3. Photoemission

In Ultraviolet Photoelectron Spectroscopy (UPS), the sample is irradiated with UV light ($\hbar w$ = 5 to 100 eV) to excite photoelectrons into the vacuum via the photoelectric effect. From an analysis of the kinetic energy and angular distribution of the photoelectrons, information on the electronic structure of the material under investigation can be extracted. Photoemission is the only method allowing the determination of absolute binding energies of electrons in solids. Due to the limited mean free path of the photoelectrons, UPS is a surface sensitive technique.

3.1. Angular resolved photoemission

In this section, some basic information about the experimental technique, the photoexcitation process inside the sample and detection in the electron energy analyzer is given. A schematic drawing of an angular resolved UPS experiment is shown in Fig. 3.1. The important parameters are visualized in the figure.

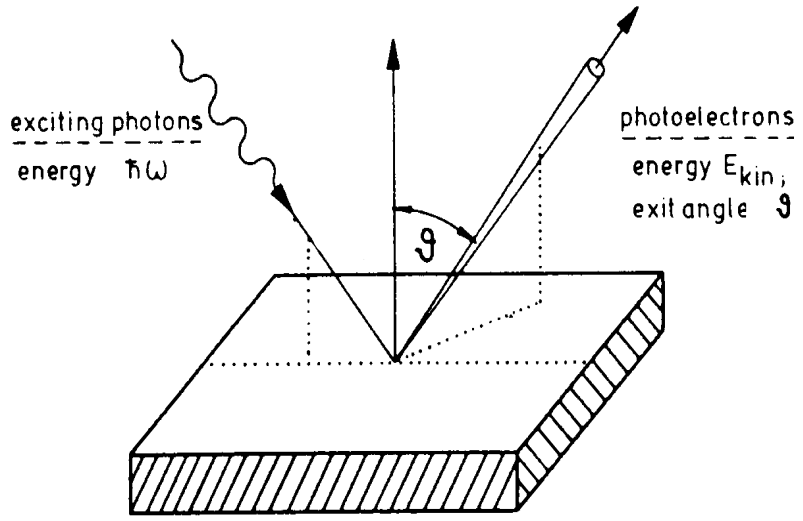

Fig. 3.1 Schematic drawing of the geometry of an angular resolved photoemission experiment. Various parameters that control the photoemission experiment are defined in the drawing, the most important are: hν: the photon energy, ϑ: polar angle of the emitted electrons, and E_{kin}: the kinetic energy of the detected photoelectron (picture taken from [Hüf96]).

Photons with an energy hν irradiate the sample surface and cause emission of electrons into the vacuum where they are analyzed. The quantity that is determined in the experiment is the kinetic energy distribution of the emitted photoelectrons as a function of the electron emission angle. Provided a tunable photon source is available, different modes of photoelectron

spectroscopy can be realized for which either the initial state or the final state is fixed: constant initial state spectroscopy (CIS) or constant final state spectroscopy (CFS) [HGö91].

In the single electron picture, electronic states in a solid are represented by plotting their energy versus the wavevector, commonly referred to as the band structure. In this scheme, the photoexcitation process can be drawn as a transition from states of an occupied band into states of an unoccupied band. A schematic view of photoexcitation in Cu in the Γ-X direction, which is the normal emission direction of a (100) plane, is given in Fig. 3.2.

