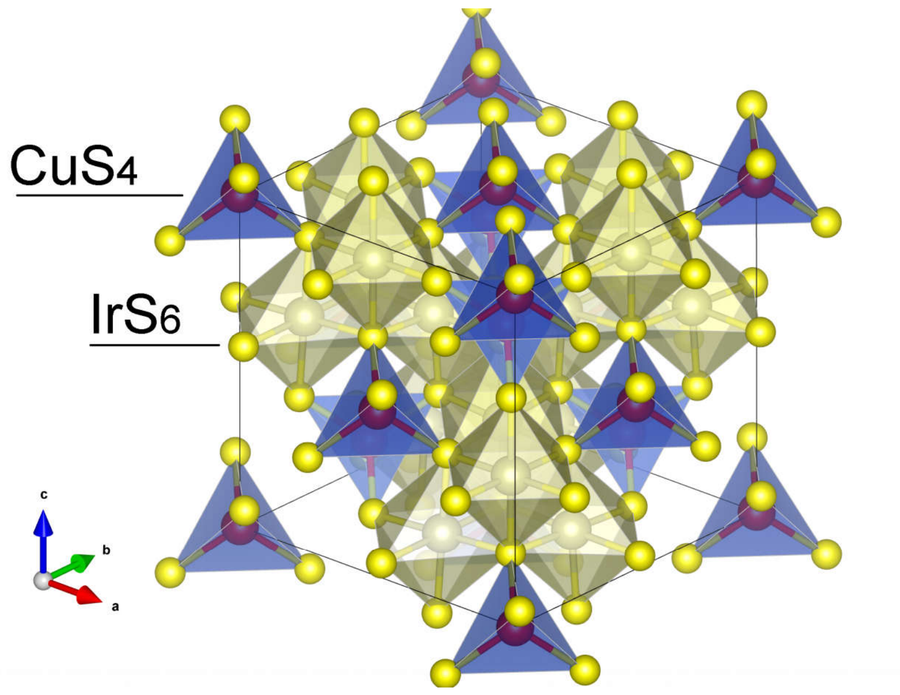
Lattice dynamics in the thiospinel $CuIr_2S_4$: Raman spectroscopic studies across the metal-insulator transition

A. Glamazda[1,3], V. Gnezdilov[1,2], V. Tsurkan[4,5], P. Lemmens[2,6]

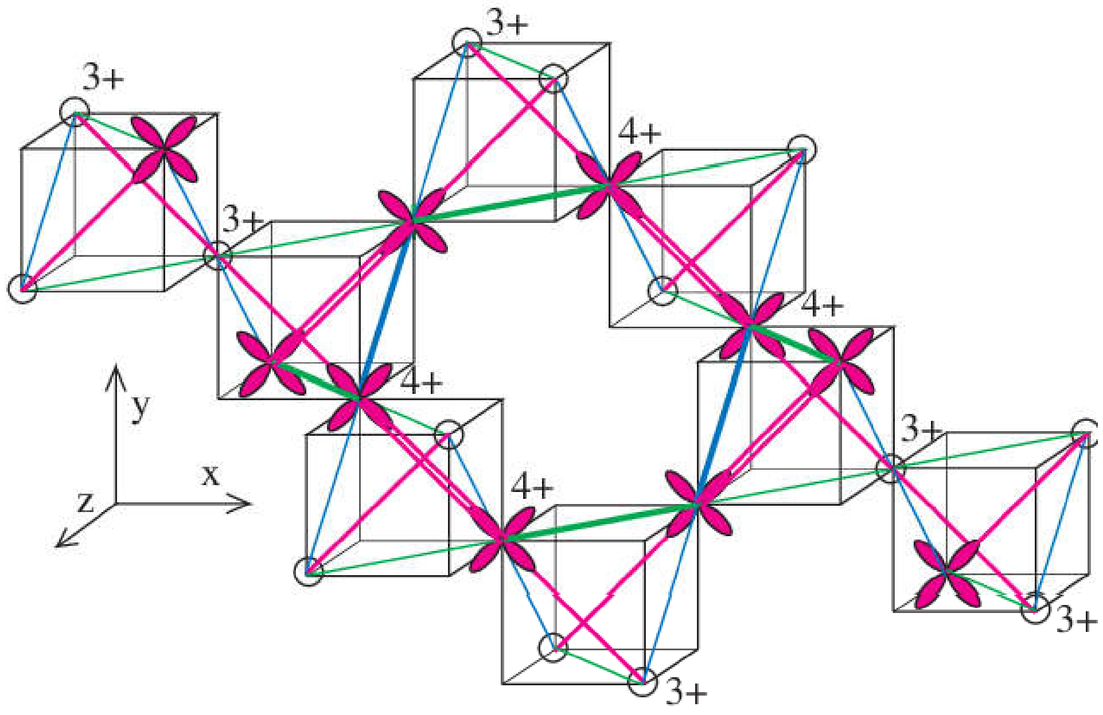
[1]B. Verkin Institute for Low Temperature Physics and Engineering of NAS of Ukraine, 47 Nauky Ave., Kharkiv, 61103, Ukraine
[2]Institute of Condensed Matter Physics, TU Braunschweig, D-38106 Braunschweig, Germany
[3]V. N. Karazin Kharkiv National University, 4 Svobody sq., Kharkiv, 61022, Ukraine
[4]Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, Augsburg, Germany
[5]Institute of Applied Physics, Moldova State University, 5 Academiei Str., Chisinau, 2028, Moldova
[6]Laboratory of Emerging Nanometrology LENA, Braunschweig D-38106, Germany
glamazda@ilt.kharkov.ua

The AB_2X_4 spinel systems (A, B = transition metal ions; X = S, Se, Te) have attracted continuous research interests due to their rich physical properties relevant to the geometrical frustration. The geometrical frustration plays an important role in the coupling of different degrees of freedom.



