

Direct imaging of orbitals using hard X-ray photoelectron spectroscopy (HAXPES)

In the study of novel materials, the electronic structure is one of the most fundamental aspects needed to understand the emergence of interesting and exotic properties. One of the most direct approaches to experimentally access the electronic structure is photoelectron spectroscopy (PES). It is a very wide-spread and established technique, but as with any other spectroscopy, the interpretation of the spectra is not always straightforward and can be a significant challenge by itself.

In this context, Fadley and co-workers proposed already in the 1980's, a specific geometry for PES that would allow to directly image orbitals of free-standing atoms [1]. Such experiment would be capable of providing highly relevant information directly from the data, effectively bypassing the need for calculations. However, for solid state materials, the presence of scattering processes that the outgoing photoelectrons endure interferes so strongly with the desired signal that such PES technique has not been realized until now. Here, we show how we have successfully implemented such experiment using hard X-ray PES (HAXPES) [2].

Our work is performed at the HAXPES end-station of SPRING-8 **BL12XU** (Taiwan Beamline). The end-station, which is part of the collaboration between the Max Planck Institute for Chemical Physics of Solids and the National Synchrotron Radiation Research Center (NSRRC), is equipped with two analyzers mounted perpendicular and parallel to the polarization of the incoming beam, making it highly suitable for studying the effects of polarization in HAXPES [3]. The parallel analyzer, in particular, corresponds to the geometry proposed by Fadley, see Fig. 1.

In order to experimentally test and realize the technique, the 5d transition metal oxide ReO_3 was chosen as a model compound. Multiple single crystalline samples were prepared in order to be able to reach all relevant crystalline orientations by rotating θ . The orientations were chosen with a certain redundancy in order to ensure that the effects observed corresponded to the orientation dependence and not to e.g. emission or incidence angle.

Figure 2 shows photoemission spectra of ReO_3 near the valence region. In order to compare the measured spectra at different orientations and angles, we normalized all spectra to a fully filled Re core level, Re 4f, at around 45 eV. This normalization criterium is key to nullify the undesired electron scattering effects including photoelectron diffraction.

The valence band spectra measured at different orientations after this normalization is shown in Figs. 3(a-c). We observe three features, A, B, and C, all of them presenting strong orientation dependences: In A, we observe almost a factor 3 in intensity changes depending on the orientation. C is, in orientations close to [001], a peak comparable to A or B, but closer to [110] or [111], it is a mere shoulder.

We study those changes by integrating first regions A and B, and plotting the anisotropic part of the integrated intensity. Figure 3(d) shows that the shape obtained from this integration matches nicely to the shape of a t_{2g} orbital as calculated from spherical harmonics, indicating the orbital character of these two valence band features. As for region C, we observe that the trends in B strongly affect its overall intensity. In order to integrate only the peak or shoulder C, we subtract a baseline starting from peak B to the background after C at around 10 eV. By plotting its anisotropic part (Fig. 3(e)), we obtain a very good match to the e_g orbital shape, which unveils the presence of e_g states at this deep region of the valence band.

Finally, our analysis procedure was validated with *ab initio* photoemission calculations using the state-of-the-art one step model [4], which includes specifically the geometry, the angle of incidence and the polarization of the light.

Our results provide a novel way to use HAXPES to identify in a very direct and visual manner the information about the electronic states of the studied

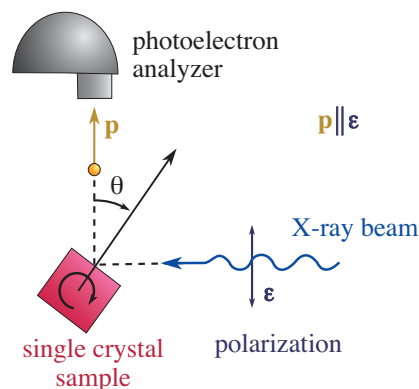


Fig. 1. Schematic representation of the experimental geometry. The photoelectrons detected by the analyzer have their momentum \mathbf{p} parallel to the electrical field $\boldsymbol{\varepsilon}$ of the X-rays. The angle θ determines the orientation of the sample facing the analyzer.

