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Inverse-photoemission spectroscopy of Fe$_x$O, Ag

Kim, Bongsoo, Ph.D.
Iowa State University, 1990
Inverse-photoemission Spectroscopy
of Fe₃O, Ag

by

Bongsoo Kim

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Iowa State University
Ames, Iowa
1990
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I. INTRODUCTION

The first observation of electron emission by electromagnetic radiation was reported by Hallwachs\(^1\) in 1888. About 10 years later, Röntgen\(^2\) discovered X-rays, and Einstein\(^3\) presented the relation between the incident light frequency and the photoelectron energy. The first demonstration of the inverse of photoelectron emission was reported by Duane and Hunt\(^4\) in 1915 using a narrow monochromator with quantum energy \(h\omega\). Bremsstrahlung yield was recorded as a function of the acceleration voltage across the X-ray tube, which showed a threshold \(U\) related to \(eU=h\omega\). In 1942, structure which was characteristic of the anode material of the X-ray tube, was found by Ohlin\(^5\) with better monochromator resolution, and later in 1946, Nijboer\(^6\) interpreted Ohlin's data in terms of unfilled electronic states above the Fermi energy of the anode. The development came to rest until when Duke and Park\(^7\) recognized the importance of inverse-photoemission spectroscopy (IPES) with respect to surface science in relationship to photoelectron spectroscopy (PES) in 1972. A big boost to inverse-photoemission spectroscopy came in the late 1970s when Dose\(^8\) made an essential technical improvement. An electron gun delivering monochromatic electrons was used as the source of excitation and radiation emitted from the sample under monochromatic electron bombardment was recorded with an energy selective quantum detection device. This spectroscopy is known as isochromatic spectroscopy initially
because a fixed radiation energy is detected. However, detectors which can vary the detection energy for IPES, have been developed so that the inverse of photoemission spectroscopy at a storage ring can be obtained in inverse-photoemission spectroscopy at the present time.

As the initial state must be below the Fermi energy and the final state should be above the vacuum level in PES, the experimental conditions in IPES should be chosen properly. The initial state should be above the vacuum level, and the final state is any region above the Fermi energy in IPES. This can be both an advantage and a disadvantage of IPES. IPES can reach the region between the Fermi energy and the vacuum level which is usually inaccessible by other techniques, especially by PES, although some techniques like X-ray absorption (XAS) and soft X-ray appearance potential spectroscopy (SXAPS) also probe this region. However, a core hole is created and one conduction electron (XAS) or two conduction electrons (SXAPS) interact with this hole (Fig. 1). Thus XAS and SXAPS reveal relaxation shifts from the ground state. Besides this, these techniques can not give angle resolution since a core level should be involved intrinsically. On the other hand, IPES could be a good angle-resolved method and it has limitations only from the energy and momentum resolution of the incident electron and the energy resolution of the detector.

I investigated two different materials with the IPES instrument which I built for this study. The first was oxidation of
In BIS, the incident electron is captured in a state $e_1$ above the Fermi level. The emitted bremsstrahlung photon has an energy $\hbar \omega = eV + e\phi + kT - e_1$. The bremsstrahlung spectrum directly probes the density of conduction band states. In PES, the photon is absorbed by a core or valence electron. In XAS, the photon is absorbed by core electrons, an electron is excited to the empty states. In SXAPS, the incident electron scatters by exciting an electron from a core into a states $e_2 = eV = e\phi + kT - e_1 - E_g$. 

Fig. 1.1 BIS  Fig. 1.2 PES  Fig. 1.3 XAS  Fig. 1.4 SXAPS
polycrystalline Fe. This was an angle-integrated study and it shows the ability of IPES in the field related to the density of states. The second was Ag(100). This was an angle-resolved IPES (ARIPES) study. The unoccupied bands of single crystal Ag were well analyzed by ARIPES.
II. EXPERIMENTAL SETUP

The vacuum chamber was built specially for this study. Figure 2 is a block diagram of the vacuum chamber. A Perkin-Elmer LEED/Auger systems (model # 11-020 and # 11-500A) are used to monitor surface contamination and surface order. The 4 grid, 120° retarding field analyser (RFA) formed the LEED optics. Very good LEED patterns from various materials (Ag, Cu, CeSn₃, LaSn₃, ...) were observed with electron energies between 70 eV and 160 eV, depending strongly on the material (for example, 130 eV electron energy was best for Ag(100)). The Auger system used a RFA and the electron gun of the LEED optics directly. Because the electron gun of the model # 11-020 can go only up to 1.6 kV, an external power supply (up to 3 kV) was used for Auger spectroscopy. The second harmonic from the RFA signal should be filtered to see the first derivative of the Auger electrons. A RFA has a lower sensitivity and smaller signal-to-noise ratio than a CMA (cylindrical mirror analyzer) A CMA usually needs the first harmonic to see the first derivative of the Auger electrons so that it has much better signal to noise ratio than the RFA. This means that a longer integration time than for a CMA is needed for spectra of the same quality. However the big advantage of the RFA is that it is easy to operate with the LEED system. Figure 3 shows a typical Auger spectrum from Fe. It should be noted however that it usually takes ~ 10 min for one spectrum. Argon sputtering is used to clean the sample. Argon
Fig. 2. Block diagram of IPES chamber. The Auger system uses a retarding filed analyzer, the same electron optics as the LEED system. Two layers of μ-metal are installed to shield magnetic fields. The positions of the e-gun and photon detector are fixed. The sample is mounted on a manipulator an it is rotated when angle resolution is needed.
Sample: polycrystalline Fe
Primary beam energy: 3 KU
Modulation voltage: 3 V
Scanning rate: 1 V/Sec

Fig. 3. Auger spectrum from Fe during sputtering: Three characteristic peaks at 598 eV, 651 eV, and 703 eV from Fe are well resolved. It also shows sulfur, carbon and oxygen at 152 eV, 271 eV, and 503 eV respectively. It indicates that more sputtering is needed before taking IPES data.
was backfilled to between $1 \times 10^{-5}$ and $5 \times 10^{-5}$ Torr during sputtering and the beam current was around 3 µA. The low-energy electron gun and photon detector for IPES was custom-designed. The whole system is controlled by an IBM personal computer and the data acquisition board installed in it.

