

### Experimental report:

Since a novel  $J_{\text{eff}}=1/2$  physics emerged, huge efforts have been concentrated in a field of condensed matter physics society [1-4]. In these materials, a large spin orbit coupling splits  $t_{2g}$  manifold into doublet and quartet states where doublet energy is higher. In the case of  $\text{Sr}_2\text{IrO}_4$ ,  $\text{Ir}^{4+}$  ( $d^5$ ) has a half filled electronic configuration on a doublet  $J_{\text{eff}}=1/2$  level and a moderate Coulomb interaction trigger a novel Mott insulator state [1]. Besides, in a hexagonal compounds, the characteristic wave function of  $J_{\text{eff}}=1/2$  state enables us to expect a novel topological phases [3,4]. Recently, superconductivity has been reported in Pd doped  $\text{IrTe}_2$  compounds, where a superconductivity competing to the charge density wave transition [5]. A dome-like phase diagram was reported and nearly similar superconducting phase diagrams have been reported in Pt and Cu doped  $\text{IrTe}_2$  [6-8]. However, although the origin of superconductivity of  $\text{M}_x\text{IrTe}_2$  ( $\text{M} = \text{Pd}, \text{Pt}$  and  $\text{Cu}$ ) has been expected as a quantum criticality associated with charge-orbital density wave order, the detail nature of charge orbital density wave has not been elucidated yet.

$\text{IrTe}_2$  is a  $\text{CdI}_2$ -type layered hexagonal structure ( $P-3m1$ ) at room temperature. The crystal structure changes to monoclinic ( $C2/m$ ) below a structural transition temperature ( $T_C \sim 280$  K, in single crystals). The monoclinic angle ( $\beta$ ) is 93.3 deg. A long range structural distortion has been reported where the  $(1/5 \ 0 \ 1/5)$  ordering was clearly identified in transmission electron microscope diffraction [5]. The physical origin of the structural distortion have been argued as an electronic instability of a 3D Fermi surface nesting and *ab-initio* calculation reveals an enhancement of  $\chi_0(\mathbf{q})$  near  $(1/5 \ 0 \ 1/5)$  position. In addition, a weak resistivity jump and a Pauli paramagnetic response of magnetic susceptibility at transition temperature support charge density wave formation. However, the known optical conductivity could not display a charge density wave gap excitation [9] and the known photoemission data did not show a significant electronic change [7] in this material. These two papers argue alternative scenarios of Te  $p$  band splitting [9] and Ir-Ir bond breaking [8]. And, the following investigations reveal that there is a valence transition from  $\text{Ir}^{3+}$  to  $\text{Ir}^{4+}$  and dimerization of  $\text{Ir}^{4+}$ .

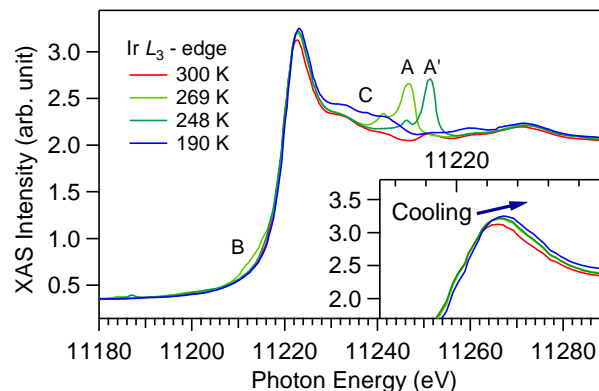


Fig.1 Temperature dependent XAS of Ir  $L_3$ -edge at four representative temperatures. The spectra were measured at 300 K (non-ordered), at 269 K and 248 K ( $\mathbf{q}=(1/5 \ 0 \ 1/5)$  phase), and at 190 K ( $\mathbf{q}=(1/8 \ 0 \ 1/8)$  phase).

