

Is IrO_2 Goodenough? An Insight into Electronic Structure via HAXPES

*This report features the work of David J. Payne and his co-workers published in Phys. Rev. Lett. **112**, 117601 (2014).*

Hard X-ray photoelectron spectroscopy (HAXPES) provide a new technique and excellent tool to study materials due to their unique ability to probe both the chemical and electronic structure of materials with bulk sensitivity. The HAXPES end-station of **BL12XUSL** at SPring-8, Japan was constructed as a collaborative research program of the NSRRC in Hsinchu, Taiwan and Max Planck Institute for Chemical Physics of Solids (MPI CPfS) in Dresden, Germany. Taiwan beamline **BL12XUSL** with an undulator source at SPring-8 that provides great brilliance and intensity is dedicated to installing the HAXPES end-station. The new HAXPES end-station is designed in a unique way to incorporate two analyzers

with disparate geometry. One analyzer is installed vertically and is used to observe the d states of the valence band in transition-metal materials. The other analyzer, set horizontally, is assigned mainly to measure information about the core level. In 2014, a research team of David J. Payne's group from the United Kingdom, revealed a new application of HAXPES that shows the electronic structure of IrO_2 with crystal-field splitting of the iridium $5d$ orbitals.¹ Their result is in satisfactory agreement with the theoretical predictions of "Goodenough for conductive rutile-structured oxides",² they explain further why the spin-orbit Mott insulating state is not observed in the IrO_2 system.

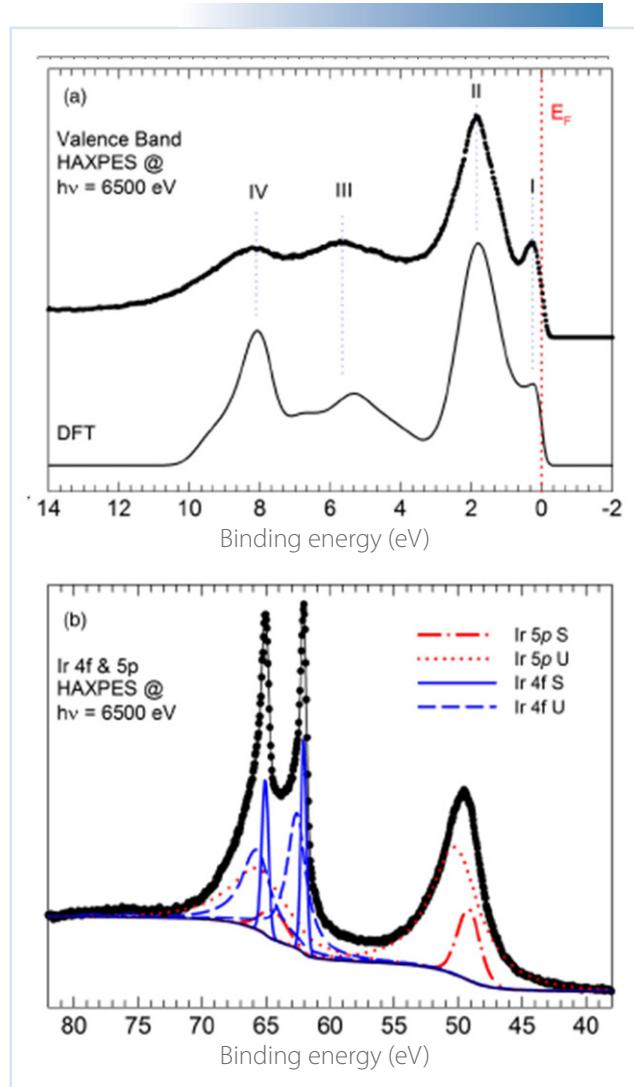


Fig. 1: HAXPES of IrO_2 recorded at $h\nu = 6.5$ keV. (a) Valence-band spectrum of IrO_2 and DFT calculation showing total densities of states. (b) Spectrum of Ir 4f and 5p core levels. The screened (S) and unscreened (U) components for Ir 4f (blue) and 5p (red) are shown.