A. Detector

There are three kinds of photon detectors widely used in IPES. The most common one is the energy-selective Geiger-Müller counter\textsuperscript{13,14} working as a band-pass photon detector, whose resolution is usually about 0.8 eV centered at 9.7 eV for a CaF\textsubscript{2} window\textsuperscript{13} or about 0.4 eV centered at 9.5 eV for a SrF\textsubscript{2} window\textsuperscript{14}. The second one is a grating monochromator\textsuperscript{9,10}. Its big advantages are a variable energy of the detected photon and higher resolution. However this is not so popular as the others, because it is usually very complex to build, and it has a small acceptance angle so that it has very low counting rates. The third one, which I used in this study, consists of an electron multiplier with CuBe cathode and dynodes and a CaF\textsubscript{2} entrance window\textsuperscript{15}. The optical transmission of CaF\textsubscript{2} and the spectral photoemission yield of the CuBe cathode work as low and high band pass filters respectively. Its full width at half maximum is 0.6 eV, centered at 9.8 eV. Figure 4 shows the spectral response of this detector. The asymmetry of this apparatus function reflects the combination of the low and
Fig. 4. Spectral sensitivity of the bandpass photon detector used in this experiment. The steep decay at high energy is caused by the transmission cut-off of the CaF$_2$ entrance window, and the exponential onset at low energy results from the spectral sensitivity of the CuBe multiplier. The detected photon energy is 9.8 ± 0.3 eV.
high pass filters. The exponential onset at low energy results from the spectral sensitivity of the CuBe multiplier while the steep decay at high energy is caused by the transmission cut-off of the CaF$_2$ entrance window. The overall detection efficiency was estimated to be 2-5 $\%^{15}$. The counting rate is comparable to, or slightly lower than, the Geiger-Müller detector. However it has better resolution and a high gain stability and no dead time. Above all, since it has excellent UHV compatibility, it offers easy and stable operation in vacuum.

B. Electron-gun

In IPES, since electrons are accelerated to the sample and a photon is detected, a good photon detector and an electron gun are needed. Two types of electron-gun are commonly used in IPES. One was originally designed by Pierce$^{16}$ and improved by Simpson and Kuyatt$^{17}$ to offer the highest possible current at moderate angular resolution($\sim 9^\circ$). The disadvantages of this type of gun are its small cathode-target spacing and the critical electrode shaping. The other type of electron gun is an electrostatic lens system. The one I built was originally designed by Erdmann and Zipf$^{18}$. An osmium-coated BaO dispenser cathode was used as the emitter. It has an advantage over tungsten wire filaments since the thermal electron energy spread of BaO dispenser cathodes is $\sim 0.22$ eV and that of tungsten wire filaments is $\sim 0.57$ eV, reflecting the
operating temperatures of 1020° K and 2570° K, respectively. It should be noted that residual magnetic fields can affect the performance of the electron gun significantly because the electron energy is very low (usually less than 20 eV). Two layers of mu-metal are installed in our chamber to reduce the magnetic field inside the chamber. Further compensation of the residual magnetic field can be achieved by a pair of Helmholtz coils, not used in my case. The measured magnetic field inside the chamber turns out to be less than 3 mGauss without any Helmholtz coils, although it is not uniform. Figure 5 shows the schematic diagram of the electron gun assembly and table 1 shows the typical voltage ratio between lenses. The performance of this type of electron gun does not depend on the absolute value of the voltage on each part, but on the voltage ratio between the parts. The voltage ratio between lenses is approximately correct over the energy range of operation, which is usually from 5 eV to 20 eV. Since the voltage applied by the power supply and the potential seen by an electron passing through the lens may be quite different as a result of charged spots on the lens surfaces, especially the part around the cathode, and the performance of the electron gun can degrade seriously, the whole electron gun should be baked thoroughly in high vacuum. Although the performance of the gun is determined by the voltage ratio between the elements, the available current is determined primarily by the absolute voltage applied to the first high-voltage elements after the filament. I kept the voltage difference 20 eV
Fig. 5. Schematic diagram of the electron-gun assembly. The aperture plates in elements A and E are 0.2 and 0.5 mm thick respectively.

Table 1. Electrode parameters

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Potential</th>
<th>Aperture diameter (mm)</th>
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<tbody>
<tr>
<td>Filament F</td>
<td>-V</td>
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</tr>
<tr>
<td>Grid A</td>
<td>-0.9 V</td>
<td>1.3</td>
</tr>
<tr>
<td>B</td>
<td>+8 V</td>
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<tr>
<td>C</td>
<td>0</td>
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<tr>
<td>D</td>
<td>+8 V</td>
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</tr>
<tr>
<td>E</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
or 30 eV during the scan between the filament and first part of the lens system. The voltage ratio between parts is usually bigger than 6, and it helps reduce the effects of potential changes at the surface due to contamination and the interaction of the electron beam itself with the lens elements. The lenses with smaller voltage ratios between elements are more sensitive to the contamination.

The overall energy resolution of the spectrometer is given by a convolution of the optical resolution function of the photon detector and the electron energy distribution of the electron gun. I measured the isochromatic spectrum from the Fermi edge of polycrystalline gold to obtain the overall resolution of the system (Fig. 6). With the assumption that the density of states of Au at the Fermi energy is a constant, I can do a deconvolution. The overall resolution of the IPES system turns out to be ~ 0.7 eV, which is very close to the theoretical $\Delta E^2 = 0.3^2 + 0.6^2$ from the electron-gun dispersion energy and the photon detector resolution energy respectively.
Fig. 6. IPES of polycrystalline Au
III. THEORY

Inverse-photoemission may be most easily understood by comparing it to the well-known photoemission process. Figure 1 shows a comparison of the two spectroscopies. In inverse-photoemission spectroscopy (IPES), an initially free electron with energy $E_i$ undergoes a radiative transition with emission of a photon of energy $\hbar \omega$ and drops in a previously unoccupied electronic state of the solid at energy $E_f$. The intensity of the emitted light $\hbar \omega$ can be measured as a function of the final state energy $E_f = E_i - \hbar \omega$ by variation of the initial energy $E_i$, keeping the quantum detector energy $\hbar \omega$ constant. This is the exact reverse process of the photoemission spectroscopy (PES), in which a photon of energy $\hbar \omega$ is absorbed by an electron at energy $E_i$, exciting it to the final state of energy $E_f = E_i + \hbar \omega$, and during which process the emitted electron is measured as a function of $E_f$. It should be noted that the difference between PES and IPES is only the interchange of initial and final states and both states are initially empty in IPES. The interaction Hamiltonian in both cases is

$$H_{\text{int}} = \frac{e}{2mc} \left( \hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}} \right)$$ (1)
where \( \vec{A} \) is the electromagnetic vector potential and \( \vec{p} \) is the momentum operator. The mutual relationship for solid surfaces of the two process has been formulated by Pendry. Suppose that the surfaces in both processes are identical in properties, except that the initial state is an occupied energy level in PES, and it is an unoccupied energy level in IPES. Let \( J_{el} \) and \( J_{ph} \) be the number of electrons per hartree per steradian per photon and the number of bremsstrahlung quanta per steradian per incident electron respectively. \( J_{el} \) and \( J_{ph} \) are not equal because the number of states in a steradian of photons is not the same as that of electrons in a steradian. In the case of electrons, the number of states is

