

Dimerization of the honeycomb iridate α -Li₂IrO₃ under pressure

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The honeycomb iridates A₂IrO₃ (A=Li, Na) show novel behavior and phases arising from the competition between spin-orbit coupling, magnetization, and dimerization. In recent years, they have been intensively scrutinized as Kitaev physics candidates [1]. Here, we present the results of x-ray diffraction and optical spectroscopy measurements on α -Li₂IrO₃ and Na₂IrO₃ single crystals under pressure [2,3].

α -Li₂IrO₃ undergoes a pressure-induced structural phase transition with symmetry lowering from monoclinic to triclinic at a critical pressure of P_c=3.8 GPa, with the formation of Ir-Ir dimers (see Fig.1) [2]. These experimental observations are independently predicted and corroborated by *ab initio* density functional theory calculations. The pressure-induced Ir-Ir dimerization is a consequence of the subtle interplay between magnetism, electronic correlation, spin-orbit coupling, and covalent bonding. In comparison, in Na₂IrO₃ a structural phase transition analogous to the one observed in α -Li₂IrO₃ is predicted to occur at a much higher pressure, namely at about 45 GPa [2], consistent with pressure-dependent x-ray diffraction measurements on Na₂IrO₃ single crystals [4].

The pressure-induced Ir-Ir dimerization in α -Li₂IrO₃ is furthermore revealed in the electrodynamic properties in the frequency range of the phonon modes and Ir *d-d* transitions, as observed by reflection and transmission measurements under pressure [3]. Further major pressure-induced changes on the Ir *d-d* transitions are found for pressures well above P_c.

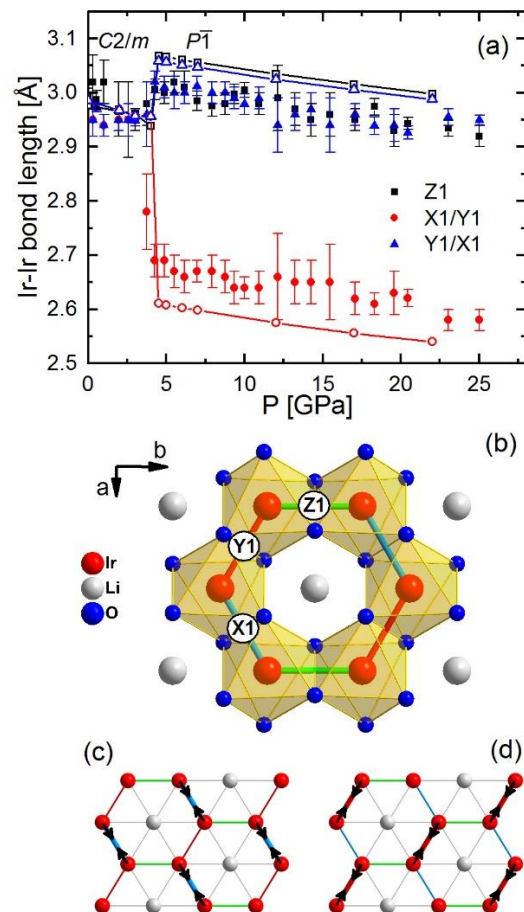


Figure 1. (a) Pressure dependence of the Ir-Ir distances for the Ir hexagons in the *ab* plane, with the nomenclature (Ir bonds X1, Y1, Z1) given in (b) for the ambient-pressure monoclinic crystal structure. Ir-Ir bond lengths as predicted from our calculations are shown as open symbols connected by a line. The two equivalent ordering patterns of the Ir-Ir dimers above P_c are illustrated in (c) and (d).

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