Ma4: X-ray photoelectron spectroscopy (XPS)

Contents

1. Overview on the topic and summary of the objectives

X-ray photoelectron spectroscopy (XPS) is a nondestructive method for studying the electronic structure of atoms, molecules, and solids. Originally XPS was used for the spectroscopy of atoms and molecules in the gas phase exciting with monochromatic ultraviolet light (He I: 21.2 eV, He II: 40.8 eV) and later for spectroscopic investigations of solids by excitation with soft X-rays (Al-K_α: 1486.7 eV, Mg-K_α: 1253.6 eV) [1]. The latter method was developed by Kai Siegbahn (Nobel Prize in Physics 1981) and was named ESCA (electron spectroscopy for chemical analysis). For XPS monochromatic photon radiation (Al-K_α, Mg-K_α, He I, He II, synchrotron radiation or laser light) is used to detach electrons from atoms, molecules or solids. Momentum and energy of the photoelectrons give direct information on the electronic structure of matter, from which they were excited. With XPS it is possible measure the shell structure fo atoms and the electronic band structure of solids in a direct manner. The latter requires that in addition to the energy of the photoelectron the emission direction (momentum) relative to a single crystalline solid is measured (so-called ARUPS method: angle-resolved ultraviolet photoelectron spectroscopy). For XPS in condensed matter one must note that the method is very surface sensitive, because only photoelectron from a thin surface layer are emitted lossless. These so-called escape depth λ varies from 2 to 20 Å, depending on the kinetic energy (E_{kin}) of the photoelectrons. λ can be approximated with the the help of the so-called universal curve (see Section 2.3), which has a minimum of about 2 Å at $E_{kin} \cong 40eV$ (largest surface sensitivity).

In this experiment you have the possibility to go deep in to the details of the XPS technology and the physics behind.

The technical basis comprises:
— generation of X rays
— fundamentals of UHV technology
— detection of electrons, monochromatization of electrons
— sample preparation, for example by deposition of thin films of samarium (Sm) and/or dosing of O_2
— computer control of the measurement.

2. Theoretical Fundamentals

The energy of an incident photon ($h\nu$) is transferred to a bound electron. If the energy of the photon is greater than the binding energy of the electron and the electron has enough energy to overcome the **work function (Φ)** of the solid, it can leave the solid (fig. 1).
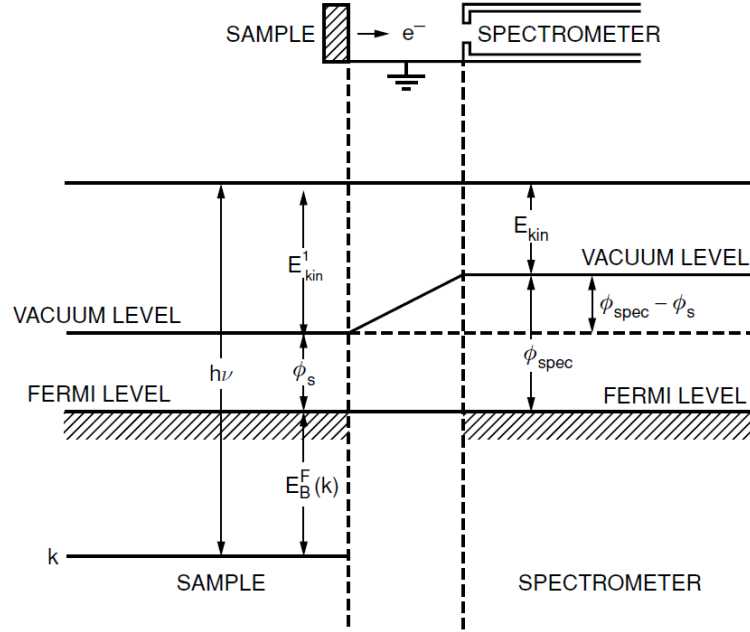
Figure 1: Schematic representation of the photoemission from[13]

Due to the emission of the electron, the inner shell of the atom (A) is ionized. The energy conservation requires:

$$E(A) + hv = E(A^*) + E_{kin} + \Phi$$

$$E_{kin} = hv - [E(A^*) - E(A)] - \Phi = hv - E_B - \Phi \qquad (1)$$

where E_B is the **binding energy** relative to the **Fermi level** E_F and E_{kin} is the kinetic energy of the photoelectron (relative to the vacuum level E_V). The **photoelectron** spectrum is given by the kinetic energy distribution of the photoelectron measured with an **electron analyzer**. For a known photon energy (hν) the binding energy can be determinate for all core electrons with $E_B < hν - \Phi$ see eq. 1.