\[
[\Omega / (2\pi)^3] |\vec{p}|^2 \cos \theta = [\Omega / (2\pi)^3] \cdot 2 \cdot E \cdot \cos \theta
\]

where \( \Omega \) is the volume of the system, \( \vec{p} \) is the electron momentum, \( E \) is the electron energy and \( \theta \) is the polar angle of electron emission. In the case of photons, the number of states is

\[
[\Omega / (2\pi)^3] |\vec{q}|^2 \cos \phi = [\Omega / (2\pi)^3] \cdot \omega^2 / c^2 \cos \phi
\]

where \( \vec{q} \) is the photon momentum, \( c \) is the velocity of light, and \( \phi \) is the polar angle of photon emission. So
\[ \frac{J_{\text{ph}}}{J_{\text{el}}} = \left[ \frac{\omega^2}{2 \beta c^2} \right] \cdot \cos \phi / \cos \theta \]  

(4)

i.e., photon emission is weaker by $c^2$ compared to the electron emission (in atomic units, $E = k^2/2$ for electron energy and $\omega = Qc$ for photon energy and $c=137$). Although this factor is prohibitive in experimental atomic physics, it is not in the case for solid surfaces. Pendry\textsuperscript{19} estimates a photon flux of $3 \times 10^6$ per second at 0.1 eV band width for an incident electron current of 100 µA for a typical 3d metal. Besides this aspect, IPES provides the same physical information as PES, but for unoccupied bands. It makes IPES a special tool in that it includes the otherwise hardly accessible region between the Fermi and the vacuum level of the sample.

Due to this close relationship between two processes, the detailed models for IPES are like that for PES. There are 2 widely used models for IPES and PES, the so called one-step model\textsuperscript{20} and the 3-step model\textsuperscript{21}. Though the one-step model is the most rigorous theoretical approach, much more physical insight can be obtained by the isotropic 3-step model. I will describe only the 3-step model because the 3-step model gives more physical insight about IPES and only the 3-step model is used in analyzing the experiment data of this study.
In the 3-step model of PES, the first step is the optical excitation of an electron from an occupied valence band state to an empty conduction band state. The next step is the transport of the hot electron to the surface, and the last step is the escape of the electron from the surface.

In IPES, there is a very analogous formalism. The summary of this 3-step model for IPES is as follows:

**Step one:** An electron enters solid and diffract out or propagate in. Optical decay of a propagated electron of energy $E$ into a final state of energy $E - \hbar \omega$. A momentum conserving direct transition assumed here, i.e., an electron with momentum $\mathbf{K}$ in the Brillouin zone and initial energy $E_i(\mathbf{K})$ decays vertically to a final state $E_f(\mathbf{K})$ on a plot of $E$ as $\mathbf{K}$.

**Step two:** Transport of the photon created in the solid to the surface. In this step, optical absorption should be considered.

**Step three:** Photon escapes from the surface.

Besides these processes, in a real situation, there are other complicated processes which forms a background, due to inelastic
scattering of the incident electron. So the measured IPES consists of a primary contribution \( I_p(E, \omega) \) and a background \( I_b(E, \omega) \),

\[
I(E, \omega) = I_p(E, \omega) + I_b(E, \omega)
\]

where \( I_p(E, \omega) \) may be interpreted with the 3-step model. We can decompose \( I_p(E, \omega) \) into an escape function \( D(\omega) \), a transport function \( T(E, \omega) \) and a bremsstrahlung distribution \( P(E, \omega) \) according to the 3-step model.

\[
I_p(E, \omega) = D(\omega) \cdot T(E, \omega) \cdot P(E, \omega).
\]

We assume that \( T(E, \omega) \) does not cause new structures in the spectrum, although it is one of the main causes of the background. The escape function \( D(\omega) \) is a function of \( \omega \), i.e., it is related to the optical constants of the sample. However it is a constant in the isochromatic mode, which is the case for this study, so it can be assumed that the structure in IPES is mainly related to the \( P(E, \omega) \), not to \( D(\omega) \), nor \( T(E, \omega) \).

If we think only of the bulk states involved in \( P(E, \omega) \), we can write

\[
\hat{p}^i f^k \propto \int d^3k \ | \langle i | \hat{\mathbf{A}} \cdot \mathbf{p}^k | f \rangle |^2 \delta (E_i(\mathbf{K}) - E_f(\mathbf{K}) - \hbar \omega) \cdot \delta (E_i(\mathbf{K}) - E),
\]
where $\mathbf{A}$ is the vector potential associated with the emission and $\mathbf{p}$ is the momentum operator. $|\langle i | \mathbf{A} \cdot \mathbf{p} | f \rangle|^2$ is the square of a dipole matrix element between the initial and the final states. The total emission per incident electron can be obtained by summing all possible final states and averaging over initial states. Thus

$$P(E, \omega) = \frac{\sum_{i,f} p_{i,f}^\text{dir}}{\sum_i \int d^3k \delta \left( E_i(k - E) \right)}$$

(8)

The normalizing denominator makes this equation different from the corresponding equation in PES, which does not have this denominator. The volume of the integration $\Omega$ is determined by the experimental conditions. For example, if our experiment is a thoroughly angle-integrated measurement, $\Omega$ should be the entire Brillouin zone and the denominator turns out to be a density of states (DOS) at energy $E$. Furthermore if the dipole matrix element is assumed to be a constant throughout the entire Brillouin zone, equation 8 simplifies to the energy distribution of the joint density of states (JEDOS) divided by the density of initial states. For an experiment on a single crystal, we need electrons of well defined $E$ and $R_S$ in vacuum, and $\Omega$ shrinks around the electron momentum $R_S$ in the solid. It should be noted that $R_S$ and $R_V$ are different since only the parallel component to the surface.
of $\mathcal{K}_v$ is conserved during the electron's passage through the surface.

