ESRF	**Experiment title:** @bservation of the charge ordering in $CuIr_2S_4$.	**Experiment number**: HE 946
Beamline: BM28	**Date of experiment**: from: 27 September 2000 to: 03 October 2000	**Date of report**:
Shifts: 18	**Local contact(s)**: Anne STUNAULT	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

SUZUKI Hiroyuki*, SCHMITT Denys*

Laboratoire Louis Néel, CNRS

RENEVIER Hubert*

Laboratoire de Cristallographie, CNRS

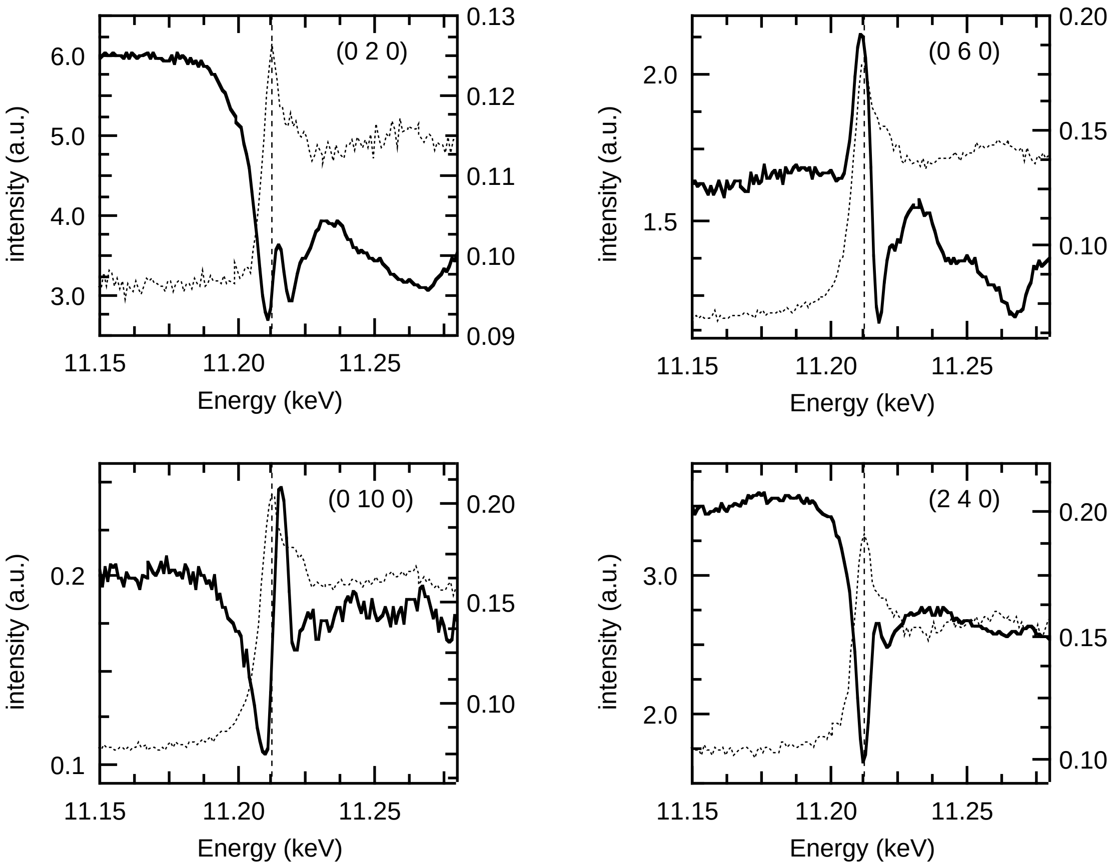
Report:

The cubic thiospinel compound $CuIr_2S_4$, which is metallic around room temperature, undergoes a structural transition to an insulating phase with the tetragonal structure at a transition temperature T_{MI}~230K [1-4]. At present, the mechanism of the M-I transition of $CuIr_2S_4$ is still an open question. NMR [5] and X-ray photo-emission spectroscopy (XPS) [6] measurements of both the metallic and insulating phase have revealed that Cu almost approaches in the valence state of Cu^{1+}, which is consistent with band calculations [7]. Thus, it seems probable that the ionic configuration of $Cu^{1+}Ir^{3+}Ir^{4+}S^{2-}{}_4$ is realized in the insulating state. The ordering of charges on the Ir site is one possible origin of the M-I transition of this compound.

