



	Experiment title: High-pressure crystal structure of $A_2\text{IrO}_3$ ($A=\text{Na},\text{Li}$)	Experiment number: HC-2754
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Report:

High-pressure versus isoelectronic doping effect on the honeycomb iridate Na_2IrO_3

We study the effect of isoelectronic doping and external pressure in tuning the ground state of the honeycomb iridate Na_2IrO_3 by combining optical spectroscopy with synchrotron x-ray diffraction measurements on single crystals. The obtained optical conductivity of Na_2IrO_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 Na_2IrO_3 and lies closer to the quasimolecular orbital picture instead. Except for the pressure-induced hardening of the phonon modes, the optical properties of Na_2IrO_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.

[Results published in *Phys. Rev. B* **96**, 195137 (2017)]

Competition between spin-orbit coupling, magnetism, and dimerization in the honeycomb iridates: α -Li₂IrO₃ under pressure

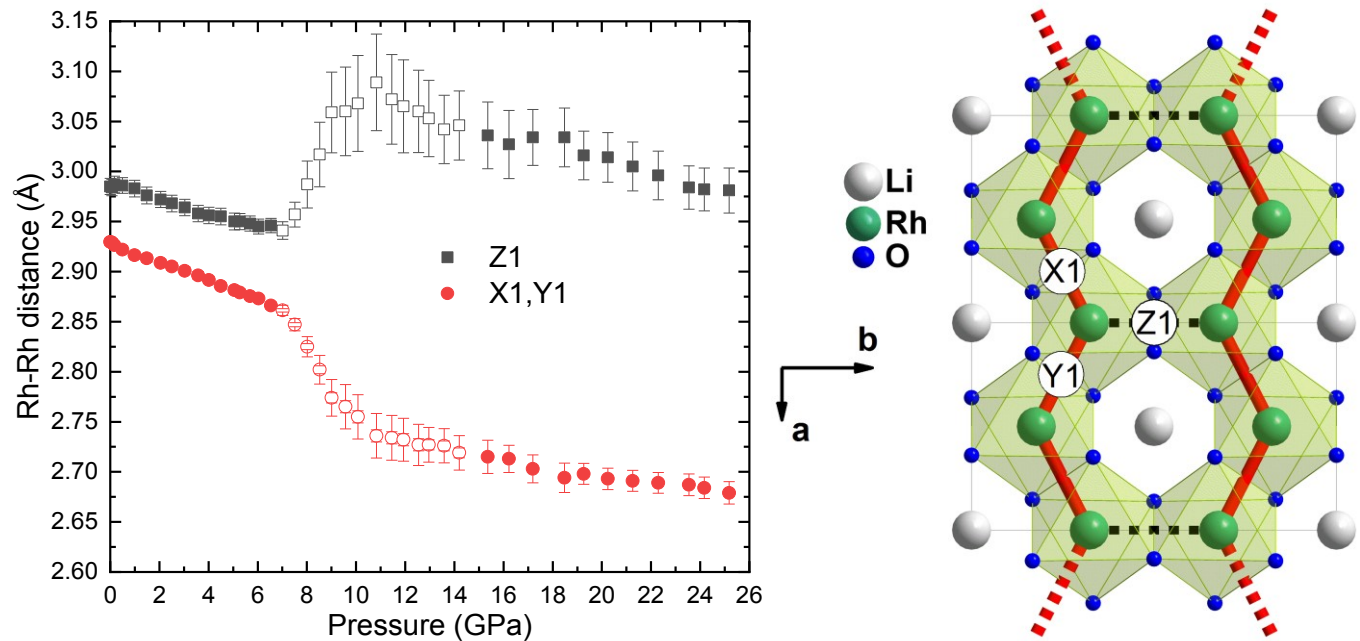
Single-crystal x-ray diffraction studies with synchrotron radiation on the honeycomb iridate α -Li₂IrO₃ reveal a pressure-induced structural phase transition with symmetry lowering from monoclinic to triclinic at a critical pressure of $P_c=3.8$ GPa. According to the evolution of the lattice parameters with pressure, the transition mainly affects the ab plane and thereby the Ir hexagon network, leading to the formation of Ir-Ir dimers. These observations are independently predicted and corroborated by our *ab initio* density functional theory calculations where we find that the appearance of Ir-Ir dimers at finite pressure is a consequence of a subtle interplay between magnetism, correlation, spin-orbit coupling, and covalent bonding. Our results further suggest that at P_c the system undergoes a magnetic collapse. Finally we provide a general picture of competing interactions for the honeycomb lattices A_2MO_3 with $A=Li, Na$ and $M=Ir, Ru$.

[Results published in Phys. Rev. B 97, 020104(R) (2018)]

Pressure-induced formation of Rh zigzag chains in the honeycomb rhodate Li₂RhO₃

Powder x-ray diffraction studies with synchrotron radiation on the honeycomb rhodate Li₂RhO₃ reveal a pressure-induced structural phase transition within the monoclinic symmetry group $C2/m$ at a critical pressure of 6.5 GPa. The evolution of the lattice parameters with pressure indicates, that the transition mainly affects the ab plane and thereby the Rh hexagon network comparable to the transition in α -Li₂IrO₃. In contrast to the iridate compound, the hardening is mainly found along the a direction leading to the pressure-induced formation of Rh zigzag chains in Li₂RhO₃ at a critical pressure of 6.5 GPa.

[manuscript in preparation]



The graph on the left shows the refinement of the three next neighbor Rh–Rh distances $X1$, $Y1$ and $Z1$, which are defined in the graphic on the right. $X1$ and $Y1$ mainly have components along a , whereby $Z1$ has only components along b . Above 6.5 GPa $X1$ and $Y1$ reduces dramatically, while $Z1$ enhances by the same amount. This leads to the formation of a zigzag chain in the a direction, which is illustrated by the thick red bonds in the graphic.