2.1 Characteristic excitation processes in solids

Figure 2 elucidates the characteristic excitation processes in solids by means of an overview XPS spectrum:

a)   emission from core levels
b)   auger processes
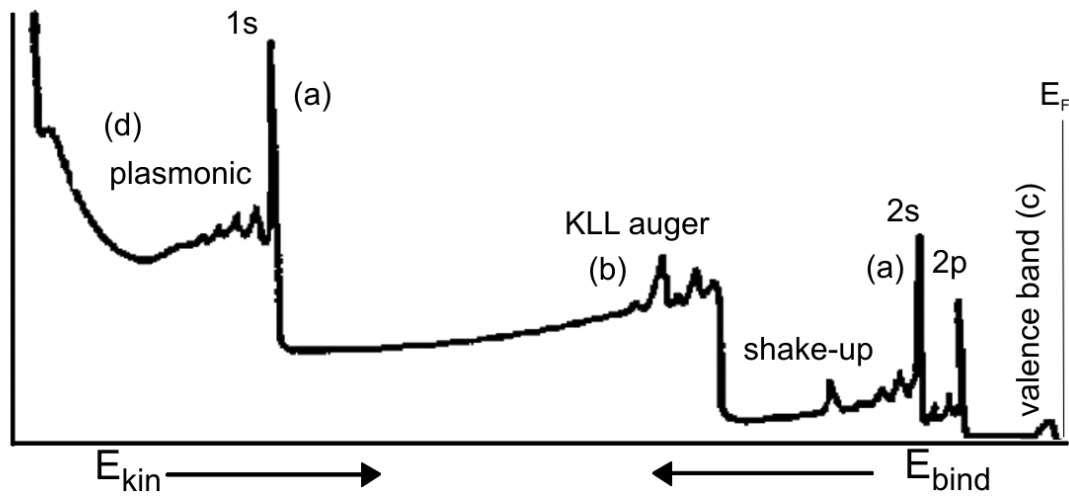c)   emission from the valence band

Figure 2: A typical XPS overview spectrum of a solid

d)   secondary electron excitation and energy losses by inelastic scattering of the electrons before they escape from the surface.

Furthermore, peaks in defined distances to a Photoemission lines are observed, such as Shake-up lines from two electron processes. In such an emission process the excited electron stimulates a second electron from a higher shell (mostly from valence band). For metals satellite peaks are observed in the spectra originating from plasmon excitation, i.e. collective oscillations of conduction electrons. For further information see [2, 3, 4].

2.2 Linewidth in photoemission

There are several contributions to the line width of a photoemission line: The lifetime width of the final state, the width of the exciting X-ray line, the energy resolution of the electron analyzer, and thermal spreading by interaction with phonons. The width of the Mg-K_α X-ray line in our setup is <1 eV (see section 3.2) and the energy resolution of the electron analyzer (at $E_{kin} \approx 1000$ eV) is also of about 1 eV (see section 3.3).

