportionation.

Many factors control the competition between Kitaev physics, magnetism, and dimerization in honeycomb networks, such as the number of transition metal $M$ d-electrons, the strength of spin-orbit coupling, the strength of correlation effects and Hund’s rule coupling, or the ionic radii of the buffer element $A$. In this context it is particularly instructive to compare α-Li$_2$IrO$_3$ with Li$_2$RuO$_3$, which contains the same buffer element (Li). α-Li$_2$IrO$_3$ is less correlated than Li$_2$RuO$_3$ (5$d$ versus 4$d$ electrons, resp.) so that one would expect in the former a reduced tendency to magnetism in favor of dimerization. On the other hand, α-Li$_2$IrO$_3$ has only a single hole in the $t_{2g}$ manifold, as opposed to two in Li$_2$RuO$_3$, and stronger spin-orbit interaction. This should weaken dimerization and strengthen Kitaev-type physics in α-Li$_2$IrO$_3$. Further, in comparison to Na$_2$IrO$_3$, the Li ionic radius is smaller than the Na ionic radius, thus favoring dimerization in Li$_2$MO$_3$. The result is a delicate balance of all these effects. At ambient pressure, α-Li$_2$IrO$_3$ shows a highly symmetric honeycomb structure with a bond disproportionation of less than 3% and magnetically orders in a spiral structure, which features a non-collinear incommensurate antiferromagnetic order inside Ir planes. It is not unreasonable to assume that α-Li$_2$IrO$_3$ may be an intermediate case between Na$_2$IrO$_3$ and Li$_2$RuO$_3$, and could be switched between the two extremes (magnetic Kitaev and nonmagnetic dimerized) by an external perturbation, such as physical pressure, an intriguing possibility.

In this work, we show that this is indeed the case. We find that, in contrast to Na$_2$IrO$_3$, in Li$_2$IrO$_3$ a structural phase transition from a monoclinic to a dimerized triclinic structure occurs at a low pressure of $P_c = 3.8$ GPa. Ab initio density functional theory (DFT) calculations also find this transition, with the transition pressure depending on the assumed correlation strength. The experimental $P_c$ is obtained for an effective Hubbard repulsion...
interaction $U - J = 1.5$ eV ($U$ and $J$ being the Hubbard and Hund’s rule coupling parameters, resp.), which is very reasonable for a 5d metal. Analyzing the calculations we observe that indeed $\alpha$-Li$_2$IrO$_3$ is a borderline case, wherein the singlet dimerized solution and the magnetic undimerized one are very close in energy. Pressure reduces the tendency to magnetism, thus diminishing the energetic advantage of forming an antiferromagnetic state, and brings Ir ions closer together, enhancing the advantage of forming covalent bonds. Compared to Li$_2$RuO$_3$, the main difference lies in the fact that in $\alpha$-Li$_2$IrO$_3$ only one $d$-hole participates in the formation of covalent bonds.

At ambient pressure $\alpha$-Li$_2$IrO$_3$ crystallizes in a monoclinic $C2/m$ space group [10, 20], with the unit cell shown in the Supplemental Material [21]. Ir forms hexagons with edge-sharing IrO$_6$ octahedra and a single Li atom in its center (Ir$_2$LiO$_3$ layer). These layers are intercalated with Li$_2$O$_3$ layers. At ambient pressure all Ir–Ir bonds have nearly the same length.

The pressure dependence of the lattice parameters obtained by refining the single-crystal XRD data is depicted in Figs. 1(a)+(b). See the Suppl. Material [21] for a description of sample preparation and pressure-dependent XRD measurements. For pressures up to $\approx 3.8$ GPa the lattice parameters decrease monotonically with increasing pressure. We included $b' = b/\sqrt{3}$ for a better comparison between the three lattice parameters. Both in-plane lattice parameters $a$ and $b'$ are affected in a very similar manner. The strongest effect is observed for the lattice parameter $c$. This is illustrated by the $c/a$ value in the inset of Fig. 1(a), which decreases with pressure up to 3.8 GPa. Within the error bar the monoclinic angle $\beta$ is not affected by pressure.

