Angle-Resolved Photoemission Study of Galena

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INTRODUCTION

The importance of sulfide minerals in environmental issues has been recognized for decades[1], but there has been relatively little study of relevant model systems using surface science techniques[2]. Key issues include mining separation processes, aquifer contamination, and corrosion. Of the sulfides, PbS (galena) is particularly good as a starting point for conventional surface techniques; the (100) surface is easy to prepare by cleavage, and the bulk structure is simply the cubic NaCl lattice. S and Pb reduction can occur under certain aqueous conditions, contaminating (and possibly acidifying) the water, but the surface chemistry is not fully understood. Numerous studies have applied a variety of surface techniques to the PbS system over the last two decades including XPS, and STM in solution[3]. However, surface chemistry on PbS has not been extensively studied by structural techniques, leaving unanswered such fundamental questions as adsorption sites and modifications to substrate surface structure.

We have conducted angle-resolved photoemission (ARP) measurements of the valence bands and core-level emission of vacuum-cleaved natural galena single crystals, as a prelude to detailed studies of the adsorption of molecules from liquids using photoelectron diffraction and high resolution spectroscopy. Our k-space images of the valence bands are particularly useful for comparison with the several theoretical treatments of the PbS system. Other images exhibit a striking example of the relationship between resonant photoemission and an Auger multi-electron process. The synchrotron-based x-ray photoelectron diffraction (XPD) images show considerable fine structure as a function of electron kinetic energy, which will be used to determine the surface structure with high precision by comparison to theoretical simulations.

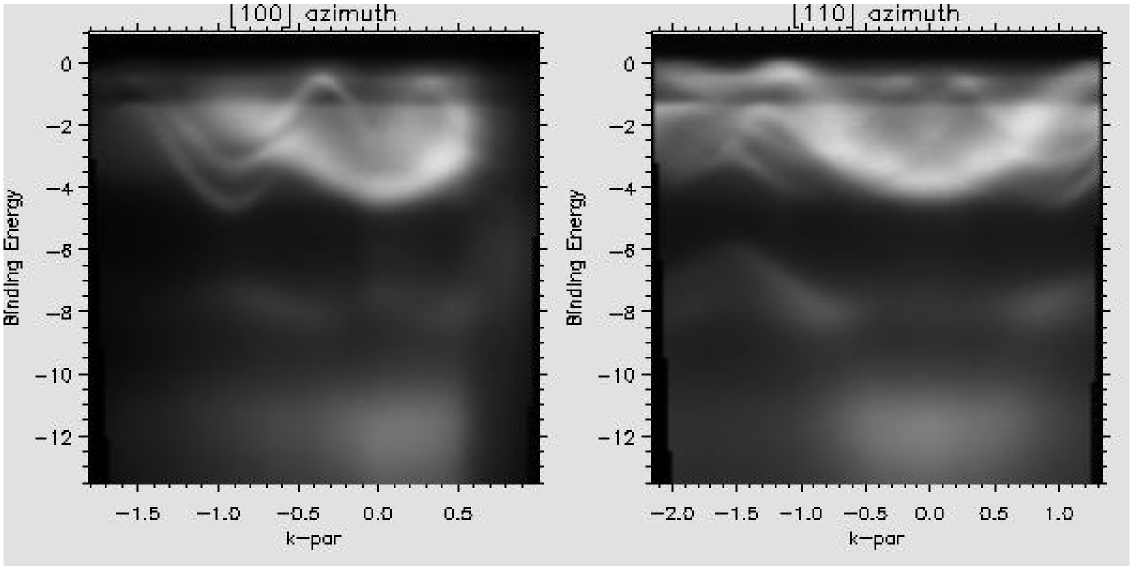

Fig. 1: Valence band spectra of PbS(001) as a function of polar emission angle taken at a photon energy of 100 eV in the [100] (left) and [110] azimuths (right). Data were collected at the UltraEsca endstation on BL7. Images were transformed to k-space coordinates (displayed in units of Å^{-1}). The binding energy (in units of eV) is relative to the valence band maximum.

RESULTS

Valence band spectra taken as a function of polar angle in the [100] (left panel) and [110] (right panel) azimuths are displayed in Fig. 1. These ARP images were produced by combining valence band spectra taken for a series of polar angles, then transforming to the corresponding k-space coordinates. The most obvious feature of these data is the PbS band structure, represented in the image as bright bands. The boundary of the first Brillouin zone can be seen in the symmetry of the bands near -1.0 Å^{-1} ([100] azimuth) and -1.5 Å^{-1} ([110] azimuth). In most respects, these results are similar to those of previous experiments[4]. In some previous discussions of PbS valence spectra, a careful distinction was made between those features due to bands and those resulting from density-of-states effects resulting from indirect transitions. Such a distinction can be difficult when viewing individual spectra. In the images of Fig. 1, however, the density-of-states effects are clearly visible as non-dispersive features. In particular, the flat "band" at 0.5 eV and the pronounced step at 1.25 eV binding energies are essentially independent of $\mathbf{k}_{\parallel}$.