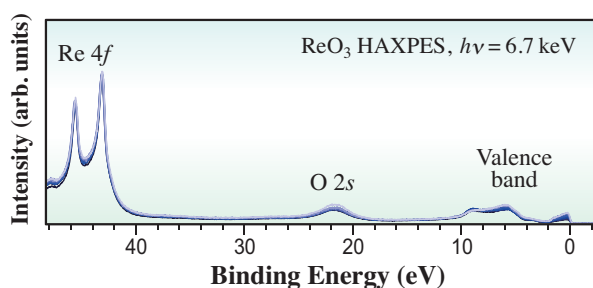


Fig. 2. Photoemission spectra of ReO₃ in a wide energy range encompassing the Re 4f core level used for the normalization and the valence band, where the orientation dependence is studied.

materials without needing to rely on theoretical calculations. This is especially promising for strongly correlated materials, where *ab initio* theoretical methods are often unreliable due to the complexity arising from many-body interactions. Our technique is complementary to other variants of PES such as

ARPES, as well as to other direct orbital imaging methods such as *s*-NIXS [5]. Our HAXPES technique can be applied to a wide range of single crystalline systems, from thin films to bulk materials, thereby opening up new opportunities also for the field of applied research.

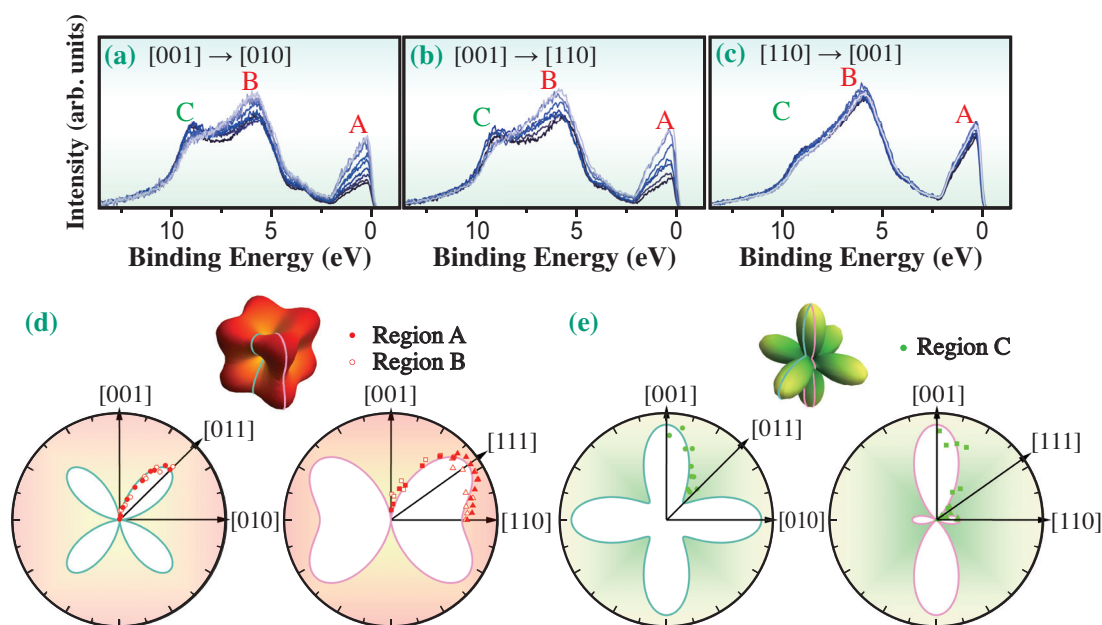


Fig. 3. (a-c) Valence band spectra taken at multiple orientations of ReO₃ by measuring multiple samples with different orientations and changing the angle θ . The spectra have been normalized to the integrated intensity of the Re 4f core level. (d) Polar plot of the anisotropic part of the integrated intensity of regions A (−0.5 to 2 eV) and B (2 eV to 7.5 eV), together with the theoretical t_{2g} line shape. (e) Polar plot of the anisotropic part of the integrated intensity of feature C, together with the theoretical e_g line shape.

Daisuke Takegami* and Liu Hao Tjeng

Max Planck Institute for Chemical Physics of Solids,
Dresden, Germany

*Email: Daisuke.Takegami@cpfs.mpg.de

References

- [1] S. M. Goldberg *et al.*: J. Electron Spectrosc. Relat. Phenom. **21** (1981) 285.
- [2] D. Takegami, L. Nicolai, Y. Utsumi, A. Meléndez-Sans, D. A. Balatsky, C.-A. Knight, C. Dalton, S.-L. Huang, C.-S. Chen, L. Zhao, A. C. Komarek, Y.-F. Liao, K.-D. Tsuei, J. Minár and L. H. Tjeng: *Phys. Rev. Res.* **4** (2022) 033108.
- [3] D. Takegami *et al.*: *Phys. Rev. B* **99** (2019) 165101.
- [4] H. Ebert *et al.*: *Rep. Prog. Phys.* **74** (2011) 096501.
- [5] H. Yavaş *et al.*: *Nat. Phys.* **15** (2019) 559.