Besides direct transitions, indirect transitions, i.e., $\mathcal{K}$ non-conserving transitions may occur. If momentum conservation is entirely relaxed, equation 8 leads to

$$P_{\text{dir}}^{i,f} \propto \int d^3k_id^3k_f |<i|\vec{K} \cdot \vec{p}|f>|^2 \delta \left(E_i(\vec{K})-E\right) \cdot \delta \left(E_i(\vec{K})-E_f(\vec{K})-\hbar \omega \right). \quad (9)$$

The volume of integration should be the entire Brillouin zone. Then the total emission $P_{\text{ind}}(E,\omega)$ becomes

$$P_{\text{ind}}(E,\omega) \propto \sum_{i,f} \frac{P_{\text{ind}}^{i,f}}{N(E_i)}. \quad (10)$$

With the further assumption that the dipole matrix element is constant in the double integration, equation 10 becomes the product of densities of the initial and the final states. Furthermore since the density of initial states is canceled by the normalizing denominator, the total emission is proportional only to the density of final states.

$$P_{\text{ind}}(E,\omega) \propto N(E-\hbar \omega) \quad (11)$$
This makes IPES different from PES, in which the same concepts lead to the product of initial and final density of states, since PES does not have the normalizing denominator as mentioned previously.
IV. OXIDATION OF POLYCRYSTALLINE Fe

The electronic structure of transition-metal oxides (MnO, FeO, NiO, ...) has been of great interest. The nature of the electronic structure and the origin of the insulating gap in these materials long has been a controversial subject, both in experiments and theory. In theory, one uses either a single-electron band theory and or a more localized electron picture that includes configuration interaction. It was generally accepted that the band gap results from Mott-Hubbard localization of electrons in partially filled d-bands\(^{23,24}\). Such a model is correct when the ratio \((U/W)\) of \(U\), the d-d Coulomb repulsion energy and \(W\), the d-band width is large, which is not always true for transition metal-oxides.

Since Fujimori et al.\(^{25}\) successfully interpreted the valence band photoemission spectrum of NiO considering configuration interaction with a \((\text{NiO}_6)^{10-}\) cluster, Fe\(_2\)O\(_3\)\(^{26}\), FeO\(^{27}\), and MnO\(^{28}\) have been studied with this scheme. The most intense features in the valence band photoemission spectrum for these materials were found to be derived from \(d^{n_L}\) final states, i.e., the d hole screened by transferring the electron from a p state of a ligand oxygen to the d state hole, and the insulating gaps of these materials were interpreted as a ligand 2p \(\rightarrow\) metal 3d charge transfer gap rather than the 3d \(\rightarrow\) 3d Mott-Hubbard gap.
Band theory was thought to be inadequate for these oxides because it failed to show the insulating monoxides as insulators, despite the fact that it could give a natural explanation for many other properties of the transition-metal oxides. For example, Andersen et al. showed that band theory could produce the lattice parameters of the insulating monoxides, and it explained the sudden jump of the lattice parameters from VO to MnO as a magnetic effect. Terakura et al. and Norman could give a good explanation for the insulating properties of MnO, NiO and CoO in the framework of the local spin density (LSD) formalism. It was also claimed that the difficulty in FeO was not due to band theory itself, but to the complexity in dealing with the local approximation in spin density functional theory.

In addition to the fact that two kinds theories can be successful in some respects and failures in others, experiments also give two different results. Eastman and Freeouf measured valence band photoemission for FeO, MnO, and Cr2O3. They showed that the metal 3d states are ~ 3 eV wide, located near the Fermi energy, and that the O states are ~ 4 eV wide at 3 eV below the Fermi energy. Metal 3d and O states overlapped significantly. A recent resonant photoemission study showed that configuration interaction could explain the satellite due to p-d mixing for NiO and FeO. An angle-resolved photoemission study on a thin FeO(111) layer epitaxially formed on a Fe(110) substrate was reported by Masuda et al. Fe 3d states showed little dispersion while the
lower-lying $O_2p$ states exhibited considerable dispersion. Since the FeO layer was less than 2 planes thick, the bulk band structure is not adequate to interpret these experiments, so that they predicted a qualitative band structure for the oxygen overlayer on Fe on the basis of a simple tight-binding picture. Recent photoemission revealed band-like behavior of the Co 3d states in paramagnetic CoO(001)\textsuperscript{34}. Two d-bands were identified, which disperse 0.4 eV and 1.7 eV along the $\Gamma$-X direction. The results were interpreted with the proposed band structure model by Terakura\textsuperscript{30}. The IPES of NiO\textsuperscript{35,36} was measured in the 9.7 eV isochromatic mode. The spectrum was interpreted with the unoccupied 4s states of the Ni\textsuperscript{2+} ions calculated by Mattheiss\textsuperscript{37}.

In this study, I measured the inverse-photoemission spectrum of oxidized Fe and carried out a band calculation for iron oxide (FeO). In the calculation I assumed stoichiometric, non-magnetically-ordered FeO, despite the fact that it is actually antiferromagnetic. Besides simplifying the calculation considerably, it may be adequate for our purpose because our experimental setup does not analyze for spin.

A. Band Calculation of FeO

FeO has the NaCl structure with a lattice constant of 4.31 A. The electronic band structure was calculated using the linearized-augmented-plane-wave (LAPW) method\textsuperscript{38} with the self-consistent
potential constructed by the KKR\textsuperscript{39} method. A muffin-tin type potential, which is appropriate for a cubic structure, was assumed throughout the calculation. About 55\% of the unit-cell volume was occupied by the muffin-tin spheres. Most of the empty space was at the center of the cubic unit cell. Because the electronic charge does not penetrate in this region very much, this arrangement is appropriate this calculation.

The starting muffin-tin crystal potential was constructed by superposing neutral atomic charge densities, which were obtained by solving the Dirac-Slater equation\textsuperscript{40} self-consistently with atomic configurations $3d^64s^2$ for Fe and $2p^4$ for O. The Hedin-Lunqvist approximation\textsuperscript{41} for the exchange-correlation terms was used for the local density functional formalism. This approximation has the advantage in self-consistent iterations that it does not need adjustable parameters. The crystal charge density was obtained by solving the Hamiltonian with the trial crystal potential at 240 k points in the irreducible $1/48$ Brillouin zone. The new trial potential was obtained by mixing the new charge density with the old charge density, along with the core charge which was also newly constructed in every iteration. This procedure was repeated until the change of the charge density converged to about $10^{-4}$ electrons, and this insured that the eigenvalues converged to less than 1 mRy in successive iterations. With this self-consistently constructed potential, the final band structure and density of states (DOS) were calculated with the LAPW method. The calculations were
scalar-relativistic\textsuperscript{42} in which the Dirac equation is reduced to keep spin as a good quantum number by omitting the spin-orbit interaction. The spin-orbit interaction is added as a perturbation, although spin-orbit interaction and relativistic effects were too small to be considered in FeO. The parameter \( K_{\text{max}}^{\text{mt}} \) was set to determine the number of augmented plane waves outside the muffin-tin spheres, about 90 to 120 plane waves. Inside the sphere, the wave functions were expanded in terms of spherical harmonics up to \( l=12 \). It should be noted that the LAPW band structure depended on the parameter of the expansion center for the linearization. This parameter was chosen so that the valence bands of the LAPW band structure resemble those of a KKR band structure as closely as possible. Figure 7 shows the calculated band structure along some symmetry lines. The Fermi level falls in the middle of the Fe band as expected. The effect of self-consistency is to narrow the energy gap between the Fe band and the O band, so there is virtually no band gap between them. The energy difference between \( \Gamma_{15} \) and \( \Gamma'_{25} \) is 0.08 Ry, compared with about 0.48 Ry in the nonself-consistent calculation. The Fe states and O states are strongly hybridized, which can be seen in the density of states plot (to be discussed later) in the self-consistent calculation. On the other hand, they are much less hybridized in the nonself-consistent calculation. The photoemission spectrum\textsuperscript{32} also supports significant overlap of Fe\textsubscript{3d} and O\textsubscript{2p} states. The unoccupied states are mainly Fe\textsubscript{4s,4p} states.
Fig. 7. Band structure of FeO. The lower bands are mainly oxygen 2p states, and the Fermi energy is in the middle of Fe 3d states. The effect of self-consistency makes Fe 3d states and O 2p states strongly hybridized.
near the Fermi energy, and a mixture of Fe\textsuperscript{4s,4p} and O\textsubscript{3d} states around 7.5 eV above the Fermi energy. Although the band structure we calculated cannot predict the band gap correctly, it may be a good basis for interpreting the photoemission spectrum and inverse photoemission spectra.