For pressures above $P_c = 3.8$ GPa the crystal structure can no longer be refined within the $C2/m$ space group, but requires a triclinic group, $\text{PT}$, with half of the unit cell volume. The structural phase transition is completely reversible [see open symbols in Figs. 1(a)+(b)]. In order to compare the high-pressure evolution of the lattice parameters to the low-pressure structures, we consider an supercell, isometric to the ambient-pressure unit cell. Note that due to the triclinic symmetry group, two different choices are possible. We select one of these (resulting in the X1 dimerization discussed below) and show the refined lattice parameters of this doubled triclinic unit cell in Figs. 1(a)+(b). All angles of this cell exhibit an anomaly at $P_c$: $\gamma$ jumps from 90° to $\approx 93.4$° and is independent of pressure above $P_c$ within the error bars, while $\alpha$ monotonically decreases with pressure, and $\beta$ exhibits an abrupt but small ($\approx 1$°) decrease at $P_c$ and then monotonically increases with pressure. The structural phase transition also induces abrupt changes in the lattice parameters. Whereas the in-plane lattice parameter $a$ is most affected with an overall reduction of about 3%, the in-plane lattice constant $b$ slightly increases at $P_c$. Interestingly, at the transition the $c/a$ ratio jumps up from $\approx 0.99$ to 1.01, but above it monotonically decreases with pressure. Thus, also above $P_c$ the lattice is more compressible along the $c$ direction.

We fitted the volume $V$ and the lattice parameters $r$ ($r=a,b,c$) separately for the low- and high-pressure phases with the second-order Murnaghan equation of state [22], to obtain the bulk moduli $B_{0,V}$ and $B_{0,r}$:

\[
V(p) = V_0 \cdot [(B'_0/B_{0,V}) \cdot p + 1]^{-1/B'_0} \quad (1)
\]

\[
r(p) = r_0 \cdot [(B'_0/B_{0,r}) \cdot p + 1]^{-1/3B'_0} \quad (2)
\]

FIG. 1. Pressure dependence of the volume $V$ of the unit cell and the lattice parameters $a$, $b'=b/\sqrt{3}$, $c$ and $c/a$ value shown in (a) and the corresponding angles $\alpha$, $\beta$ and $\gamma$ in (b). For a better comparison a non-primitive unit cell was used for the high-pressure phase above 3.8 GPa, as explained in the text. The solid lines in (a) are fits with a Murnaghan type equation of state (see text). Open symbols are values observed during pressure release. If not shown, the error bar is smaller than the symbol size. (c) Calculated lattice parameters for pressures up to 22 GPa (corrected by 3 GPa to closely resemble the experimental crystal volume at zero pressure).
For the low-pressure phase we find $B_0$ with $c$ pressible along the $c$ direction. Above $P_t$ the bulk modulus is increased to $B_0 \approx 125(3)$ GPa, while $B_{0,a}$ and $B_{0,b}$ sharply increase to $\approx 170$ GPa, and $B_{0,c}$ is slightly decreased compared to the low-pressure phase to about $86(5)$ GPa. Thus, $\alpha$-Li$_2$IrO$_3$ hardens at $P_t$, and the hardening takes place within the Ir planes.

For a comparison with isostructural Na$_2$IrO$_3$ we refigured the data of Ref. 29 with $B_0^0$ fixed to 4 and listed the so-obtained results in Table I. Compared to $\alpha$-Li$_2$IrO$_3$ in the low-pressure phase, the bulk modulus $B_{0,V}$ of Na$_2$IrO$_3$ is only slightly lower. Interestingly, for Na$_2$IrO$_3$ the values $B_{0,a}$ and $B_{0,b}$ are much higher, whereas $B_{0,c}$ is much lower. Hence, in its low-pressure phase $\alpha$-Li$_2$IrO$_3$ is more compressible in the $ab$ plane and less compressible along the $c$ direction as compared to Na$_2$IrO$_3$. The former effect could be attributed to the smaller Li atoms occupying the center of the hexagons (instead of Na), and the latter to the stronger Li–O bonds with strong out-of-$ab$-plane character. The higher in-plane compressibility is instrumental in triggering Ir dimerization. Above $P_c$ the bulk moduli $B_{0,a}$ and $B_{0,b}$ of $\alpha$-Li$_2$IrO$_3$ are sharply enhanced and become similar to those for Na$_2$IrO$_3$, i.e., the compressibility of the $ab$ plane becomes similar for both compounds.