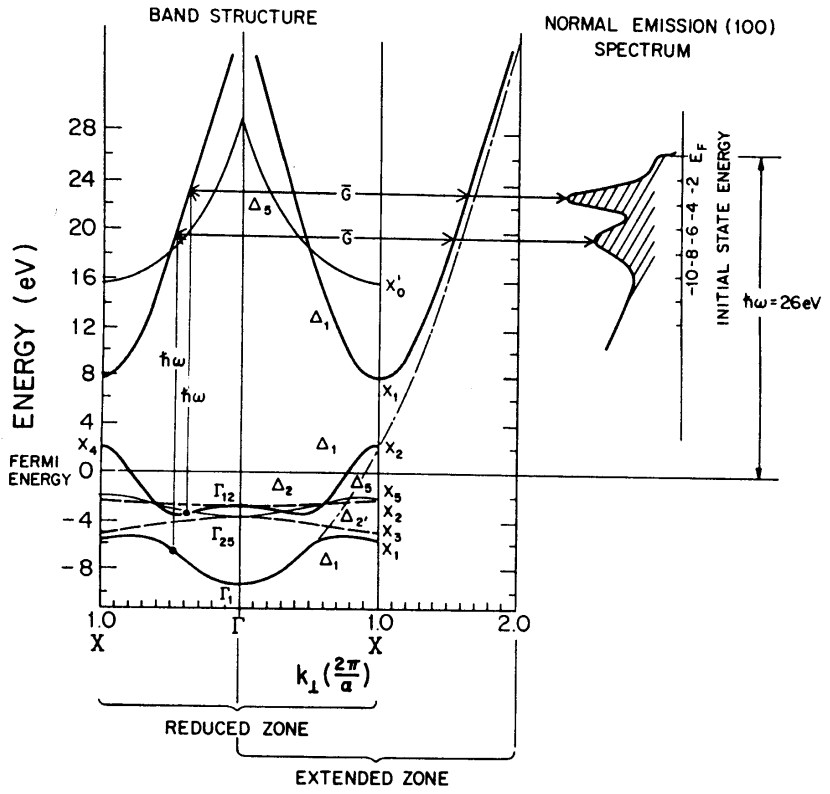

Fig. 3.2 Schematic drawing of the photoemission process in Cu in the reduced and extended zone scheme. The Γ-X direction is normal to the (100) surface (compare to Fig. 3.5). The dot-dashed curve is the free electron band. At the right side of the figure, the hypothetical photoemission intensity after excitation with 26 eV photons is shown (see arrows). The absorption of the photon induces a transition between two energy bands in the crystal. The momentum of the photon is small enough to be neglected, the transition is thus said to be vertical in the reduced zone scheme. Allowed transitions can be identified using dipole selection rules (see chapter 3.2, Tab. 3.1). In normal emission geometry, the Δ_5 final state band does not contribute to photoemission because it has no amplitude in direction of the detector, only final states with Δ_1 symmetry contribute to the signal. Since no excitation from Δ_2 and Δ'_2 (dashed bands in Fig. 3.2) is allowed into the Δ_1 band, these initial states can never be observed in normal emission (picture from [PEb82]).

In the UPS photon energy regime (5 to 100 eV), the momentum of the photon is small compared to the electron momentum and can therefore be neglected. As an example, the momentum of an electron near the Brillouin zone boundary in CaF_2 is about 100 times higher than that of a 21.2 eV photon. Transitions in the reduced zone scheme between the initial state with the wave vector k_i and the final state with (reduced) wave vector k_f are therefore k-conserving or vertical: $k_i = k_f$. However, one has to keep in mind that the transition in the extended zone scheme - which is the more realistic description - involves a reciprocal lattice vector G, i.e. $k_f = k_i + G$ (see Fig 3.2). This representation emphasizes the fact that direct interband optical transitions are indeed processes involving diffraction against the lattice. At the surface, the final state Bloch wave has to match with a free electron wave propagating into the vacuum. The electron will only be able to escape if it has sufficient kinetic energy normal to the surface to overcome the work function barrier. The momentum is not conserved as the electron crosses the surface. One the one hand, the potential step reduces the component of the kinetic energy perpendicular to the surface and, on the other hand, because in the crystal the electron moves in a periodic potential, the dispersion of the electron is not free electron like. During the escape into the vacuum, only the wave vector $k_{\parallel}$ parallel to the surface is conserved: $k_{\parallel(in)} = k_{\parallel(out)}$ (to be exact, $k_{\parallel}$ is conserved modulo a reciprocal bulk lattice vector $G_{\parallel}$ and a reciprocal surface vector $G_{s\parallel}$: $k_{\parallel(in)} = k_{\parallel(out)} + G_{\parallel} + G_{s\parallel}$). The perpendicular component of the wavevector inside the solid remains undetermined by the experiment, unless more involved methods are applied, for example the energy coincidence method that compares spectra from two different crystal faces [Hüf96].