B. Density of States (DOS) Measurement by IPES

As mentioned earlier in theory, IPES measures the DOS directly for polycrystals, a non-\mathcal{K} conserving spectrum with the assumption of constant dipole matrix elements. Figure 8 shows the experimentally determined DOS of FeO along with the DOS from the band calculation. The overall agreement is not too bad. The main two structures are well matched with the calculation. The difference, however, starts getting bigger rapidly for $E > 6$ eV. This is because of one or more energy losses by the incident electron through creating an electron-hole pair prior to the optical transition. Figure 9 displays the basic mechanism of this energy loss process. With the assumption that electron hole pair creation is by far the dominant energy loss process, the rate of radiation is

$$I(E_1, \hbar \omega) = \gamma N(E_1 - \hbar \omega) + \int P(E_1, E_2) dE_2 \left( \gamma N(E_2 - \hbar \omega) + \cdots \right)$$

(12)
Fig. 8. Density of states of FeO (solid line) along with experimental result (dashed line). The dashed-dot line is the contribution of radiative transitions through the creation of one electron hole pair. Although the inclusion of this contribution to the DOS (long-dashed line) makes the experimental result much closer to the theoretical results, it does not produce any new structures.
Fig. 9. Energy level diagram for Bremsstrahlungemission with and without preceding electron hole pair creation. Electron hole pair production can proceed in two different ways (solid and dashed arrows) leading to the same final state.
where \( P(E_1, E_2) \) is the probability that an electron of initial energy \( E_1 \) is scattered to a final state with energy \( E_2 \) creating an electron hole pair, and \( \gamma \) is the probability for a radiative transition with quantum \( \hbar \omega \). Berglund and Spicer\(^{15}\) showed that \( P(E_1, E_2) \) is simply given by the sum of all interband transitions between \( E_1 \) and \( E_2 \) within the assumption of total relaxation of \( \gamma \) conservation.

\[
P(E_1, E_2) = \frac{2N(E_2) \int N(E_3)N(E_3-E_1+E_2) \, dE_3}{\int N(E_2) \, dE_2 \int N(E_3)N(E_3-E_1+E_2) \, dE_3}
\]

The dashed-dot line in Fig. 8 is the contribution of radiative transitions through the creation of one electron hole pair. It shows little structure because \( P(E_1, E_2) \) is a convolution effect of two density of states and the creation of electron hole pairs is integrated over \( E_2 > \hbar \omega \). We can see already much improvement only with one electron hole pair. Further improvement can be achieved with more pairs and probably, the inclusion of dipole matrix elements. However because the spectrum does not show any other structures beyond 6 eV, and the inclusion of electron hole pairs does not change the spectrum dramatically at low energy, it is safe to use the spectrum for analyzing the behavior of DOS of FeO near the Fermi energy without any improvement.
C. Experiment

The Fe polycrystal was cleaned by repeated Ar⁺-ion sputtering and annealing cycles. Carbon and sulfur were the hardest elements to remove. Argon was backfilled to 5x10⁻⁵ Torr. The ion current was ~ 30 mA and the beam current was about 3 μA at 1 kV energy. Carbon could not be thoroughly removed just with Ar⁺ ion sputtering. The sample was oxidized on purpose up to a few Langmuir and annealed to 600° C during the sputtering cycles, so carbon was removed by conversion to CO and CO₂. Extensive sputtering (2-3 weeks) could get rid of sulfur. The Fe-oxide layer was prepared by exposing the clean surface to 2x10⁻⁸ Torr of O₂ up to 1000 L, and 5x10⁻⁷ Torr for higher exposures. Although the surface layer must be a mixture of FeO, Fe₂O₃ and Fe₃O₄, most of it is believed to be FeO, since Fe(110) and Fe(100) surfaces favor the growth of FeO⁴³. A recent extended appearance-potential measurement⁴⁴ also supports the formation of FeO on polycrystalline Fe when the surface is exposed to oxygen.

D. Unoccupied States of FeO

Figure 10 shows the change of the IPES spectrum as a function of oxygen exposure up to 20,000 L at 300K. The shoulder at ~ 1 eV
Fig. 10. IPES spectrum as a function of oxygen exposure up to 20,000 L on polycrystalline Fe at 300 K. From bottom to top, clean Fe, 10L, 20L, 100L, 300L, 800L, 20,000L oxygen respectively.
above the Fermi energy, which is from the Fe substrate, was continuously attenuated and two structures at 2.5 eV and 7.5 eV from iron oxides grew with increasing oxygen exposure. Since the pure Fe spectrum does not have a dominant structure, it is hard to separate the contribution of the Fe substrate from the FeO spectrum. The spectrum was decomposed into Fe and iron oxide contributions by least-squares fitting to a linear contribution of the clean iron signal and the iron oxide at 20,000 L exposure. The decomposition for 100 L O₂ exposure is given in Fig. 11. The dash-dot curve represents the difference between the fit and experiment. The quality of fit is not as good as that achieved for NiO. The reason for this poor fit may be that the backgrounds of Fe and iron oxide IPES are not so small in the high energy region, and they are not linearly related to each other. Moreover, there may be significant amounts of Fe₂O₃ and Fe₃O₄ in the surface region.