For a more detailed investigation, we refined the Ir–Ir bond lengths [see Fig. 2 (a)], since they are relevant for the magnetic and electronic properties of the material. In a perfectly hexagonal lattice one can distinguish three Ir–Ir bonds related by a 120° rotation [Fig. 2 (b)]. Following the nomenclature of Ref. 23, we shall call them Z1, X1, and Y1. In the monoclinic phase below $P_c$, the X1 and Y1 bonds are equivalent by symmetry, while Z1 is distinct. The high-pressure phase lacks the $C_2$ symmetry, and therefore the two bonds X1 and Y1 become inequivalent. The Ir–Ir bond lengths as a function of pressure, as obtained from the refinement of the XRD data, are plotted in Fig. 2 (a). At $P_c$ one of the X1/Y1 bonds is slightly increased from $\approx 2.95$ Å to $\approx 3.00$ Å, while the other one is strongly decreased to 2.69 Å. Note that this distance is smaller than the Ir–Ir distance of 2.714 Å in Ir metal. As opposed to Li$_2$RuO$_3$, where (i) the dimerized bonds alternate between X1 and Y1, (ii) a $C_2$ axis is preserved and (iii) the $P2_1/m$ monoclinic symmetry is realized, in $\alpha$-Li$_2$IrO$_3$ either X1 or Y1 bonds dimerize, thus breaking the $C_2$ symmetry [Figs. 2 (c,d)]. The Z1 bond’s length increases at $P_c$ and becomes nearly degenerate with that of the longer X1/Y1 bond. The energy difference between these various types of dimerization is related to different mutual arrangements of the dimers: armchair (herringbone) or ladder (parallel). As dicussed in Refs. 15, 27 the choice is being made by long-range, likely elastic, interactions. It is worth noting that very recently Veiga et al. 27 have observed a structural phase transition at $P_c \approx 4$ GPa in a similar 5$d$-system $\beta$-Li$_2$IrO$_3$, which is consistent with dimerization above $P_c$, although no actual evidence of dimerization was obtained.

In order to gain more insight into the physics of dimerization and interactions that control it, we have per-

| $B_{0,V}$ | $V_0$ [Å$^3$] | $B_{0,a}$ [GPa] | $B_{0,b}$ [GPa] | $B_{0,c}$ [GPa] |
|----------|---------------|-----------------|-----------------|-----------------|
| low-p phase | 106(5) | 220.1(2) | 114(2) | 113(2) | 92(1) |
| high-p phase | 125(3) | 214.3(9) | 167(2) | 166(2) | 86(5) |
| Na$_2$IrO$_3$ | 100.6(1) | 269.55(3) | 152(2) | 146 (2) | 58(1) |
formed first-principles DFT calculations, as described in the Suppl. Material [21]. First, we find, in agreement with experiment and qualitative considerations, that \( \alpha-\) Li\(_3\)IrO\(_3\) is more prone to dimerization than Na\(_2\)IrO\(_3\), and, in fact, dimerizes in DFT within the generalized gradient approximation (GGA) already at zero pressure. This can be traced to the underestimate of correlation effects, and, therefore, underestimation of the tendency to magnetism. Indeed, Ref. [28] showed that at the mean-field level, usually called the LDA+U approximation (or GGA+U), correlations increase the Stoner coupling \( I \), which characterizes the tendency to form magnetic moments in DFT, as \( I \rightarrow I + (U - J)/5 \), where \( U \) and \( J \) are the Hubbard and Hund’s rule coupling parameters. For 5d metals \( I \) is of the order of 0.3 eV, while \( U_{\text{eff}} = U - J \), as we discuss in more detail in the Suppl. Material [21], should be taken to be close to 1.5 eV. Thus, including correlations enhances magnetic interactions by about a factor of two.