In order to examine the electronic configuration of Ir, we measured x-ray absorption spectra. Figure 1 displays temperature dependent XAS spectra at Ir  $L_3$ -edge. Upon cooling temperature we observed two sudden spectral changes. At 280 K, the peak position shift slightly high energy and another spectral features of A(A') and B emerge. Below  $T_{C1} = 280$  K, the system is known to show a monoclinic structural transition as well as a charge order, it might give us additional Bragg reflections and super structure peaks. The peak shift can be explained by a valence change from pure  $\text{Ir}^{3+}$  to  $\text{Ir}^{3.4+}$ , where  $\mathbf{q}=(1/5 \ 0 \ 1/5)$  order has three  $\text{Ir}^{3+}$  and two  $\text{Ir}^{4+}$  sites. In addition, the fine structures are also changed because of deformations of local symmetries [10, 11]. At 190 K, we can observe another phase where Ir valence becomes even higher, the feature of A disappears and a new feature of C can be found. Another charge ordering has  $\mathbf{q}=(1/8 \ 0 \ 1/8)$ ,

in which the correlation length of ordering gets worse and gives us broadened superstructure reflection feature as like C. From these data, we confirmed the measured crystal displays two cascade charge ordering transitions combining valence transitions. However, the photon energy was not so stable in our measurement to estimate the white line shift of Ir  $L_3$ -edge accurately.

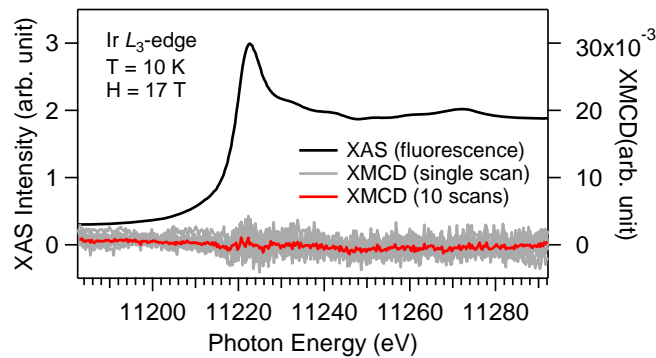


Fig. 2 XMCD spectra measured at 10 K are displayed. The XMCD was measured under 17 T magnetic field. In order to reduce a noise level, we accumulated 10 scans which reduce the noise below an order of  $10^{-3}$ . Within this noise level, we could not observe any sizable XMCD signal.

We also measured x-ray magnetic circular dichroism spectra in order to test a robustness of Ir<sup>4+</sup> dimer as displayed in Fig. 2. Even though more than a half of Ir sites change to Ir<sup>4+</sup> at 10 K, we could not observe any sizable XMCD signal where a maximum of noise level is smaller than  $10^{-3}$  of XAS signal. This result is coincident with a magnetic susceptibility data measured under 2 T magnetic field, and implies that the valence transition from Ir<sup>3+</sup> to Ir<sup>4+</sup> occurs with an Ir<sup>4+</sup> dimer formation simultaneously which is robust up to 17 T. Since the dimer forms a  $J_{\text{eff}} = 0$  singlet, the XMCD signal keeps zero under 17 T magnetic field. This Ir<sup>4+</sup>  $J_{\text{eff}} = 0$  dimer is known to be very robust as proved in an Ir<sup>4+</sup> dimer (octamer) – CuIr<sub>2</sub>S<sub>4</sub> [12] – system. As a results, we could not find any triplet ( $J_{\text{eff}} = 1$ ) feature up to 17 T at 10 K in the  $J_{\text{eff}} = 1/2$  dimer system.

## References

1. B. J. Kim *et al.*, Phys. Rev. Lett. **101**, 076402 (2008).
2. B. J. Kim *et al.*, Science **323**, 1329 (2009).
3. A. Shitade *et al.*, Phys. Rev. Lett. **102**, 256403 (2009).
4. G. Jackeli, and G. Khaliullin, Phys. Rev. Lett. **102**, 017205 (2009).
5. J. Yang *et al.*, Phys. Rev. Lett. **108**, 116402 (2012).
6. S. Pyon, K. Kudo, and M. Nohara, J. Phys. Soc. Jpn. **81**, 053701 (2012).
7. D. Ootsuki *et al.*, Phys. Rev. B **86** 014519 (2012).
8. M. Kamitani *et al.*, Phys. Rev. B **87**, 180501(R) (2013).
9. A. F. Fang *et al.*, Sci. Rep. **3**, 1153 (2013).
10. G. L. Pascut *et al.*, Phys. Rev. Lett. **112**, 086402 (2014).
11. B. Joseph *et al.*, Phys. Rev. Lett. **88**, 224109 (2013).
12. K. Takubo *et al.*, Phys. Rev. Lett. **95**, 246401 (2005).