In this work, they present high-resolution HAXPES measurements on IrO_2 , compared with theoretical band structure calculations using the framework of density functional theory (DFT). Their experimental data show clearly the 5d valence band utilizing the vertical geometry analyzer. The HAXPES spectrum of the valence band of IrO_2 follows closely the curve calculated with DFT, as shown in Fig. 1(a). The data reveal an explicit understanding of the electronic structure of the IrO_2 valence band, particularly the nature of electronic states near the Fermi level. Further detailed analysis of the individual

Ir d orbital contributions to electronic states indicates that the degeneracy of the five Ir d orbitals is completely lifted by the crystal field of coordination symmetry D_{2h} .

Figure 2 shows the rutile crystal structure, partial densities of states with each atomic orbital respectively and band structure of IrO_2 . The conduction properties of IrO_2 are dominated by the two t_{2g} bands (d_{xz} and d_{yz}) that display a broad density of states about the Fermi level. The rise of metallic behavior in IrO_2 is also indicated to be derived from the spin-orbit coupling of valence electrons and the electron-electron repulsion that are determined by the effects of crystal-field splitting and the effective orbital overlap.

IrO_2 core-level photoelectron spectra of the Ir 4f and 5p regions are shown in Fig. 1(b). The result exhibits a distinctly asymmetric shape of the 4f line, whereas a symmetric line shape is typically expected in a metallic case. Such a strongly asymmetric shape is attributed to the effect of the final state, occurring during photoemission. This effect of the screening of conduction electrons in metallic conductors on the core-level spectral line shape has been well studied. It is difficult to fit well the Ir 4f core level with a single function such as a Voigt or Fano function. Improved fits were obtained on using two Voigt components with fixed relative intensities and positions of the main lines, but constraining the separation between screened and unscreened components of each individual core line to the same value led to a rapidly deteriorated quality of the fits. This effect indicates that the Kotani model³ might be appropriate for the IrO_2 system. According to this model, the photoemission triggers a local coulombic interaction with the valence states contributing to the conduction band. The photoemission is hence described in interpreting the line shape of core-level photoelectron spectra of IrO_2 with a formalism of screened and unscreened final states.⁴

Commercial samples of IrO_2 are postulated to contain an Ir_2O_3 impurity phase because of the presence

of an Ir⁶⁺ component in the surface phase. HAXPES is a bulk-sensitive technique, which provides an increased probing depth and thus decreased surface effect in a photoelectron process. HAXPES hence shows promise for the study of the metal-insulator transition in iridate systems. HAXPES is a new technique rapidly developing at synchrotron facilities worldwide and is more sensitive to the bulk than XPS. The work of Payne's group exploits the advantage of HAXPES on studying a metal-insulating system. We believe that HAXPES is also a powerful approach to investigate complicated materials, buried nanostructures and multi-layered structures relevant for device applications. (Reported by Yen-Fa Liao)

References

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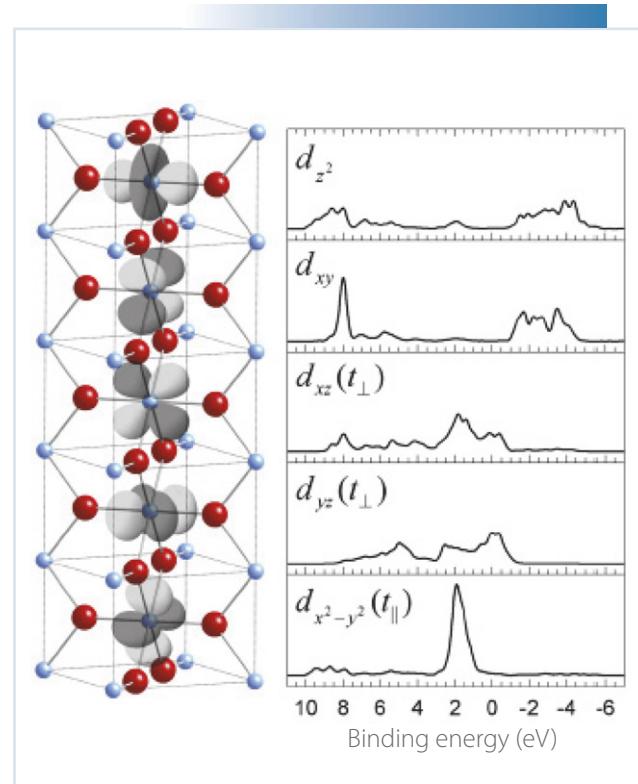


Fig. 2: Left: a stack of five unit cells shows the IrO₂ rutile structure in the revised coordinate system. Right: Ir 5d partial densities of states projected onto their representative atomic orbitals.