We have also probed the band structure in the $k_{\perp}$ direction. Figure 2 shows a series of normal emission valence spectra as a function of incident photon energy. If a free-electron approximation can be made about the final state of the photoelectron, this CIS series can be regarded as band map along $k_{\perp}$. This image of raw data will be analyzed in this vein, but in the present form serves to illustrate the dispersion of the valence bands. The density-of-states features discussed above are also evident in this image.

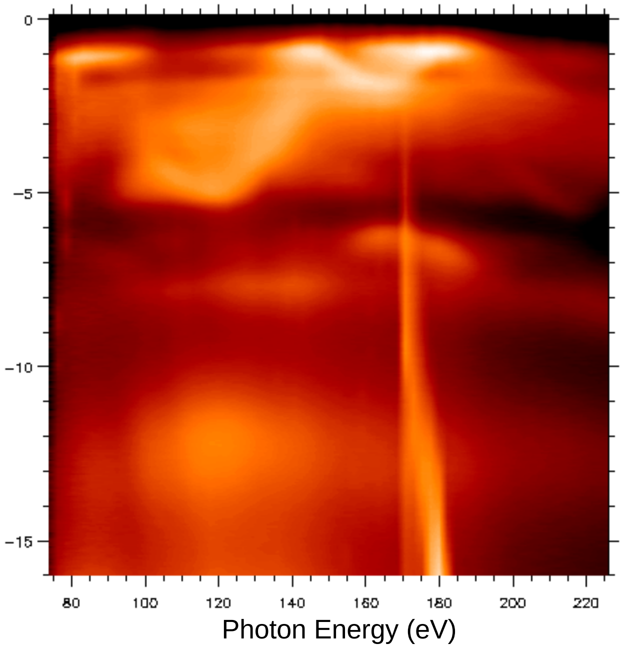

Figure 2: CIS series of raw spectra of normal-emission valence bands of PbS(001). The binding energy (in units of eV) is relative to the valence band maximum.

An additional feature of interest in Figure 2 is the significant intensity enhancement seen between 4 and 13 eV binding energy at a photon energy of 162 eV. The photon energy of the resonance is coincident with the measured binding energy of the S2p core level (not shown). According to theoretical calculations, this valence band range is predominantly a mixture of S3p and Pb6s character. These aspects indicate a photoemission resonance, which generally results from transitions between core and valence electronic levels. The image in Figure 3 displays a detailed CIS series in the photon energy region of the resonance. The resonance appears as a doublet (vertical lines near 160 eV in Figure 2), directly corresponding to the 1.2 eV separation of the S2p core level due to spin-orbit interaction. The prominent feature which "disperses" to lower binding energy for

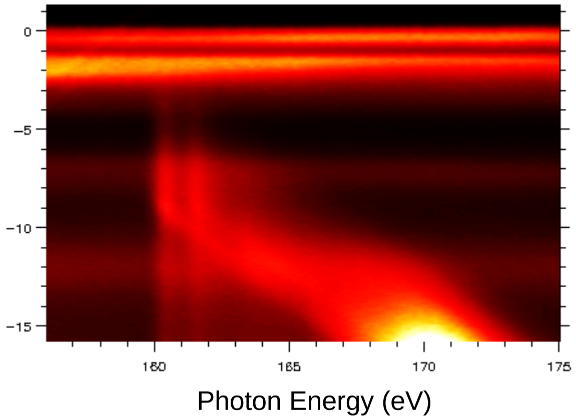

Figure 3: CIS series of raw spectra of normal-emission valence bands of PbS(001) in the vicinity of the S2p photoemission resonance.

photon energies greater than the resonance is a constant kinetic energy peak due to the S LVV Auger level.

Angle-resolved photoemission at high kinetic energies is dominated by structural effects, and is called x-ray photoelectron diffraction (XPD). We are measuring XPD patterns from galena substrates to understand the diffraction and surface structure of the clean, natural crystals, in preparation for studies of adsorption from liquids. At high kinetic energy, as shown in Figure 4, the XPD pattern of galena shows good fine structure from forward-scattering, correlated with chains of atoms in the bulk crystal structure.

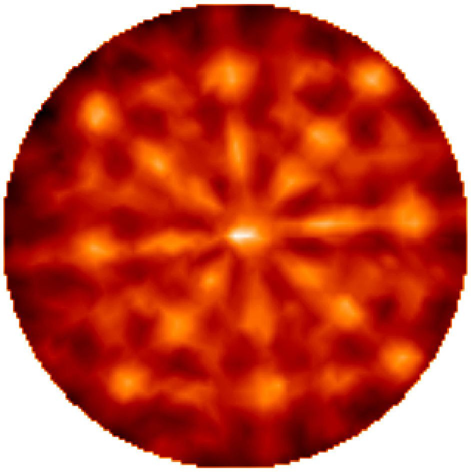

Figure 4: High energy XPD pattern (Al K) of the Pb 4f core-level.

