

Photoemission and Inverse Photoemission

Purpose of these techniques: to measure the occupied and unoccupied electronic density of states of a sample surface

The resulting spectra can contain both bulk and surface states. However, they can be distinguished by their angular dependence in angle-resolved photoemission.

First, we discuss the physical process for photoemission

1. monochromatic light incident on surface ($E_\gamma = \hbar\omega$)
2. electron excited from an occupied state to an unoccupied state
3. electron propagates towards the surface
4. electron traverses the surface
5. electron is detected at some angle θ

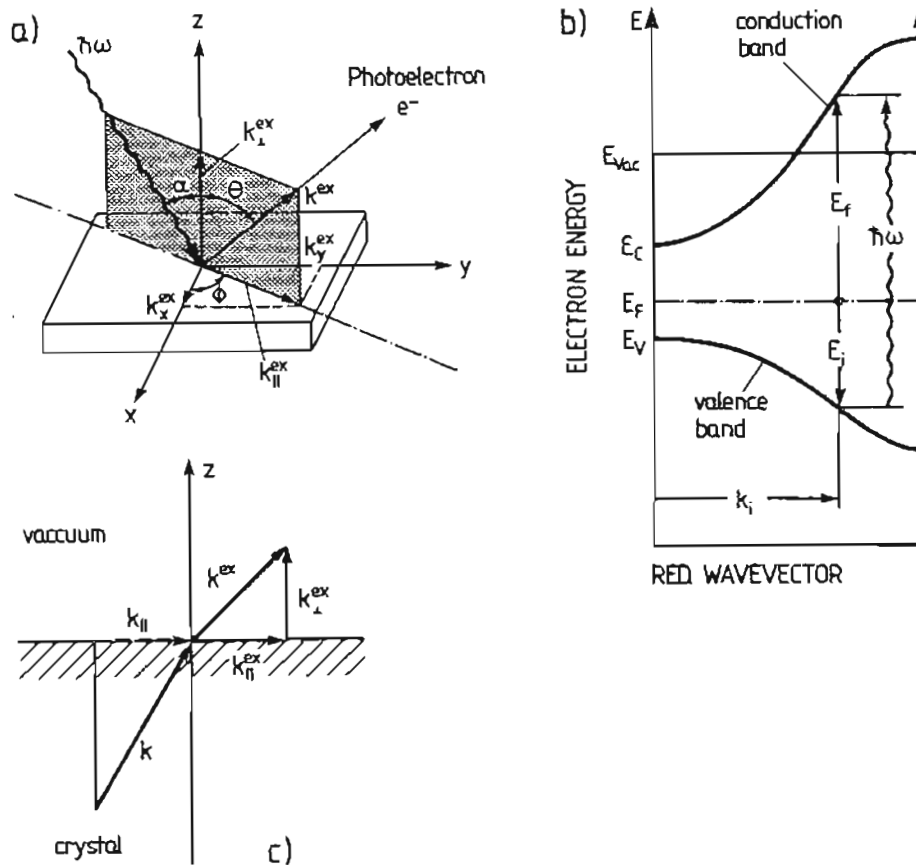


Fig. 6.6a-c. Description of a photoemission experiment. (a) Definition of the angles and wave vectors of the incident photon ($\hbar\omega$) and emitted electron e^- . (b) Representation of the photoexcitation process in the electronic band scheme $E(k)$ of a semiconductor. Only direct transitions with $k_i \simeq k_f$ are taken into account. The energies of the initial state (E_i) and final state (E_f) are referred to the Fermi level E_F . (c) Conservation of the wave vector component $k_{||}$, (parallel to the surface) upon transmission of the emitted electron through the surface

The emission intensity is calculated (in one method called 3-step method) by taking the product of the probabilities of the 3 separate steps:

1. absorption of γ
2. propagation to surface
3. crossing the surface

Lüth develops the 3 probabilities and arrives at the following formula for the observable (external) emission current:

$$I^{ex}(E, \hbar\omega, \vec{k}_{||}^{ex}) = \underbrace{I^{int}(E, \hbar\omega, \vec{k}_{||})}_{\text{absorption}} \underbrace{D(E, \vec{k}_{||})}_{\text{propagation}} \underbrace{T(E, \vec{k}_{||}) \delta(\vec{k}_{||} + \vec{G}_{||} - \vec{k}_{||}^{ex})}_{\text{crossing the surface (transmission through surface)}}$$

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which is proportional to:

$$I^{ex} \propto \underbrace{\sum_{f,i} m_{fi} f(E_i(\vec{k}_{||})) \delta(E_f(\vec{k}_{||}) - E_i(\vec{k}_{||}) - \hbar\omega) \delta(E - E_f(\vec{k}_{||}))}_{\text{absorption}} \times \underbrace{D(E, \vec{k}_{||})}_{\text{propagation}} \times \underbrace{T(E, \vec{k}_{||}) \delta(\vec{k}_{||} + \vec{G}_{||} - \vec{k}_{||}^{ex})}_{\text{transmission}}$$

Of course, the external current is then proportional to

$$m_{fi} = |\langle f, \vec{k}_{||} | \mathcal{H} | i, \vec{k}_{||} \rangle|^2$$

the matrix elements between initial and final states.

