

There is a direct connection between materials' electronic structure and their functionality in a variety of contexts including electronic devices and catalysis. This functionality often emerges at/from interfaces. In the works highlighted below, we use x-ray techniques to elucidate electronic properties of functional materials, particularly at interfaces.

Hard x-rays can measure electronic structure and correlation effects via HAXPES (hard x-ray photoelectron spectroscopy), and have the advantage of enhanced depth sensitivity, useful for measuring materials where bulk information is desired or an atomically clean surface is difficult to prepare. This technique was applied to LaB₆, a common hot cathode material (Phys. Rev. Materials 5, 055002 (2021)). We investigated the bulk electronic structure of LaB₆ using tender/hard x-ray photoemission spectroscopy, measuring both core-level and angle-resolved valence-band spectra. We compare the La 3d core level spectrum to cluster model calculations in order to understand the bulklike core-hole screening effects. The results show that the La 3d well-screened peak is at a lower binding energy compared to the main poorly screened peak; the relative intensity between these peaks depends on how strong the hybridization is between La and B atoms. We show that the recoil effect, negligible in the soft x-ray regime, becomes prominent at higher kinetic energies for lighter elements, such as boron, but is still negligible for heavy elements, such as lanthanum. In addition, we report the bulklike band structure of LaB₆ determined HAXPES. We compare HAXPES experimental results to the free-electron final-state calculations and to the more precise one-step photoemission theory including matrix element and phonon excitation effects. We demonstrate that the one-step theory of photoemission and HAXPES experiments provides, at present, the only approach capable of probing, both experimentally and theoretically, true "bulklike" electronic band structure of rare-earth hexaborides and strongly correlated materials.

We have also used x-ray photoemission to elucidate interfaces. Near total reflection (NTR) has been widely used in x-ray science, specifically in grazing incidence small angle x-ray scattering and in hard x-ray photoelectron spectroscopy (XPS). In this work, we introduce some practical aspects of using NTR in ambient pressure XPS and apply this technique to study chemical concentration gradients in a substrate/photoresist system (J. Phys. D: Appl. Phys. 54 464002 (2021)). Experimental data are accompanied by x-ray optical and photoemission simulations to quantitatively probe the photoresist and the interface with the depth accuracy of ~1 nm. Together, our calculations and experiments confirm that NTR XPS is a suitable method to extract information from buried interfaces with highest depth-resolution, which can help address open research questions regarding our understanding of concentration profiles, electrical gradients, and charge transfer phenomena at such interfaces.

Some bulk materials can be regarded as a natural heterostructure, and PdCoO₂ is an example of this, consisting of alternating layers of metallic Pd and Mott-insulating CoO₂ sheets. To understand the nature of the electronic coupling between the layers that gives rise to the unique properties of PdCoO₂, we revealed its layer-resolved electronic structure combining standing-wave X-ray photoemission spectroscopy and ab initio many-body calculations (Communications Physics 4, Article number: 143 (2021)). Experimentally, we have decomposed the measured VB spectrum into contributions from Pd and CoO₂ layers. Computationally, we find that many-body interactions in Pd and CoO₂ layers are highly different. Holes in the CoO₂ layer interact strongly with charge-transfer excitons in the same layer, whereas holes in the Pd layer couple to plasmons in the Pd layer. Interestingly, we find that holes in states hybridized across both layers couple to both types of excitations (charge-transfer excitons or plasmons), with the intensity of

photoemission satellites being proportional to the projection of the state onto a given layer. These findings pave the way towards a better understanding of complex many-electron interactions in layered quantum materials.

A related work, completing a project underway when C. Fadley passed away, used standing wave XPS to resolve the Se and Bi contributions to the valence band of topological insulator Bi_2Se_3 (Phys. Rev. B 104, 245105 (2021)). Ongoing followup work focuses on the related topological superconductor, $\text{Cu}_x\text{Bi}_2\text{Se}_3$, where preliminary standing wave measurements indicate that Cu is located throughout the 3D structure, rather than just concentrated in the van der Waals gap.

Standing wave techniques can also be used to elucidate interfaces and chemical specificity in synthetic multilayers, as was done in a hybrid multiferroic multilayer of BiFeO_3 (BFO) and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO). Our results show that the interfaces of BFO on top of LSMO are atomically abrupt, while the LSMO on top of BFO interfaces show an interdiffusion length of around 1.2 unit cells. The two interfaces also exhibit different chemical gradients, with the BFO/LSMO interface being Sr-terminated by a spectroscopically distinctive high binding energy component in Sr 2p core-level spectra, which is spatially contained within 1 unit cell from the interface. Our X-ray optical analysis revealed a unique electronic signature at the BFO/LSMO interface, which we attribute to the coupling between those respective layers. Valence band decomposition based on the Bragg-reflection standing-wave measurement also revealed the band alignment between BFO and LSMO layers (arXiv:2012.07993).