A logarithmic growth law was checked with the superposition result by the same procedure used in for NiO. For a logarithmic growth law, the oxide layer thickness corresponding to an exposure L is given by

\[ d = d_0 \ln(1 + L/L_0), \]  

(14)

where \( d_0 \) and \( L_0 \) are free parameters, which depend on the oxidation conditions. If we assume that the incident electron current
Fig. 11. IPES spectrum at an intermediate state of oxidation is decomposed into pure Fe and pure FeO contributions. Solid line: experimental result; dashed-dot line: difference between the fit and the experiment.
density is damped exponentially due to the finite elastic mean free path in the oxide film, the strength of the spectrum from the iron oxide as a function of oxide thickness is given by

$$ S(d) = S_\infty \left( 1 - \exp\left(-d/\lambda_{FeO}\right) \right), $$

where $S_\infty$ is the signal intensity of an infinitely thick oxide film. By combining above two equations, we can get the intensity of the thin film as a function of oxygen exposure $L$.

$$ S(d) = S_\infty \left( 1 - (1+L/L_0)^{-\beta} \right) $$

where $\beta$ is a free parameter. Here we take $S_\infty$ as the intensity at 20,000 L $O_2$ exposure. $L_0 = 53.6$ L and $\beta = 0.5$ give the best fit.

Figure 12 shows the comparison of $S/S_\infty$ from the superposition result and from the logarithmic growth law. The two sets agree reasonably well, so it appears that the logarithmic growth law is valid for the iron oxide system. A slight disagreement between the two sets may come from difficulty in the decomposition of the spectrum into Fe and FeO contributions. The final oxide spectrum is shown in Fig. 13, along with PES data$^{32}$ and the density of states of FeO. The position of the Fermi energy in the DOS of occupied states was shifted about 0.5 eV to higher energy and the DOS of unoccupied states was shifted about 1 eV to higher energy inorder that the leading structure in the DOS was aligned with the
Fig. 12. Measured intensity of the FeO IPES spectrum compared to values derived from a logarithmic growth law.
Fig. 13. IPES spectrum of FeO (dashed), PES spectrum (dashed) and the calculated density of states (solid). The DOS of unoccupied states were shifted about 1 eV to high energy in order that the leading structure in the DOS be aligned with the IPES, and the DOS is broadened by a Lorenzian of width (FWHM) 0.2 eV for occupied and width 0.6 eV for unoccupied states in order to simulate experimental resolution.
IPES, and the DOS was broadened by convolution with a Lorenzian of width (FWHM) 0.2 eV for occupied states and FWHM 0.6 eV for unoccupied states in order to simulate the experimental resolution. The PES spectrum was decomposed into $O_{2p}$ and $Fe_{3d}$ states on the basis of the photon-energy dependence of the emission intensities. Our calculated DOS gives reasonable agreement with the photoemission data in the width, position, and the overlap between $Fe_{3d}$ and $O_{2p}$ structures. This overlap in the PES experiments and band calculation implies that FeO does not exhibit perfect ionic bonding, but has some covalent bonding between Fe and oxygen. The IPES data show two structures. One is near the Fermi energy, and the other is around 7.5 eV above the Fermi energy. They are well matched with the DOS of FeO. According to the band calculation, the one near the Fermi energy is mainly from $Fe_{4s,4p}$ states, and the other is from a mixture of $Fe_{4s,4p}$ and $O_{3d}$ states.

Since $Fe^{3+}$ defects exist on the oxidized surface and act as acceptors, the band gap cannot be seen experimentally. We can assume that the low intensity region in PES and IPES belongs to the band gap region, the full band gap is the energy difference between the top of the valence band in PES and the first structure in IPES, which turns out to be ~ 2.5 eV from Fig.5. Optical data give a 2.4 eV band gap$^{47}$, very close to our estimate.

If FeO is a Mott-Hubbard type insulator, the structure resulting from transitions into empty localized Fe states of type $d^n \rightarrow d^{n+1}$ could be seen. Then the Coulomb correlation energy $U$,
defined as $d^n + d^n \rightarrow d^{n-1} + d^{n+1} + U$ could be determined experimentally with IPES and PES data. It turns out to be $2.5 \text{ eV}$ for NiO$^{45}$, using $1.5 \text{ eV}$ from $d^8 \rightarrow d^7$ in PES and $1 \text{ eV}$ from $d^8 \rightarrow d^9$ in IPES. From this result for NiO, the best estimation of the energy of $d^n \rightarrow d^{n+1}$ for FeO is lower than $1 \text{ eV}$. There is, however, no structure within $1 \text{ eV}$ of the Fermi energy in IPES. Assuming that the band structure model can give a good interpretation for IPES, it indicates that FeO is not a Mott-Hubbard type insulator, or that $U$ is too small to be detected with our resolution.

E. Conclusion

We measured IPES of iron oxides grown on a polycrystalline Fe substrate, and calculated the band structure to analyze the spectrum of FeO. The band calculation showed some overlap of Fe$^{3d}$ states and O$^{2p}$ states, and s,p-like unoccupied states. Isochromatic IPES showed two structures at $2.5 \text{ eV}$ and $7.5 \text{ eV}$, which could be identified as mainly Fe states, with a small fraction of O states in the second structure according to the band calculation. We estimated the full band gap as $2.5 \text{ eV}$ from PES and IPES data. We could not identify $d^n \rightarrow d^{n+1}$ transitions in this study, although they could be seen in the NiO system. It may be because the Coulomb correlation energy in FeO is smaller than in NiO.
V. ANGLE RESOLVED INVERSE-PHOTOEMISSION FROM THE Ag(001) SURFACE

Ag has been studied many times by PES\textsuperscript{48-50} and IPES\textsuperscript{51-55}. The occupied states below the Fermi energy are a mixture of s, p states and d states, and the unoccupied states are free electron-like near the Fermi energy. Besides bulk states, surface states are well known for Ag, both above and below the Fermi energy. Although free electron-like unoccupied states have been well suited to analyze PES data, recent PES experiments\textsuperscript{49,50} suggest that the unoccupied states near the Fermi energy can not be treated as free electron-like, and a very flat band exists at 17 eV above the Fermi energy, along the Γ - X direction, in experiments\textsuperscript{56,57} and band calculations\textsuperscript{58}. Obviously, we can not treat this band as a free electron-like state. Since IPES is the best tool for seeing unoccupied states, especially near the Fermi energy, it is a very interesting problem to see whether the unoccupied states of Ag are indeed free-electron-like or not, and to see the existence of the flat band. I calculated two band structures for Ag to analyze IPES. One is the simplest free electron band structure, and the other is a relativistic LAPW band structure. The LAPW calculation procedure is the same as explained for the FeO band calculation.
A. Experiment

The orientation of the Ag(001) surface was determined by a back scattering Laue X-ray diffraction pattern. Just before putting the sample into the chamber, I etched the sample with an echant of $\text{H}_2\text{O}_2(1) + \text{NH}_4\text{OH}(1)$ for 2 minutes. The surface was cleaned by Ar$^+$-ion sputtering. Oxygen was the last impurity to be removed. The Ag(001) surface structure could be regained by annealing the sample up to 400° C for 5 minutes after sputtering, and LEED confirmed it. The IPES spectra were measured up to 30 eV above the Fermi energy along the T-X direction of the (100)-surface Brillouin zone. Two bulk-related structures and one surface-related structure were observed.

