X-ray absorption and photoemission studies of spinel-type compound CuIr$_2$S$_4$

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Spinel-type chalcogenide CuIr$_2$S$_4$ exhibits a metal-insulator transition (MIT) at the temperature $T_{\text{MI}} \sim 230$ K from the high-temperature metallic phase to the low-temperature insulating phase [1]. The magnetic susceptibility decreases at the transition and the compound turns from Pauli paramagnetic to diamagnetic. The transition is accompanied by change of the crystal structure: the cubic spinel structure in the metallic phase turns to be triclinic structure in the insulating phase, where one of the unit vector is expanded and the other two are slightly shortened [2,3]. Interestingly, the volume of the insulating phase is smaller than that of the metallic phase and the application of the high pressures stabilizes the insulating phase: the behaviour is contrary to the most of other materials that exhibit MIT.

The mechanism of the MIT is still unclear. The Cu ion is suggested to be in the monovalent state [4], and thus the probable ionic configuration is Cu$^{+}$Ir$^{3+}$Ir$^{4+}$(S$^2$)$_4$. One possible explanation for the MIT mechanism is the charge ordering of Ir$^{3+}$ and Ir$^{4+}$ ions, accompanied by the dimerization of Ir$^{4+}$ ions to cancel the spin moment. However, the charge separation of Ir has not been confirmed experimentally.

We have performed the measurements of soft x-ray absorption spectroscopy (XAS) and photoemission spectroscopy (PES) for CuIr$_2$S$_4$ to elucidate the variation of the electronic structure at the MIT. The line-shape of the Ir 4$f$ core-level PES spectra shows a drastic change at $T_{\text{MI}}$, while the valence-band PES spectra show only a slight variation just below the Fermi level. The XAS spectra for the Cu L$_{2,3}$ edge also shows a significant temperature variation which continues in the wide temperature range below $T_{\text{MI}}$.