Furthermore, in accordance with our previous study [28] for the isoelectronic doping series Na\(_{1\,(1-x)}\)Li\(_4\)IrO\(_3\), we find that at ambient pressure, using the experimental crystal volume, it is not enough to include an effective Hubbard correlation of about \( U_{\text{eff}} = U - J = 1.5 \) eV to stabilize magnetism and the observed undimerized structure. The spin-orbit coupling also appears essential. Here we choose the zigzag antiferromagnetic order to mimic the incommensurate spiral order [31] observed in experiment [10]. This indicates that the observed structural transition at finite pressures is driven by two competing energy scales: (i) the energy gained by the formation of magnetic moments and (ii) the energy gained by placing two electrons of neighboring Ir atoms in the bonding orbital resulting from the Ir–Ir dimerization. In both processes, correlation effects are significantly involved. At low pressures the overlap of adjacent Ir atoms is slightly too small to favor the dimerization, while a small decrease of the Ir–Ir distances with pressure changes the situation and results in a breakdown of the magnetic order and structural dimerization. Note that in the above-mentioned experiment on \( \beta-\) Li\(_2\)IrO\(_3\) [21] static magnetism was disappearing prior to the putative dimerization transition, at \( P_m \approx 2 \) GPa, and one can speculate that at a higher pressure, corresponding to dimerization, the local moments collapse as well, in agreement with the present calculations. Alternatively, between \( P_m \) and \( P_c \) the system may be in a valence bond liquid state, similar to that in Li\(_2\)RuO\(_3\) at high temperature [15].

In Fig. 1(c) we show the lattice parameters calculated within relativistic GGA+U as a function of the simulated hydrostatic pressures. As typical for GGA, we observe slight underbinding, so that the experimental volume at ambient pressure corresponds to the calculated pressure of \( \approx 3 \) GPa. In the following, we subtract this systematic error from the calculated pressure. With this in mind, the calculated transition pressure as well as the resulting bond disproportions are in good agreement with the experiment. At the phase transition, the X1/Y1 dimerized structure is the most stable with a relative Ir–Ir dimerization of long/short bond= 3.07/2.61 \( \approx 1.18 \) in very good agreement with the experiment, as shown in Fig. 2(a). In addition, we find an abrupt collapse of magnetism at \( P_c \) (see Suppl. Material [21]).

At this point, it is insightful to investigate the dimerization pressure for the closely related Na\(_2\)IrO\(_3\) compound. In fact, at 29 GPa the crystal structure of Na\(_2\)IrO\(_3\) has been shown to resemble that of \( \alpha-\) Li\(_2\)IrO\(_3\) with respect to the lattice metrics [23]. Our simulations for Na\(_2\)IrO\(_3\) (see Suppl. Material [21]) predict lattice parameters that are in excellent agreement with the observations in the experimentally studied pressure range up to 30 GPa. At about 45 GPa, we find a structural transition perfectly analogous to the one we observed in \( \alpha-\) Li\(_3\)IrO\(_3\). It is accompanied by a magnetic collapse and the Ir–Ir dimerization triggers a strong decrease of the in-plane \( a \) lattice parameter, while the \( b \)-lattice parameter is slightly enhanced. The \( c \) parameter in Na\(_2\)IrO\(_3\) is significantly larger than in \( \alpha-\) Li\(_2\)IrO\(_3\), due to the larger intercalated ion in Na\(_2\)IrO\(_3\). Notably, the Ir–Ir distance, at which the transition occurs, about 2.95 Å, is almost exactly the same as for \( \alpha-\) Li\(_2\)IrO\(_3\) and also the unit cell volume is remarkably similar (\( V \approx 210 \) Å\(^3\)). Indeed, due to the larger Na ion size compared to Li, the IrO\(_3\) layer is less compressible in Na\(_2\)IrO\(_3\), as discussed above, and thus formation of sufficiently short dimers (in order to take full advantage of the covalent energy) is hindered. This is also validated by our bulk modulus study (Table I). Otherwise, as expected due to their similar electronic properties, these two compounds behave in the same way. The pressure of \( \approx 45 \) GPa, at which we expect the dimerization transition in Na\(_2\)IrO\(_3\) to occur, should be accessible in diamond anvil cells but is beyond the scope of the present study. Conducting such an experiment in the future will be invaluable to confirm the general physical picture that we deduce in this paper.