Because of the 2-D translational symmetry of the potential (surface potential) parallel to the crystal surface,

\vec{h}_{\parallel} is conserved
upon crossing the surface

But

\vec{h}_{\perp} is not conserved
because of the asymmetry.

Thus we get $\int (\vec{h}_{\parallel} + \vec{G}_{\parallel} - \vec{h}_{\parallel}^{ex})$

$D(E, \vec{h})$ leads to the surface sensitivity, ~~roughly~~

~~roughly~~

Basically, the mean free path is typically very small
 $\sim 5-20 \text{ \AA}$

The Fermi function also appears since the current comes only from the occupied states:

$$f(E_i(\vec{k})) = \frac{1}{e^{(E_i - \mu)/kT} + 1}$$

It is also interesting to note that the electron can be (will be) excited from its initial energy \bar{E}_i to final energy E_f which is in the conduction band of the solid although above the vacuum level ^{and} inside the solid.

Also, the delta function $\delta(E_f - E_i - \hbar\omega)$

This requires the final and initial energy difference $(E_f - \bar{E}_i)$ to equal $E_f = \hbar\omega$

$\delta(E - E_f(\vec{k}))$ requires the electron energy of the internal current to equal the final energy of the electron after the absorption. ~~Also, the energy of the electron after the absorption is measured relative to the vacuum level.~~

What does the experiment measure?

We measure the kinetic energy and external wavevector of the emitted photoelectron.

$$\bar{E}_{kin} \text{ and } \vec{k}_{ext}$$

\vec{k}_{ext} is measured by knowing the angle θ of the emitted electron and knowing \bar{E}_{kin}

$$\begin{aligned}\bar{E}_{kin} &= \bar{E}_f - E_{vac} \\ &= \frac{\hbar^2}{2m} (k_L^{ex^2} + k_{||}^{ex^2})\end{aligned}$$

Energy conservation requires

$$\hbar\omega = \bar{E}_f - E_i = \bar{E}_{kin} + \underbrace{\phi}_{\substack{\text{work} \\ \text{function} \\ = E_{vac} - E_F}} + \underbrace{\bar{E}_B}_{\substack{\text{binding} \\ \text{energy} \\ = \bar{E}_F - E_i}}$$

$$\begin{aligned}&= \bar{E}_f - E_{vac} + E_{vac} - E_F + \bar{E}_F - E_{vac} \\ &= \bar{E}_f - E_i\end{aligned}$$

So, we get

$$E_B = h\nu - E_{kin} - \phi$$

so that by measuring E_{kin} and knowing $h\nu$ and ϕ , we get the binding energy.

The $E_B = E_F - E_i$

Many times you will thus see the spectrum plotted vs. binding energy like

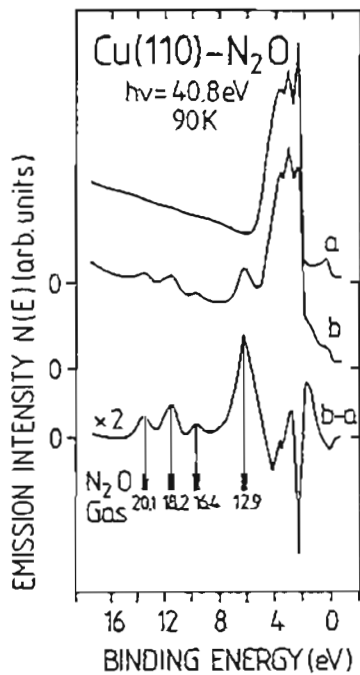


Fig. 6.7. He II UPS spectra of a clean Cu(110) surface at 90 K (a), and after a 1 L exposure to N₂O (b). Marked under the difference curve (b-a), enlarged by a factor of 2, are the vertical ionization energies of gaseous N₂O (referred to vacuum level) [6.10]

Compare the momenta

γ :

