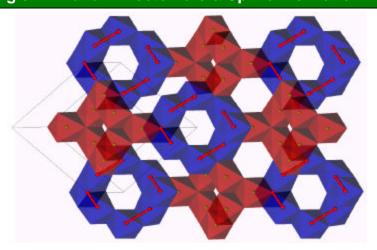
Formation of isomorphic Ir³⁺ and Ir⁴⁺ octamers and spin dimerization in the spinel Culr₂S₄

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Inorganic compounds with the AB_2X_4 spinel structure have been studied for many years, because of their unusual physical properties. The spinel crystallographic, first solved by Bragg in 1915, has cations occupying both tetrahedral (A) and octahedral (B) sites. Interesting physics arises when the B-site cations become mixed in valence. Magnetite (Fe₃O₄) is a classic and still unresolved example, where the tendency to formordered arrays of Fe²⁺ and Fe³⁺ ions competes with the topological frustration of the B site network. The Culr₂S₄ thiospinel is another example, well known for the presence of a metal±insulator transition at 230K with an abrupt decrease of the electrical conductivity on cooling accompanied by the loss of localized magnetic moments.

Here, we report the determination of the crystallographic structure of Culr_2S_4 below the metal±insulator transition. Our results indicate that Culr_2S_4 undergoes a simultaneous charge-ordering and spin-dimerization transition–a rare phenomenon in threedimensional compounds. Remarkably, the charge-ordering pattern consists of isomorphic octamers of Ir^{3+}_8 S₂₄ and Ir^{4+}_8 S₂₄ (as isovalent bi-capped hexagonal rings). This extraordinary arrangement leads to an elegant description of the spinel structure, but represents an increase in complexity with respect to all the known charge-ordered structures, which are typically based on stripes, slabs or chequerboard patterns.



3D stacking of Ir³⁺- and Ir⁴⁺-octomers & Spin dimerization in Ir⁴⁺-octomers