In summary, \( \alpha-\) Li\(_2\)IrO\(_3\) undergoes a pressure-induced structural phase transition at \( P_c=3.8 \) GPa with symmetry lowering to \( P\bar{T} \). This transition mainly affects the \( ab \) plane with the Ir hexagons. As corroborated by our density functional theory calculations, our refinements of the Ir positions show that the structural phase transition is accompanied by a dimerization of the previously equally long X1/Y1 Ir–Ir bonds. Analysis of the total energies of the high-symmetry and the dimerized \( P\bar{T} \) lattices at the experimental crystal volume shows that several factors affect the propensity to dimerization, namely the size of the central ion (i.e., Li vs. Na), as well as the strength of the spin-orbit interaction, electronic correlations, and Hund’s rule coupling (all of them discourage dimerization, cf. 4d vs. 5d metals), and the number of \( d \)-electrons in the metal species (e.g., Ru vs. Ir). Li\(_2\)RuO\(_3\), having (a) a small central ion, (b) four \( d \)-electrons, and (c) weaker spin-orbit coupling has the strongest tendency towards dimerization among the known 213 systems, de-
spite being more magnetic than Ir. $\alpha$-Li$_2$IrO$_3$ has one more $d$-electron and stronger spin-orbit interaction, but weaker Hubbard and Hund’s rule couplings, and thus dimerizes only under pressure, albeit at a relatively small $P_c$. Na$_3$IrO$_3$ only differs in terms of the central ion size, and thus compressibility, and is predicted to dimerize as well, at an accessible, but much higher pressure.

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[1] A. Kitaev, “Anyons in an exactly solved model and beyond,” Ann. Phys. (NY) **321**, 2 – 111 (2006) January Special Issue.

[2] G. Jackeli and G. Khaliullin, “Mott Insulators in the Strong Spin-Orbit Coupling Limit: From Heisenberg to a Quantum Compass and Kitaev Models,” Phys. Rev. Lett. **102**, 017205 (2009)

[3] J. Chaloupka, G. Jackeli, and G. Khaliullin, “Kitaev-Heisenberg Model on a Honeycomb Lattice: Possible Exotic Phases in Iridium Oxides $\alpha$-Li$_2$IrO$_3$,” Phys. Rev. Lett. **105**, 027204 (2010)

[4] S. K. Choi, R. Coldea, A. N. Kolmogorov, T. Lancaster, I. I. Mazin, S. J. Blundell, P. G. Radaelli, Yogesh Singh, P. Gegenwart, K. R. Choi, S.-W. Cheong, P. J. Baker, C. Stock, and J. Taylor, “Spin Waves and Revised Crystal Structure of Honeycomb Iridate Na$_2$IrO$_3$,” Phys. Rev. Lett. **108**, 127204 (2012)

[5] K. W. Plumb, J. P. Clancy, L. J. Sandilands, V. Vijay Shankar, Y. F. Hu, K. S. Burch, Hae-Young Kee, and Young-June Kim, “$\alpha$-RuCl$_3$: A spin-orbit assisted Mott insulator on a honeycomb lattice,” Phys. Rev. B **90**, 152 (2014)

