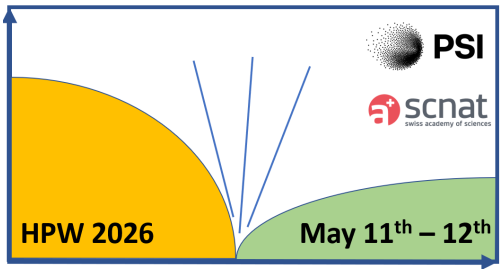

Contribution ID: **55** Type: **Talk**

Pushing electrons uphill: High-pressure routes to transition metal anions

Tuesday, 12 May 2026 15:00 (30 minutes)

The abilities of the elements to accept or donate electrons and thus adopt various oxidation states are fundamental to bonding and chemical transformations. The discovery in the 1940s of the first compound containing a monatomic metal anion, transparent CsAu with the Au^- ion, upended prior understanding and stimulated new chemistry with reduced 5*d* transition metals, including the preparation of Pt^{2-} in semiconducting Cs_2Pt. We investigated the possibility of extending this remarkable series of ions to monatomic Ir^{3-} by combining the existing approach of chemical reduction with the application of high pressures. Reaction of a potassium-rich mixture of potassium and iridium at 19.5(6) GPa and 493 K in a diamond anvil cell yields K_5Ir, which adopts the rare but simple $BaSn_5$ crystal structure. Hybrid functional electronic structure calculations, net atomic charge analysis, and Ir L_3-edge X-ray absorption spectroscopy reveal K_5Ir is a semimetal with a carrier density $\sim 10^{20}$ cm^{-3} which features anionic Ir and both cationic and neutral K on different sites. While the net atomic charge of Ir in K_5Ir falls short of that in hypothetical, semiconducting K_3Ir, it exceeds those of Pt^{2-} in Cs_2Pt and formal Ir(III-) in the carbonyl complex $Na_3[Ir(CO)_3]$, suggesting an extreme for the distribution of charge in the vicinity of a transition metal. First-principles crystal structure prediction corroborates the thermodynamic stability of K_5Ir under the preparatory conditions and indicates that several other K–Ir compounds await discovery. Synthetic methods and prospects for realization of new ions are discussed.

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