Several models have been proposed to treat the photoemission process theoretically. A phenomenological description that splits the process into three steps has been developed by Berglund and Spicer [BSp64] in 1964. In this approach, optical excitation between two Bloch states, transport of the electron to the surface, and escape of the electron through the surface into the vacuum are treated separately. In more recent models, photoemission is described as a one step process [Mah70]. Excitation occurs between the initial one-electron Bloch state into a so called "time reversed LEED state" that is free electron like in vacuum and decays inside the crystal. The two concepts are illustrated in Fig. 3.3.

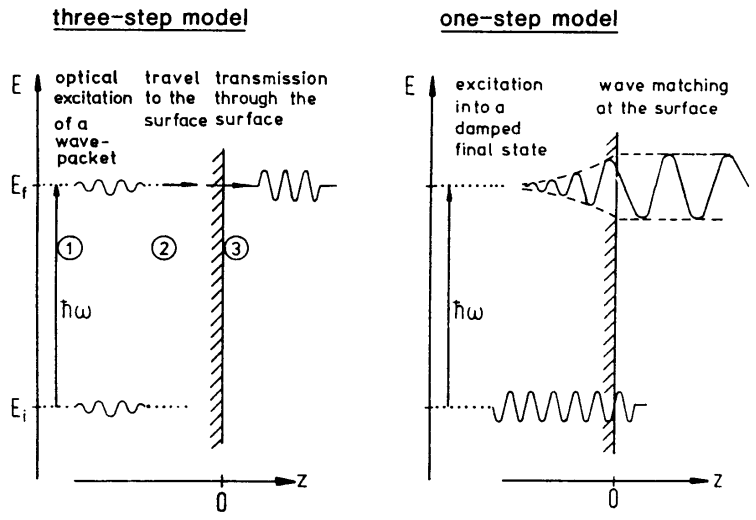

Fig. 3.3 Illustration of the three step and one step model [Hüf96]. The steps of the three step model are: 1. excitation of the electron to a Bloch final state inside the crystal, 2. transport of the electron to the surface, 3. escape of the electron into the vacuum. In the one step model, the electron is excited from the Bloch initial state into a state that is composed of a free propagating part outside the crystal and a damped part inside the crystal, the damping taking account of the limited mean free path of the photoelectrons (picture taken from [Hüf96]).

The three step model is the most commonly used in the interpretation of photoemission data. Photoemission theories are discussed for example in the book of S. Hüfner [Hüf96] and the review article of Plummer and Eberhardt [PEb82].

Photoelectrons emitted from the sample are recorded with an electrostatical energy analyzer. In Fig. 3.4, a survey of the various potentials involved in photoelectron spectroscopy is given

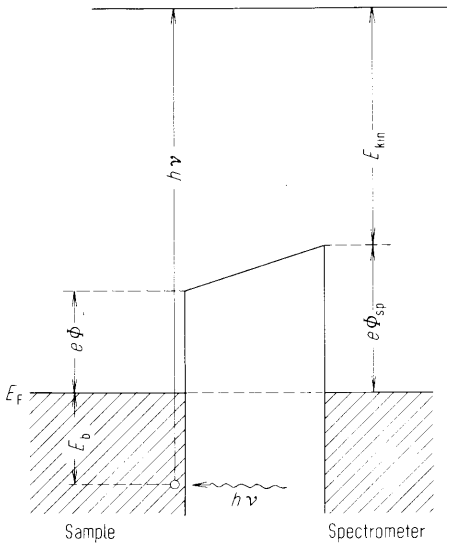

Fig. 3.4 Energy level diagram for photoelectron spectroscopy from an conducting sample. The Fermi energies of sample and spectrometer coincide as soon as they are in electrical contact (picture from [EKü85]).

for UPS from a conducting solid. Both metallic sample and electrostatical energy analyzer are conductive, thus when both are in electrical contact, the Fermi energies coincide. It can be concluded from the figure that, for given analyzer and photon energy, the Fermi step in the UPS spectrum appears for all conductive samples at the same kinetic energy, independent from the work function of the sample.