At the ALS, we have the ability to change the outgoing XPD electron wavelength, by tuning the photon energy. We obtained a series of XPD images of the S2p and Pb4f core levels at several photon energies. A selection of these images for the S2p level is displayed in Figure 5. The final-state kinetic energy of the photoelectron is indicated for each image. The high quality of the images indicates good crystal quality and purity. There is a strong variation in diffraction patterns as a function of kinetic energy, which is very sensitive to structural parameters in the theoretical simulations, leading to high precision in bond-length determinations. An additional advantage of low-energy XPD is the high sensitivity to surface atomic structure due to the intrinsic surface sensitivity and strong backscattering effects. Modelling parameters needed for the more complex systems (such as H_2O/PbS) can be established from these initial data.

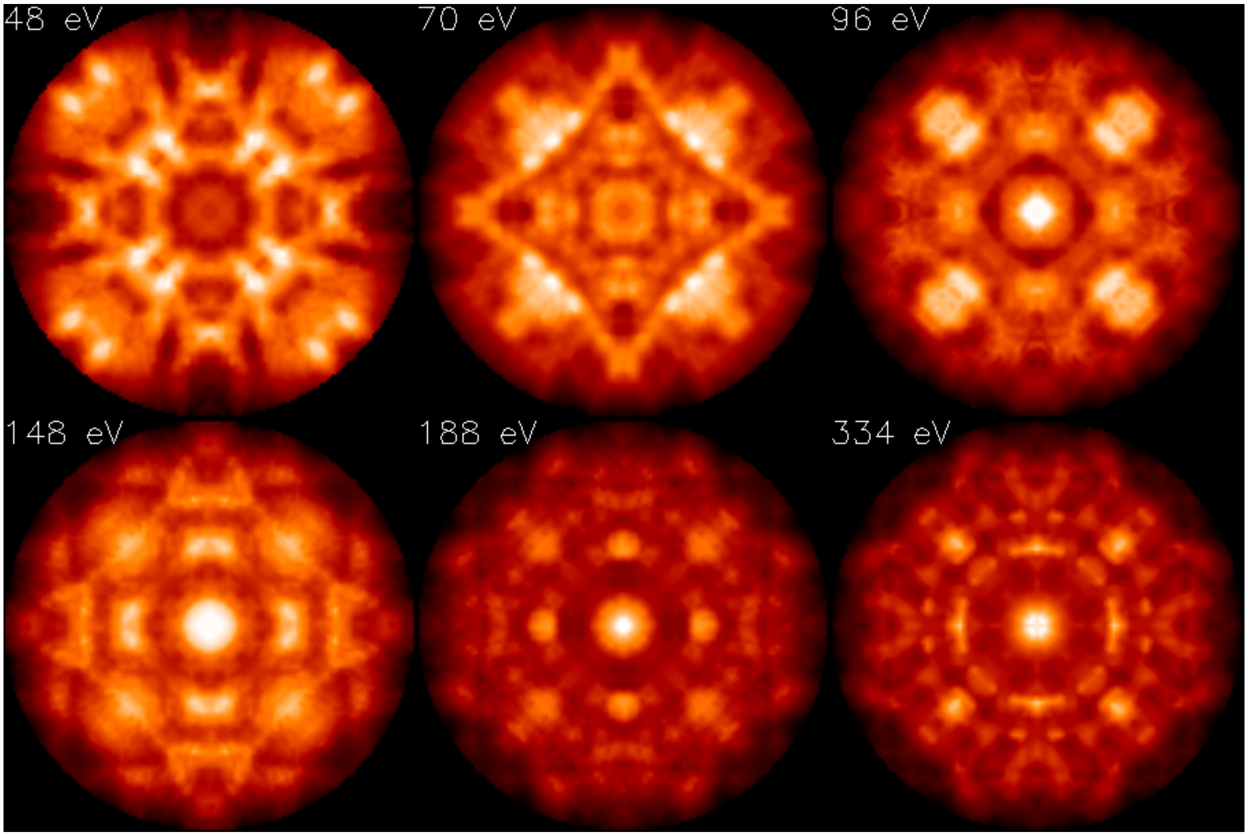

Figure 5: XPD images of the S2p core level of clean PbS(001). Data are plotted such that the radius is linear in polar emission angle, with the [100] azimuth horizontal. Data from a 90° sector were symmetrized by reflection about symmetry axes.

CONCLUSION

We have studied the clean surface of natural PbS(001) using ARP and XPD. The ARP images are in good agreement with previous studies, although certain aspects such as density-of-states features are more readily apparent as a result of our image displays of the band structure. We have observed an interesting valence-band photoemission resonance related to the S2p core level. Both high and low-energy XPD images show high-quality diffraction patterns, which will be used as a basis for future experiments involving chemisorption of environmentally relevant substances, such as water.

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