On the surface of a material there can exist localised electron states, that are completely split off from bulk states. The two-dimensional band structure of these “surface states” can be fully characterised by means of angle resolved photoemission. The purpose of the present experiment is to map the dispersion of such a state on Cu (100).

**Photoelectron Spectroscopy**

When light is incident on a surface, an outflow of electrons can be observed. Einstein explained the phenomenon in terms of photons, which are fully absorbed in the interaction with electrons. The photoelectron spectroscopy technique has developed during the last 30-40 years into one of the most powerful tools for characterization of the electronic structure of matter and there are numerous review articles and books written on the subject, see e.g. [1].

Two important technological steps can be distinguished, that have promoted use of photoemission as an analytical tool: development of ultrahigh vacuum equipment in the early 1960’s, and construction of synchrotron radiation sources in the 1970’s.

Einstein's energy relation describing the energy balance in the photoelectric process is

\[ E_{\text{kin}} = h\omega - E_{\text{B}} - \phi_W \]

where \( E_{\text{kin}} \) is the kinetic energy of the emitted electron, \( h\omega \) is the photon energy, \( E_{\text{B}} \) is the electron binding energy (relative Fermi level), and \( \phi_W \) is the work function. Fig. 1 shows a pictorial version of this relation, and Fig. 2 shows schematically an experimental set-up used for photoemission studies.

**Fig. 1** Energy level diagram for the photoelectron process. \( E_F \) is the Fermi level and \( E_{\text{vac}} \) denotes the vacuum level.

**Fig. 2** The experimental setup for ARPES, XPS and LEED measurements. The electron energy analyser in this system (VG ADES400) is a 150° spherical sector analyser, rotatable around the sample.
The set-up in Fig. 2 is a typical home-laboratory system, using a noble gas discharge lamp for production of monochromatic UV radiation and an Al K-line X-ray source for excitation of deeper core levels. Nowadays most advanced photoemission experiments are carried out at synchrotron radiation laboratories, for example MAX-lab in Lund. The advantage of using a synchrotron-type source is that it provides a continuous spectrum of polarized radiation. This allows tuning the photon energy, which is a prerequisite for detailed studies of energy bands in single crystals, and characterization of their symmetry properties.

**Theoretical descriptions**

Although photoemission should be considered as a one-step quantum mechanical process, the semiclassical description in terms of three independent consecutive events has proven to be satisfactory in most situations: (1) the optical excitation of the electron in the interior of the crystal; (2) transport of the electron to the surface; and (3) transmission of the electron through the surface into vacuum.

**Step one: Excitation of the electron**

In the first step, a photon of energy $h\omega$ penetrates into the crystal and is absorbed by an electron in the initial state $\Psi_i(k_i)$ with energy $E_i$ into an excited (final) state $\Psi_f(k_f)$ with energy $E_f$. In a first approximation ("sudden approximation") $\Psi_i$ as well as $\Psi_f$ can be taken as the eigenfunctions of the ground state Hamiltonian $H_0$. In the so-called dipole approximation the differential cross section is found to be:

$$\frac{d\sigma}{d\Omega} = \left| \langle \Psi_i | p | \Psi_f \rangle \cdot A_0 \right|^2 \delta(E_f - E_i - h\omega)$$

(2)

where $A_0$ is the amplitude of the vector potential describing the photon. Expression (2) is strictly valid only for negligible $\nabla \cdot A_0$, which is not necessarily true at a surface. However, for photon energies well above the plasma frequency the effects an inhomogeneous vector potential are in general relatively small, and the cross-section is well described by (2) also in the surface region.

**Step two: Transport to the surface**

When the electrons travel through the solid they are scattered. The primary mechanism that reduces the number of unscattered photoexcited electrons reaching the surface is electron-electron interaction. The inelastically scattered electrons contribute to the background of the energy distribution spectrum. Electrons, scattered elastically by the periodic atom lattice have their momentum altered by a reciprocal lattice vector $g$.