3.2. Dipole selection rules

Dipole selection rules can be used to identify possible transitions between electron energy bands. Bands in the crystal exhibit distinct symmetry properties, which a-priori rule out the contribution of specific bands in the photoemission spectrum. A compilation of dipole selection rules for bcc and fcc lattices was given by Eberhardt and Himpsel [EHi80]. The fcc Brillouin zone with the high symmetry lines indicated is shown in Fig. 3.5.

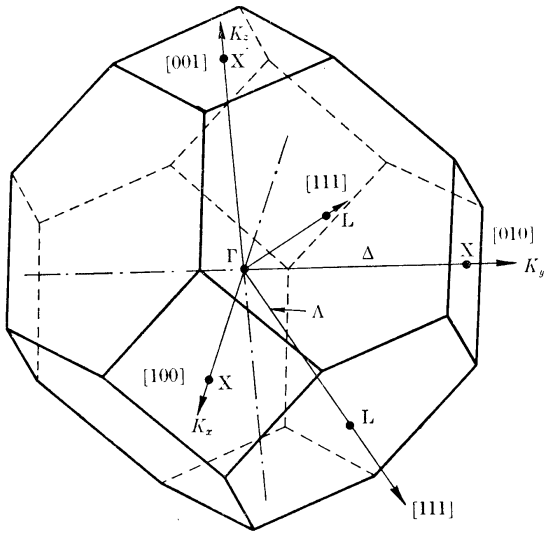

Fig. 3.5 Bulk Brillouin zone for the face centered cubic (fcc) lattice. Several high-symmetry lines are indicated in the figure. The Γ-L direction is the normal emission direction when investigating (111) faces.

Apart from not being dipole allowed, the contribution of bands to the photoemission signal can be prevented by a suitable choice of the electron collection geometry of the experiment. In normal photoemission along Δ (normal to (100) faces), Σ (normal to (110) faces), or Λ (normal to (111) faces) (see Fig. 3.5), the final state has to be totally symmetric, i.e. Δ_1, Σ_1, or Λ_1. It can thus be seen that the normal emission recording geometry simplifies the process of data analysis.

As an example, allowed transitions corresponding to emission from an (100) face (compare example of photoexcitation in copper shown in Fig. 3.2.) are given in Tab. 3.1.

	$\mathbf{D_1}$	$\mathbf{D_{1'}}$	$\mathbf{D_2}$	$\mathbf{D_{2'}}$	$\mathbf{D_5}$
$\mathbf{D_1}$	+				0
$\mathbf{D_{1'}}$		+			0
$\mathbf{D_2}$			+		0
$\mathbf{D_{2'}}$				+	0
$\mathbf{D_5}$	0	0	0	0	+

Tab. 3.1 Allowed dipole transitions at Δ. (+) is for A parallel Δ, (0) is for A normal Δ.

From table 3.1, it can be concluded that a transition from the Δ_1 band to the Δ_5 band is possible, however, in the normal emission geometry (compare Fig. 3.2) the Δ_5 band does not contribute to photoexcitation because it has no amplitude in the direction of the detector.
For the interpretation of the normal emission spectra from CaF_2, the allowed dipole transitions at the Λ-direction, which is parallel to the (111) surface normal, are given in table 3.2.

	$\mathbf{L_1}$	$\mathbf{L_2}$	$\mathbf{L_3}$
$\mathbf{L_1}$	+		0
$\mathbf{L_2}$		+	0
$\mathbf{L_3}$	0	0	+0

Tab. 3.2 Allowed dipole transitions at Λ. (+) is for A parallel Λ, (0) is for A normal Λ.

Similar to the example given above, for the (111) surface, the Λ_1 band is the only detectable final state band in normal emission.