[6] Stephen M. Winter, Alexander A. Tsirlin, Maria Daghofer, Jeroen van den Brink, Yogesh Singh, Philipp Gegenwart, and Roser Valentí, “Models and materials for generalized Kitaev magnetism,” J. Ph. Conden. Matter **29**, 493002 (2017)

[7] R. D. Johnson, S. C. Williams, A. A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valentí, and R. Coldea, “Monoclinic crystal structure of $\alpha$-RuCl$_3$ and the zigzag antiferromagnetic ground state,” Phys. Rev. B **92**, 235119 (2015)

[8] J. A. Sears, M. Songvilay, K. W. Plumb, J. P. Clancy, Y. Qiu, Y. Zhao, D. Parshall, and Young-June Kim, “Magnetic order in $\alpha$ – RuCl$_3$: A honeycomb-lattice quantum magnet with strong spin-orbit coupling,” Phys. Rev. B **91**, 144420 (2015)

[9] A. Banerjee, C. A. Bridges, J-Q Yan, A. A. Aczel, L. Li, M. B. Stone, G. E. Granroth, M. D. Lumsden, Y. Yiu, J. Knolle, S. Bhattacharjee, D. L. Kovrizhin, R. Moessner, D. A. Tennant, D. G. Mandrus, and S. E. Nagler, “Proximate Kitaev quantum spin liquid behaviour in a honeycomb magnet,” Nat. Mater. **15**, 733 – 740 (2016)

[10] S. C. Williams, R. D. Johnson, F. Freund, S. Choi, A. Jesche, I. Kimchi, S. Manni, A. Bombardi, P. Manuel, P. Gegenwart, and R. Coldea, “Incommensurate counterrotating magnetic order stabilized by Kitaev interactions in the layered honeycomb $\alpha$-Li$_2$IrO$_3$,” Phys. Rev. B **93**, 081109 (2016)

[11] Stephen M. Winter, Kira Riedl, Pavel A. Maksimov, Alexander L. Chernyshev, Andreas Honecker, and Roser Valentí, “Breakdown of magnons in a strongly spin-orbital coupled magnet,” Nat. Commun. **8**, 1152 (2017)

[12] Y. Kasahara, K. Sugii, T. Olimishi, M. Shimozawa, M. Yamashita, N. Kurita, H. Tanaka, J. Nasu, Y. Motome, T. Shibayachi, and Y. Matsuda, “Unusual thermal effect in a Kitaev spin liquid candidate $\alpha$-RuCl$_3$,” ArXiv e-prints (2017), arXiv:1709.10286 [cond-mat.str-el]

[13] Y. Miura, Y. Yasui, M. Sato, N. Igawa, and K. Kakurai, “New-Type Phase Transition of Li$_2$RuO$_3$ with Honeycomb Structure,” J. Phys. Soc. Jpn. **76**, 033705 (2007)

[14] J. Park, T.-Y. Tan, D. T. Adroja, A. Daoud-Aladine, S. Choi, D.-Y. Cho, H.-S. Lee, J. Kim, H. Sim, T. Morioka, H. Nojiri, V. V. Krishnamurthy, P. Manuel, M. R. Lees, S. V. Streltsov, D. I. Khomskii, and J.-G. Park, “Robust singlet dimers with fragile ordering in two-dimensional honeycomb lattice of Li$_2$RuO$_3$,” Sci. Rep. **6**, 25238 (2016)

[15] S. A. J. Kimber, J. I. Mazin, J. Shen, H. O. Jeschke, S. V. Streltsov, D. N. Argyriou, R. Valentí, and D. I. Khomskii, “Valence bond liquid phase in the honeycomb lattice material Li$_2$RuO$_3$,” Phys. Rev. B **89**, 081408(R) (2014)

[16] C. I. Hiley, D. O. Scanlon, A. A. Sokol, S. M. Woodley, A. M. Ganose, S. Sangiao, J. M. de Teresa, P. Manuel, D. K. Khaliullin, and M. R. Lees, and R. I. Walton, “Antiferromagnetism at T>500K in the layered hexagonal ruthenate SrRu$_2$O$_6$,” Phys. Rev. B **92**, 104413 (2015)