In Fig. 14 I show a set of spectra from Ag(100) obtained for different angles of incidence in the IXUL plane. Peak B1, near the Fermi energy, and peak B2 at around 17 eV above the Fermi energy were assigned to bulk-band-derived transitions, and S1 to a surface-state transition.

B. Surface State

If we disregard localized states due to lattice defects, steps, or adsorbed atoms, there are two kinds of surface states, called Tamm states$^{59,60}$ and Shockley states$^{61-63}$. Tamm surface states are split off into a gap from bulk bands, when the perturbation of the
Fig. 14. IPES spectra of Ag(001) in the isochromatic mode along the Γ - X symmetry line. The spectra are marked with the incidence angle of the electron in degree. The energy scale is that of the final state.
surface potential is sufficiently strong compared with the bandwidth. Shockley surface states are in energy gaps caused by the hybridization of crossed bands, e.g., in sp gaps. The lower band should have odd symmetry, and the upper band should have even symmetry for the existence of Shockley surface states (Shockley inverted gap), because the opposite case cannot meet the matching condition for waves at the surface\(^6\). Shockley-type surface states can be created when the surface potential attracts charge from the bulk and accumulates them in the surface states located in real space outside the surface atom cores. This is the physical reason for Shockley inversion. For Ag\(^6\), Tamm surface states as well as Shockley surface states exist. Tamm surface states which are related to the d-like bands for Ag, however, are located well below \(E_F\) so that they cannot be observed in this study. A Shockley-type state\(^6\) is observed in this study, which gives the S peak in Figure 14.

Among several numerical calculations of unoccupied surface states on metals, Echenique and Pendry\(^6\) give the most simple and transparent explanation for the surface states found at \(K//\) within band gaps. They describe an electron trapped in a surface state as a wave between the crystal edge and the surface-barrier potential. If we use \(r_C e^{i\phi_C}\) and \(r_B e^{i\phi_B}\) as the amplitude of the reflectivity of the crystal edge C and the barrier potential B respectively, then the total amplitude of the wave after an infinite number of reflections is
A pole of equation 17 leads to the surface state. Thus the conditions for the surface state are

\[ r_B = r_C = 1 \quad \text{and} \quad \phi_B + \phi_C = 2\pi n \quad n: \text{integer} \]  

(18)

When an electron is in a bulk band gap \((r_C = 1)\) and below the vacuum level \((r_B = 1)\), this condition is satisfied. The other condition \((\phi_B + \phi_C = 2\pi n)\) may be met by a rapid variation with energy of either \(\phi_C\) or \(\phi_B\). Figure 15 depicts the whole situation for the Ag(100) surface. Although the precise \(z\) dependence of the potential and \(\phi_C\) and \(\phi_B\) are unknown, the asymptotic behavior can be predicted with some assumptions. The first assumption is that the surface potential is continued in perfect Coulomb form up to \(z = 0\), then

\[ V_B(z) \propto -(4z)^{-1}, \quad z > 0 \]

\[ = + \infty, \quad z < 0. \]

(19)

Then

\[ \phi_B/\pi = \left[ \frac{3.4 \text{ eV}}{E_V - E} \right]^{1/2} - 1 \]

(20)

Neglecting \(\phi_C\), equation 21 gives an infinite number of roots for the condition (19). Among them, the two lowest roots corresponding to
Fig. 15. Schematic image potential diagram: (a) Schematic potential diagram for an image potential surface state on Ag(001), indicating the image potential barrier outside the crystal (z>0) and the bulk band gap between states $X_1 - X_4'$. (b) Bulk band structure of Ag along $\Gamma - X$, corresponding to normal electron incidence as a function of the electron $k$ vector. (c) The imaginary part of $k$ inside the gap without (solid line) and with (dashed line) damping of the bulk states.
n=0, 1 are 3.4 and 0.4 eV. For n \geq 3, the Rydberg-series-like infinite number of roots are in the range 0.4 eV > E_y - E > 0, which are unresolvable with my resolution. Clearly the neglect of \phi_C is justified for bigger n, but not for n=0,1. With the assumption that the band gap X_4-X_1 is given by the two-band approximation, we can estimate \phi_C. Then the wave function within the gap

$$\phi(z) = \exp(ik_1z)\cos(k_xz+\delta), \quad z<0 \quad (21)$$

where $k_x=2\pi/a$ is the real part of $\mathbf{K}$ on the zone boundary, and $k_1$ is the imaginary part of it,

$$k_1^2 = -E-(2\pi/a)^2+[4E(2\pi/a)^2+V_G^2]^{1/2}, \quad (22)$$

where E is measured relative to the bottom of the inner potential well, and $2V_G$ is a gap width. The behavior of $k_1$ is shown in Fig. 15(c). The important idea is that the wave functions are $\alpha \sin(k_xz)$ at $X_4$ and $\alpha \cos(k_xz)$ at $X_1$ for $V_G > 0$, which is the Shockley inversion. Then the phase $\delta$ changes by $\pi/2$ across the gap. With the wave matching condition at $z=0$, $\phi_C$ is given by about $2\delta$. Figure 16 shows the behavior of $\phi_C$ and $\phi_B$ for the (100) direction. Depending on which phase contributes predominantly to
Fig. 16. Energy variation of the phase, and image-potential states for Ag(001)
the total phase change, Echenique divided "barrier-induced image-potential states" and "crystal-induced" gap states. In that sense, the surface state S1 for Ag(100) is a image-potential state. Furthermore, the model predicts that the lateral dispersion of the image-potential states is

\[ E(k_{//}) = E_0 - E_n + \frac{\hbar^2 k_{//}^2}{2m^*}, \]  

where \( m^* \) is the effective mass. Figure 17 shows the comparison between the experimental results and fitting results. The surface state I observed follows the equation 23 very well and \( m^* \) is 1.5 free electron masses from this experiment.