From given example,

$$\bar{E} = h\nu = 40.8 \text{ eV} = \frac{hc}{\lambda}$$

$$p = \frac{h}{\lambda} = \frac{\bar{E}}{c}$$

$$\Rightarrow p_{\gamma} = \frac{(40.8 \text{ eV})}{c}$$

$$p = \hbar k \Rightarrow k_{\gamma} = \frac{p}{\hbar} = \frac{40.8 \text{ eV}}{\hbar c}$$

e^{-} :

$$\bar{E}_{\text{kin}} = \hbar\omega - \phi - \bar{E}_B$$

$$\text{for Cu}^{(110)}, \phi = 4.48 \text{ eV}$$

peak of \bar{E}_B about 4 eV ($\bar{E}_B \sim 4 \text{ eV}$ for that peak)

$$\Rightarrow \bar{E}_{\text{kin}} = 40.8 \text{ eV} - 4.48 \text{ eV} - 4 \text{ eV}$$

$$\bar{E}_{\text{kin}} = 32.3 \text{ eV}$$

$$\bar{E}_{\text{kin}} = \frac{p^2}{2m}$$

$$p = \sqrt{2m\bar{E}_{\text{kin}}}$$

$$p = \sqrt{\frac{2(511 \text{ keV})}{c^2} (32.3 \text{ eV})}$$

$$p_e = 5745 \frac{\text{eV}}{c}$$

$$k_e = \frac{p}{\hbar} = 5745 \frac{\text{eV}}{\hbar c}$$

$$k_e \gg k_{\gamma}$$

It may also be that one will plot the kinetic energy
 This will agree with the formula:

$$E_{kin} = h\nu - \phi - E_B$$

Nicely illustrated as follows

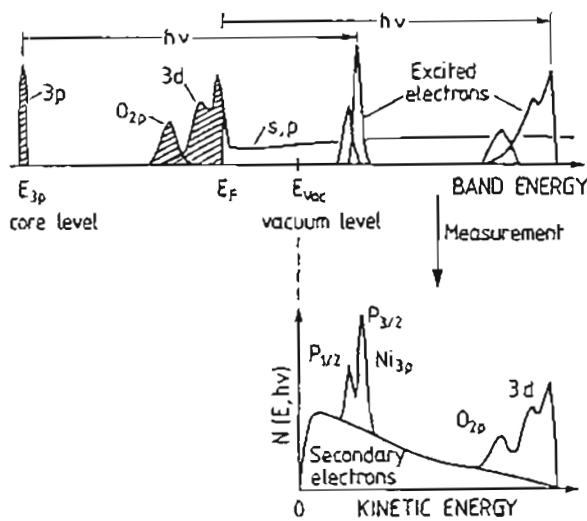


Fig. XI.1. Illustration of the photoemission process for the example of a transition metal surface (e.g., Ni) on which atomic oxygen (O 2p) is adsorbed. Shaded areas show occupied electronic states (up to the Fermi level E_F). Photons incident with energy $h\nu$ cause electrons to be excited into unoccupied quasi-continuous electron states within the crystal. These electrons can leave the crystal and are detected in the measurement as free electrons with a kinetic energy E_{kin} . Electrons that have undergone scattering processes on their way into vacuum are detected at lower energy and form a continuous background of so-called secondary electrons

Angle - Integrated Photoemission

The emission current is integrated over all of the \vec{k} -space

$$\tilde{I}^{\text{ex}}(E, \hbar\omega) \propto \int_{\text{half sphere}} I^{\text{ex}}(E, \hbar\omega, \vec{k}_{\parallel}^{\text{ex}}) d\vec{k}^{\text{ex}}$$

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Then

$$\tilde{I}^{\text{ex}}(E, \hbar\omega) \propto \sum_{f,i} m_{fi} \int d\vec{k} f(E_i(\vec{k})) \delta(E_f(\vec{k}) - E_i(\vec{k}) - \hbar\omega) \delta(E - E_f(\vec{k}))$$

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assuming slowly varying m_{fi} with \vec{k}

Note: as in also the case of non-integrated, the total current depends on ~~both~~ both the initial and final states.

This makes a difference for UPS (ultraviolet PS) and XPS (X-ray PS)

since for X-ray energies, final states are probably quasi-continuous, whereas for UV energies, final states may have a lot of structure.

Determining Bulk and Surface States

For angle-resolved photoemission, we will find the surface state energy to depend on the angle θ and thus on the $k_{||}$ component. This information is used to obtain the dispersion of a surface state. One can also measure at fixed angle θ for various incident photon energies.