[17] S. V. Streltsov, J. I. Mazin, and K. Foyevtsova, “Localized itinerant electrons and unique magnetic properties of SrRu$_2$O$_6$,” Phys. Rev. B **92**, 134408 (2015)

[18] S. V. Streltsov and D. I. Khomskii, “Orbital physics in transition metal compounds: new trends,” ArXiv e-prints (2017), arXiv:1711.05409 [cond-mat.str-el]

[19] F. Freund, S. C. Williams, R. D. Johnson, R. Coldea, P. Gegenwart, and A. Jesche, “Single crystal growth from separated educts and its application to lithium transition-metal oxides,” Sci. Rep. **6**, 35362 (2016)

[20] Matthew J. O’Malley, “Henk” Verweij, and
Patrick M. Woodward, “Structure and properties of ordered Li$_2$IrO$_3$ and Li$_2$PtO$_3$,” *J. Solid State Chem.* **181**, 1803–1809 (2008).

[21] See Supplemental Material at — for details about sample preparation, experimental setup, and the results of additional calculations.

[22] F. D. Murnaghan, “The Compressibility of Media under Extreme Pressures,” *P. Natl. Acad. Sci. USA* **30**, 244–247 (1944).

[23] V. Hermann, J. Ebad-Allah, F. Freund, I. M. Pietsch, A. Jesche, A. A. Tsirlin, J. Deisenhofer, M. Hanfland, P. Gegenwart, and C. A. Kuntscher, “High-pressure versus isoelectronic doping effect on the honeycomb iridate Na$_2$IrO$_3$,” *Phys. Rev. B* **96**, 195137 (2017).

[24] S. Nishimoto, Vamshi M. K., V. Yushankhai, H. Stoll, U. K. Rößler, Liviu Hozoi, I. Rousochatzakis, and J. van den Brink, “Strongly frustrated triangular spin lattice emerging from triplet dimer formation in honeycomb Li$_2$IrO$_3$,” *Nat. Commun.* **7**, 10273 (2016).

[25] S. M. Winter, Y. Li, H. O. Jeschke, and R. Valentí, “Challenges in design of Kitaev materials: Magnetic interactions from competing energy scales,” *Phys. Rev. B* **93**, 214431 (2016).

[26] G. Jackeli and D. I. Khomskii, “Classical dimers and dimerized superstructure in an orbitally degenerate honeycomb antiferromagnet,” *Phys. Rev. Lett.* **100**, 147203 (2008).

[27] L. S. I. Veiga, M. Etter, K. Glazyrin, F. Sun, C. A. Escanhoela, G. Fabbris, J. R. L. Mardegan, P. S. Malavi, Y. Deng, P. P. Stavropoulos, H.-Y. Kee, W. G. Yang, M. van Veenendaal, J. S. Schilling, T. Takayama, H. Takagi, and D. Haskel, “Pressure tuning of bond-directional exchange interactions and magnetic frustration in the hyperhoneycomb iridate β-Li$_2$IrO$_3$,” *Phys. Rev. B* **96**, 140402 (2017).

[28] A. G. Petukhov, I. I. Mazin, L. Chioncel, and A. I. Lichtenstein, “Correlated metals and the LDA + U method,” *Phys. Rev. B* **67**, 153106 (2003).

[29] S. Manni, Sungkyun Choi, I. I. Mazin, R. Coldea, M. Altmeier, H. O. Jeschke, R. Valentí, and P. Gegenwart, “Effect of isoelectronic doping on the honeycomb-lattice iridate A$_2$IrO$_3$,” *Phys. Rev. B* **89**, 245113 (2014).

[30] “We note that without a further increase of the unit cell, only three antiferromagnetic patterns are possible: Neel (q=0), stripes, and zigzag (both q={1,0} in plane), where the latter two are closer to the experimental wave vector. the choice between stripes and zigzag is rather arbitrary, and does not affect the final conclusions.”