The aim of this experiment is to shed some light on the origin of the M-I transitions by performing the resonant X-ray scattering on the Ir *L* edge. The results of this experiment have revealed the anomaly in Ir ionic state, while they have questioned the origin of M-I transition of this system, as shown below.

As shown in figures, we observed dramatic energy profile at the Ir L_3 edge on the reflections (0 0 2), (0 0 6), (0 0 10) and (2 4 0), which are forbidden reflections in *Fd*-3*m* symmetry of the cubic phase. Such energy dependences of these reflections clearly indicate that the charge states of the Ir are not uniform. Moreover, it is noted and very interesting that even above T_{MI}, i.e. in the metallic phase, these characteristic energy profiles were observed and almost same ones as those in the insulating phase. This fact of no drastic change in the energy profile between above and below T_{MI} gives a proposition that the occurrence of the anomaly in Ir ions, like the charge ordering, is not the direct driving force of the M-I transition. Only for (2 4 0) reflection, we observed structures of the σ- π component in the energy profile around Ir-edge, although it is difficult to discuss about their structures due to their small intensity. On the other hand, the fact that those forbidden reflections were observed at an off-resonant energy indicates the distortion of the crystal structure, which would be very small, from the cubic symmetry even in the metallic phase. The determination of the crystal structure in the metallic phase will be also necessary hereafter. For the other reflections corresponding to the superlattice, such as (h/2, h/2, h/2), no significant energy profiles were obtained below T_{MI}.

This is the first time to reveal the anomaly in Ir ionic state in $CuIr_2S_4$. It is probably related to the charge ordering. At present we are analyzing those experimental results based on various models of the charge ordering of Ir sites. However, there is not enough information to determine the wave vector of the charge ordering and so on, and it is necessary to perform further experiments. Especially, it is very attractive to investigate the by the X-ray magnetic scattering. The static magnetic measurements showed that the $CuIr_2S_4$ is non-magnetic in both states. Then, the low-spin state (S=1/2) of Ir^{4+} would take singlet pairs, for example, dimmer-like configuration. It has been proposed that the distortion in the low temperature state is in favor of dimmer model of the spin singlet pairs of Ir chain in the [1 1 0] direction [8].



The energy dependence of the reflections (0 0 2), (0 0 6), (0 0 10) and (2 4 0) (solid lines) and the absorptions (dashed lines) at the Ir L_3 edge below T_{MI}.

[1] S. Nagata, T. Hagino, Y. Seki and T. Bitoh, Physica B **194-196** (1994) 1077.
[2] T. Furubayashi, T. Mastumoto, T. Hagino and S. Nagata, J. Phys. Soc. Jpn **63** (1994) 3333.
[3] G. Oomi, T. Kagayama, I. Yoshida, T. Hagino and S. Nagata, J. Magn. Magn. Mater. **140-144** (1995) 157.
[4] S. Nagata, N. Matsumoto, Y. Kato, T. Furubayashi, T. Matsumoto, J. P. Sanchez and P. Vulliet, Phys. Rev. B **58** (1998) 6844.
[5] K. Kumagai, S. Tsujii, T. Hagino and S. Nagata, *Spectroscopy of Mott Insulators and Correlated Metal,* ed. A. Fujimori and Y. Tokura (Springer, Berlin, 1995) p. 255.
[6] J. Matsuno, T. Mizokawa, A. Fujimori, D. A. Zatsepin, V. R. Galakhov, E. Z. Kumaev, Y. Kato and S. Nagata, Phys. Rev. B **55** (1997) R15979.
[7] T. Oda, M. Shirai, N. Suzuki and K. Motizuki, J. Phys. Condens. Mater **7** (1995) 4433.
[8] T. Furubayashi, T. Mastumoto and H. Suzuki, in preparation.