Cuproiridsite – orbital parts unknown

Emil S. Bozin

Brookhaven National Laboratory

Transition metal chalcogenides (TMCs) with partially filled *d*-bands host some of the most amazing emergent responses including high-temperature superconductivity, colossal magnetoresistance, formation of spin-dimerized lattices, and spin and charge glass states. They often undergo structural, electronic and magnetic transitions, and display symmetry broken ground states with orders in orbital, charge and spin sectors. Most studies of these systems focus on the observed behaviors in the low temperature regime, where symmetry broken states order over long range as a product of subtle interplay of various fundamental interactions. Less is known about what happens upon heating when the long-range order melts or disappears upon doping or other excitation, yet this is possibly more crucial to understand the physics governing the properties than the much lower energy effects responsible for the ordering of the broken symmetry states. Observed nematic response in copper and iron based superconductors may be one such example that has gained appreciable attention in this context recently. The high temperature regime is typically characterized by a high crystallographic symmetry structure where, due to partial filling of the *d*-orbitals, orbital states are degenerate and are prone to symmetry breaking to lift the degeneracy. Mechanisms of orbital degeneracy lifting (ODL) could be numerous, such as the crystal field effects, the well-known orbital-lattice Jahn-Teller effect, the superexchange interactions between the orbitals, as well as the relativistic spin-orbit coupling, and could in principle also arise from some combination of these effects. Regardless of the exact origin, studies searching for existence and exploring the character of the ODL state at high temperature, above the temperature where the broken symmetry states order (i.e., the spin or orbital ordering) are therefore of great importance as they could provide important missing ingredients instrumental for understanding the big picture. By taking the ODL viewpoint this presentation will focus on nanoscale structure study of the metallic regime above the metal-insulator transition at ~230 K in cuproiridsite $CuIr_2S_4$ by means of X-ray total scattering based atomic pair distribution function (PDF) analysis. Fortuitous scattering contrast in this system allows for direct probing of the Ir *d*-orbital overlaps by means of atomic PDF. Tunable electron filling (via Cr and Zn doping) and temperature phase parameters utilized within this approach reveal thus far unobserved existence of ODL-like short-range correlations resembling orbital-liquid-like state. The results not only provide a rationale for long standing puzzle related to unusual metallicity at high temperature, but further suggest that the metal-insulator transition can be seen, at least in part, as a crystallization of nanoscale orbital fluctuations into a long-range orbitally ordered lattice. Notably this behavior is reminiscent of that seen in several TMCs seemingly unrelated to cuproiridsite. Although admittedly eclectic, this observation is suggestive of possible ubiquity of the ODL phenomena.