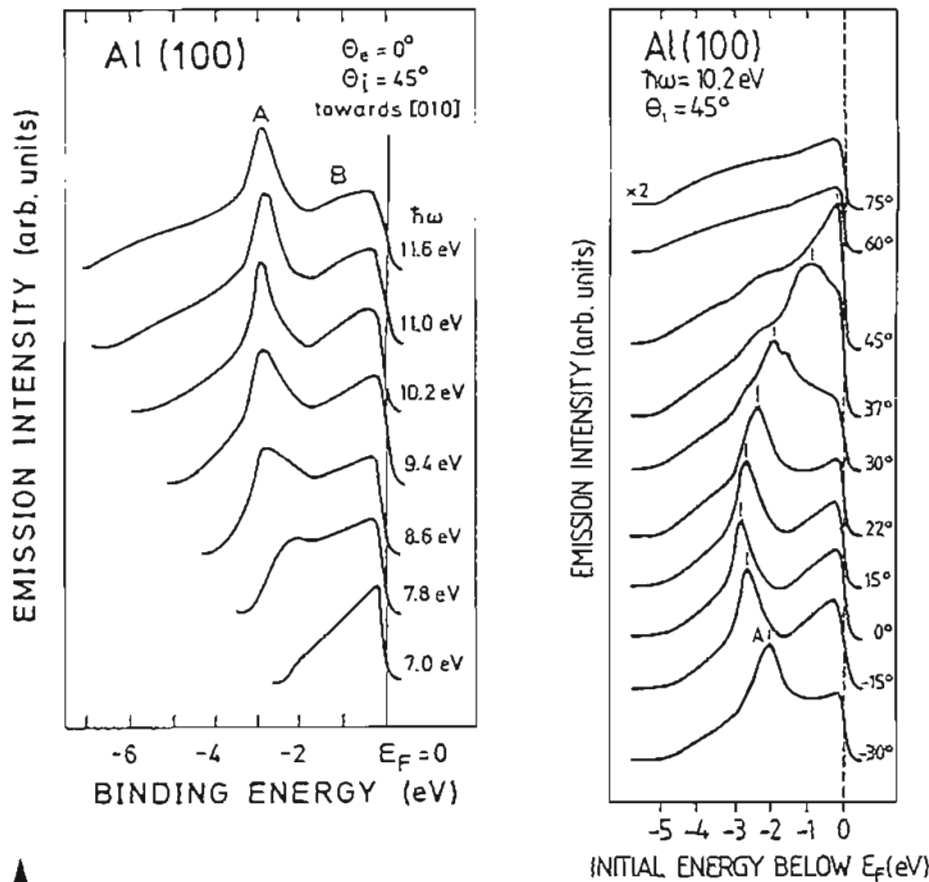


Fig. 6.12. Experimental spectra of photoelectrons emitted normal to the Al(100) surface for photon energies between 7 and 11.6 eV (direction of incidence 45° to the [011] direction) [6.13]

Fig. 6.13. Photoemission spectra from the Al(100) surface with different polar angles in the (011) plane; photon energy $\hbar\omega = 10.2$ eV, (direction of incidence 45° to the [011] direction) [6.13]

The surface state binding energy does not vary with the incident photon energy but does of course vary with the angle θ

$$k_{||}^{ex} = k_{||} = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \sin\theta$$

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Plotting the binding energy vs. $k_{||}$,

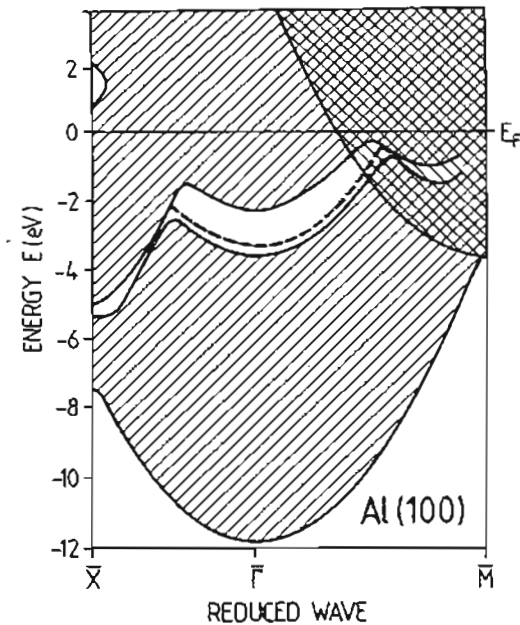


Fig. 6.14. Measured surface state dispersion (broken curve [6.13]) and projected bulk bands for Al(100) (shaded area [6.15]) [6.14]

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Why doesn't the surface state binding energy depend on the incident photon energy $\hbar\omega$? (at $\theta_e = 0^\circ$)

$$E_B = \hbar\omega - \phi - E_{kin}$$

If E_B remains constant, we have

$$\hbar\omega - \phi - E_{kin} = E_B = \text{const.}$$

$$\Rightarrow \hbar\omega - E_{kin} = \text{const.}$$

$$\Rightarrow \Delta\hbar\omega = \Delta E_{kin}$$

\Rightarrow if $\hbar\omega$ increases by 1 eV,
 E_{kin} increases by 1 eV.

$$k_{||}^{ex} = \sqrt{\frac{2m}{\hbar^2} E_{kin}} \sin\theta$$

It is related to the fact that for surface state, there is no k_{\perp} ~~dispersion~~ dispersion (i.e. $k_{\perp} = 0$)

Whereas, for bulk states, t_{\perp} does exist, (also dispersion)
In this case, the ~~energy~~^{bulk} band is expected to vary
with photon energy.