C. Bulk State

B1 and B2 in Fig. 14 are related to interband transitions between two bulk bands. B1 is dispersive and its behavior is like that of nearly-free electrons, i.e., of the empty lattice bands. Around 17 eV there is a very broad, nondispersive peak (B2). According to band calculations there is a very flat band around 17 eV above \( E_F \) which remains flat throughout the \( \Gamma X U L \) plane. Photoemission and thermomodulation experiments also show the existence of such a flat band at 17.5 eV above \( E_F \). The latter measurements indicate, at least for Au, a lifetime for this band
Fig. 17. Final-state energies $E(k)$ obtained along the direction of the surface Brillouin zone of the (001) face of Ag. $S$ represents an image-potential state and $B_1$ is the observed bulk-interband transition. The unshaded area represents gaps of the projected bulk-band structures.
longer than that of the nearly-free electron band just below it. The lower energy resolution of inverse photoemission precludes us from seeing such lifetime effects. This flat band could produce two nondispersive features in the spectrum. One could occur if this band were the initial states for the inverse photoemission. The other is if it were the final states. However we do not see this feature appearing as the initial state in our spectra. This may be explained by the fact that electrons captured in this band decay dominantly by inelastic electron-electron scattering events, i.e., the dipole matrix element for transitions to states 9.8 eV lower in energy is small. (Such final states exist in the band structure.) The background of the inverse photoemission spectrum increases above 7-8 eV, indicating that there is an increase in inelastic decay for states 17-18 eV above the Fermi energy. Peak B2 is associated with the flat band as the final states. To analyze the dispersion of IPES, we should search for the isochromat surface given by

\[ E_i(\mathbf{k}) - E_f(\mathbf{k}) - \hbar \omega = 0 \quad . \quad (24) \]

The search process is illustrated in Fig. 15(b).

Theoretical structure plots were calculated with a free-electron model and with a first-principles band structure, using k-conserving optical transitions to identify the bulk band-derived features. For the case of normal incidence on Ag(001), \( \mathbf{k} \parallel \)}
vanishes so that the transition occurs along the $\Gamma - X$ direction illustrated in Fig. 15(b). At $\hbar \omega = 9.8$ eV (which is the energy selected by the photon detector), there is only one interband transition at $E_g = 0.2$ eV. Away from normal incidence, we have

$$\mathcal{R} = \frac{[2m(E - E_V)/\hbar^2]^{1/2} \sin \theta}{},$$

(25)

where $\theta$ is the angle of electron incidence and $E_V$ is the vacuum level. In calculating the structure plots with the free-electron model, the inner potential was kept constant at 8.5 eV and any perturbation between bands was not considered. This was the simplest band calculation we could consider. The dipole matrix elements vanish for the free-electron model, but with a weak pseudopotential with Fourier coefficients $V_G$ at reciprocal lattice vectors G, the dipole matrix elements do not vanish and can be calculated easily for regions near the zone boundaries, where the transitions are strongest. These occur between bands which were degenerate at the zone boundary. The same formalism can be used for transitions between bands that are associated with different reciprocal lattice vectors, in which case, the dipole matrix elements are much smaller. The allowed final states from the free-electron calculation (without calculating dipole matrix elements see below) are shown in Fig. 18, along with the experimental results. The reciprocal lattice vectors associated with the initial and final states are shown as labels.
Fig. 18. Calculated structure plots for Ag(001). (a) was from the first principles band structure. Matrix elements were not used. Shaded area indicates that several pairs of transitions are possible around those energy. (b) was obtained from free electron bands, and only final states are displayed. The labels are the reciprocal-lattice vectors associated with the initial and final states of k-conserving transitions. Dots on both plots are the experimental results, S1 is a surface derived feature.
This simple calculation gives a fairly good description of the spectra, especially for the structure (B1) near the Fermi energy. Although only one structure is found in the experiments, this simple model predicts many energetically possible transitions. However, only two spectral features are expected to have large oscillator strengths, those labelled (200,000) and (111,111). All others should be weak for reasons stated above. The second of these two transitions was not seen at the angles used, possibly because of large initial state broadening and a larger background when the final state energy is high at the small angles used. It should be easier to find at larger angles, but the small size of our sample precluded working at larger angles. Also the incoming electron can match the components of the plane wave \( \exp(i(R + \vec{G} 200)) \) more effectively for the (100) face than it can match the components of \( \exp(i(R + \vec{G} 111)) \). The incoming electrons in the IXUL plane do not scatter strongly with \( \vec{G} \) -vectors which are associated with parts outside the IXUL plane as observed for other materials and various faces\(^{54,55} \). This effect also leads to an emphasis on the transition labelled (200,000) in Fig. 18a. Although the free-electron model shows some possible inverse photoemission transitions around 17 eV, their dipole matrix elements should be small, as described above. A flat band at this energy is not present in the free-electron model. It results from the crystal potential and a more realistic calculation is needed to describe the structure around 17 eV.
I used the LAPW method with a relativistic self-consistent potential\textsuperscript{68} to calculate the bands up to 30 eV above the Fermi energy. Two energy windows were used to cover this large energy range. Instrumental broadening effects were included by finding all k-conserving transitions within a window of $\pm 0.3$ eV around 9.8 eV. Because the calculation is based on the ground state, but the measurements involve the excited states, the neglected self-energy may be an important factor in comparing experiment with theory. The self-energy gives a lifetime broadening as large as 2 eV around 17 eV above the Fermi energy, at least in the free electron-like bands\textsuperscript{57}. Although it is difficult to assign one-to-one band pairs to this peak because other bands are involved and the self energy is very large, the existence of the nondispersive peak B2 throughout various angles indicates that it is related to that flat band. A high density of states at 17 eV in the 2-dimensional density of states also supports this connection. This high density of states means that no matter where the wave vector of the incident electron lies in the $\Gamma X U L$ plane, there is an initial state because of the large energy broadening of the nearly free-electron bands so far above the Fermi level, and there is a final state at the same wave vector because of the very flat band 17 eV above $E_p$. The peak is strong at 12°.

By treating the initial state as nearly free-electron-like, we can calculate $k_+$ as well as $k_\parallel$. The $k$ point approaches the zone boundary around 12°. The plane wave is perturbed increasingly as
the band approaches the zone boundary so that the energy
distribution of the joint density of states is increased and the
intensity of spectra also can increase if we treat matrix elements
as constant. This flat band has been found in other band
calculations, where it appears at about the same energy in Cu, Ag,
and Au, although it is not very prominent (flat) in Cu. At the
zone center, this band has $f$-character, with $p$-states mixing in
away from the zone center. It is clearly not free-electron like,
and some of its unusual properties are a result of this.

D. Conclusion

I observed the image-potential surface state near vacuum level
and the bulk related state which can be described by the free
electron model. There is also a very nondispersive structure at 17
eV above the Fermi energy in inverse photoemission spectra along $\Gamma - X$. Direct interband transitions are responsible for the
observation of this feature. First-principles band structure
calculations to high energies are needed to show this non-
dispersive feature.
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