**Step three: Escape into vacuum**

Finally, if the final state energy is large enough, and in the absence of surface irregularities, the electron escapes through the surface barrier ($W$) into the vacuum under conservation of crystal momentum parallel to the surface. Energy and momentum conservation in the solid result in

$$E = E_f - W = E_i + h\omega - W$$

(3)

$$k_f = k_0 + g + q_{\text{photon}} = k_i + g$$

(4)
where $E$ is the electron energy outside the crystal and $g$ is a reciprocal lattice vector. The momentum of the photon can usually be neglected in UPS experiments using low photon energies, $h\omega < 50 \text{eV}$. In a reduced zone scheme we thus have so-called vertical transitions, $k_i = k_f$.

Translational invariance in the plane of the surface guarantees that $k_{\parallel\text{outside}} = k_{\parallel\text{inside}}$. The perpendicular component of the photoelectron momentum, on the other hand, bears no particular relationship to $k_{\perp}$ of the initial band state. Implementation of the $k_{\parallel}$ conservation is the basis for band-structure mapping of single crystals by angle resolved photoemission [3]. For an electron in vacuum $k_{\parallel}$ is given by the formula $k_{\parallel} = 0.5128 \cdot \sin(\Theta) \cdot \sqrt{E}$ where $\Theta$ is the angle of emission.

The light source in our equipment is a resonance lamp operating with He or Ne, giving a photon energy of 21.2 or 16.8 eV. Emitted photoelectrons have thus typical energies of 10-15 eV so by changing the emission angle $\Theta$, we can sample initial states with $k_{\parallel}$ in the range 0-2 Å$^{-1}$ corresponding to the dimension of the Brillouin zone (BZ).

**Experiment.**

A single crystal of copper, with the surface cut in the (100) plane, is mounted in the vacuum chamber. The task is to study an electronic surface state that exist in a region of the reciprocal space where no states are allowed in the bulk. Due to the extremely short mean free propagation path of excited electrons, the surface has to be atomically clean and well ordered during the experiment. This is achieved by bombarding the sample with argon ions to remove a few atomic layers of contaminants and copper from the surface. After the cleaning we have a structurally disordered surface that has to be heated to 400 C to restore the crystalline order.

![Fig 3. Bulk and surface Brillouin zone of fcc copper](image)

A LEED (low energy electron diffraction) equipment in the vacuum chamber is used to monitor the order as well as the orientation of the copper crystal. The bulk and surface BZ of Cu(100) is shown in fig. 3 with the conventional notations for high symmetry points. Points on the $\Gamma$–X lines in reciprocal space represent $k$-vectors with [100]-directions in real space. The points X on the zone boundary are projected at points $\bar{M}$ in the surface BZ. If the band structure is projected on the surface plane we obtain a map of energies for occupied states as a function of $k_{\parallel}$. In fig. 4 such a map for Cu(100) is shown for the region around $\bar{M}$ with $k_{\parallel}$ along $\bar{\Gamma}$–$\bar{M}$. We can observe a “pocket” without allowed bulk states close to $\bar{M}$, from the Fermi level down to the Cu 3d bands at $\approx 2 \text{eV}$. In this region surface specific states cannot mix with bulk states, and the energy dispersion of these states depends only on $k_{\parallel}$. By measur-
In order to find the surface state peak in the photoemission spectrometer we have to use the LEED system. The first order LEED diffraction spots are due to scattering by surface reciprocal lattice vectors in the directions $\Gamma - \bar{X}$. The copper crystal must first be rotated azimuthally until $\Gamma - \bar{M}$ is in the horizontal plane where our electron spectrometer is positioned. Secondly we have to calculate the approximate angle of emission for photo-electrons from the surface state, at the photon energy used.

**Preparation for the laboratory work:**

1. Make a sketch of the diffraction pattern from a (100) surface of a fcc crystal.
2. Draw a picture of the surface BZ of Cu(100) and calculate its dimensions.
3. Calculate the emission angle for states at 2eV binding energy (relative Fermi level), located at the $\bar{M}$ point of Cu. Assume a photon energy of 21.2 eV.

References: