

Formation of isomorphous Ir³⁺ and Ir⁴⁺ octamers and spin dimerization in the spinel CuIr₂S₄

Paolo G. Radaelli, Y. Horibe, Matthias J. Gutmann, Hiroki Ishibashi, C. H. Chen, Richard M. Ibberson, Y. Koyama, Yew-San Hor, Valery Kiryukhin & Sang-Wook Cheong

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Inorganic compounds with the **AB₂X₄ 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 form ordered arrays of Fe²⁺ and Fe³⁺ ions competes with the topological frustration of the B site network. The **CuIr₂S₄ 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 CuIr₂S₄ below the metal-insulator transition. Our results indicate that **CuIr₂S₄ undergoes a simultaneous charge-ordering and spin-dimerization transition—a rare phenomenon in three-dimensional compounds**. Remarkably, the charge-ordering pattern consists of **isomorphous octamers** of Ir³⁺₈ S₂₄ and Ir⁴⁺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 checkerboard patterns**.

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