Structure of $CuIr_2S_4$ [Furubayashi T., et al *J Phys. Soc. of Japan* *63*, 3333 (1994)]. The visualization was created using the modeling software VESTA [K. Momma and F. Izumi, *J. Appl. Crystallogr.* **44**, 1272 (2011).]

Previous studies have shown that the thiospinel $CuIr_2S_4$ undergoes a metal-insulator transition at T_{MI} ~230 K upon cooling with a drop of the electrical resistivity by almost three orders of magnitude and a concomitant jump in the magnetic susceptibility from Pauli-like paramagnetism at high temperatures to diamagnetism in the low-temperature phase. Subsequent studies determined that $CuIr_2S_4$ undergoes a simultaneous charge-ordering (CO) and spin-dimerization (SD) transition [1]. Below T_{MI} the charge-ordering pattern consists of isomorphic octamers. Orbitally-driven, three-dimensional Peierls-like spin dimerization between the magnetic ions in the octamers is responsible for the nonmagnetic nature of the insulating phase.

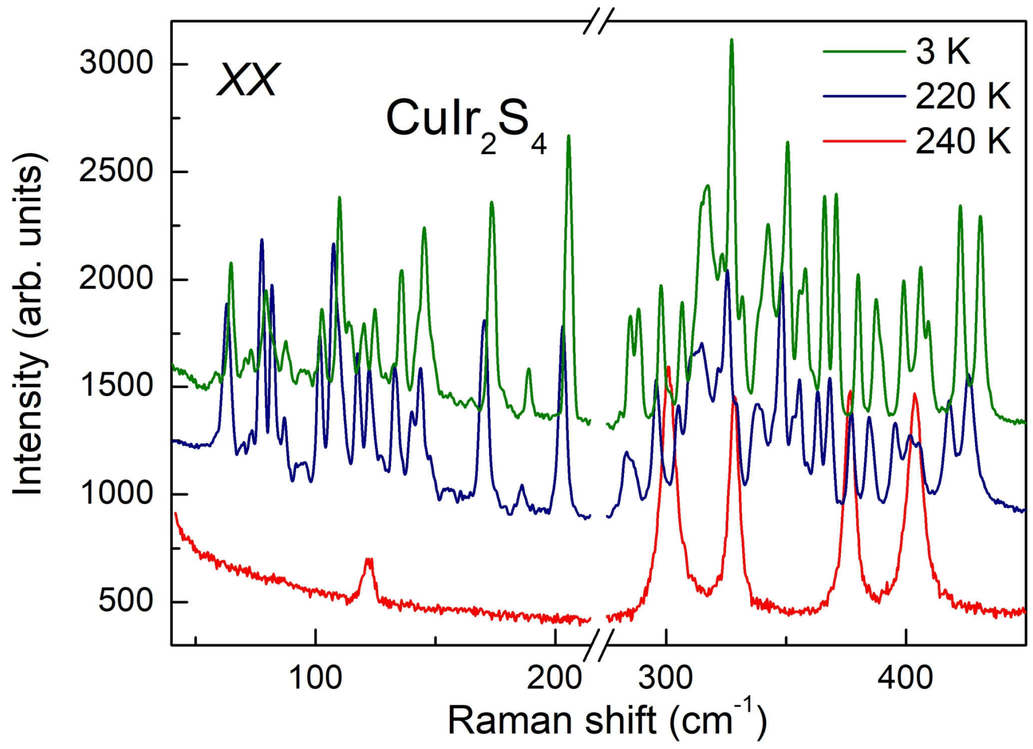


Charge and orbital ordering in $CuIr_2S_4$. Octamer is shown by thick lines, short singlet bonds-by double lines. [Khomskii D. I. and Mizokawa T. Orbitally Induced Peierls State in Spinels// Phys. Rev. Lett. 94, 156402 (2005).]

It is known that the symmetry of the crystal lattice is strongly related to the magnetic and transport properties of solids. At room temperature, $CuIr_2S_4$ has a normal cubic spinel structure. However, there is still debate in the literature about the symmetry of the low-temperature phase of this compound. This is due to the complexity of the superstructure formed as a result of the CO and SD transitions.

Here we report the results of the detailed analysis of the temperature evolution of the polarized-dependence Raman spectra of the high-quality $CuIr_2S_4$ single crystals. In the high-temperature Raman spectra we observed all five phonon modes allowed for a cubic normal spinel-type structure. To assign the observed Raman active phonon modes to the definite type of the atomic vibrations and symmetry we have performed the lattice dynamical calculations of the phonon spectra in the high-temperature phase. Below T_{MI}, we observed for the first time amazing changes in Raman spectra, an appearance of a large number of modes that strongly indicate an extraordinary change in symmetry of $CuIr_2S_4$ from cubic (Fd-3m), to triclinic (P-1),

$$\Gamma_{\text{Raman}}\,(Fd\text{-}3m) = A_{1g} + E_g + 3T_{2g}.$$
$$\Gamma_{\text{Raman}}\,(P\text{-}1) = 81A_g$$



Temperature-dependent Raman spectra of $CuIr_2S_4$ at selected temperatures measured in the XX scattering geometries. The spectra are shifted vertically for clarity.

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