2.3 Surface sensitivity

Electron spectroscopic methods allow surface sensitive measurements down to one monolayer. An important parameter to describe the surface sensitivity is the **mean escape depth (λ)**, which is identical to the mean free path of a photoelectron in a solid. The so-called universal curve in figure 3 shows λ as function of E_{kin}. It can be seen that XPS is very surface sensitive at electron
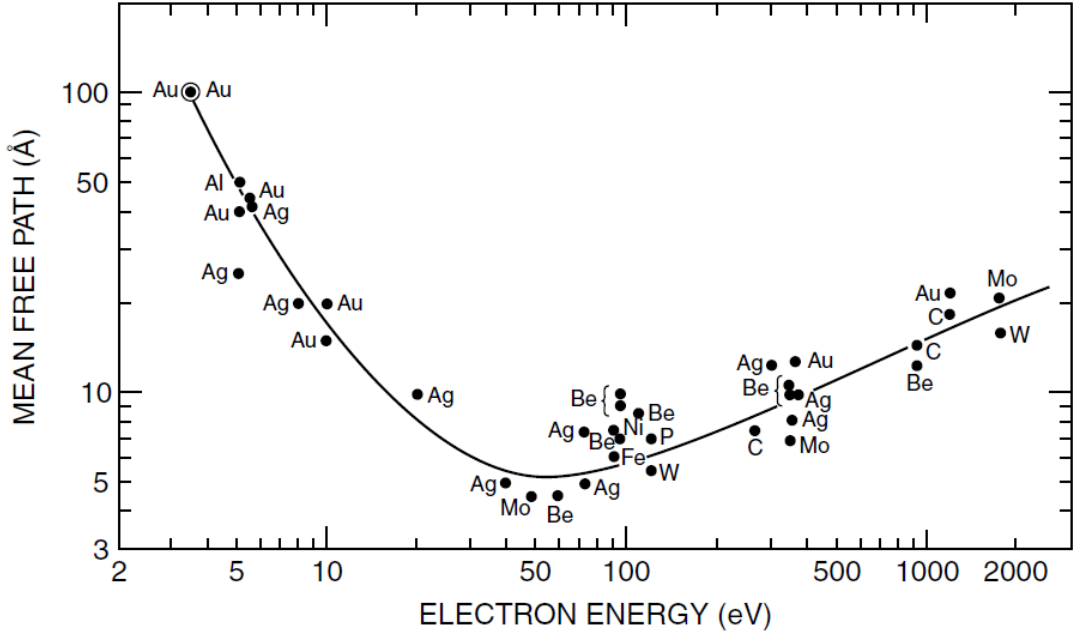
Figure 3: Universal curve of escape depth as a function of E_{kin} from [14].

energies in the range of $20eV < E_{kin} < 100eV$. In this experiment, we can vary the kinetic energy of the photoelectrons by switching the anode of the X-ray tube between Mg and Al.

2.4 Binding energy

The binding energy E_B depends on different terms:

$$E_B = E_B(atom) + \Delta E_{chem} + \Delta E_{Mad} + \Delta E_{rel} \qquad (2)$$

In equation (2) the **chemical shift** (ΔE_{chem}) (see fig 4) reflects the influence of the chemical bonds with neighboring atoms. The **Madelung constant** (ΔE_{Mad}) describes the electrostatic energy of the lattice in the solid. The **relaxation effects** (ΔE_{rel}) describe many-body effects in the 1-hole final state of the investigated many-body object. In addition, multiplet structures can occur due to following effects:

— **spin-orbit coupling:** In this case the coupling within the same Orbital state. The spin s of an electron interacts with its orbital moment l. This is described by the Hamiltonian:
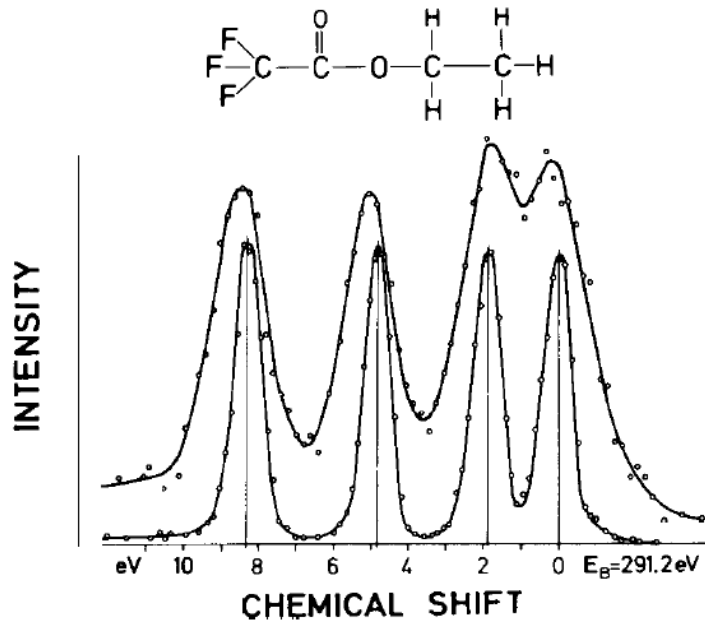
$$H_{sl=}\boldsymbol{a}s \cdot l$$

Figure 4: The ESCA shifts of the Cls in ethyl trifluoroacetate. Upper spectrum without and lower with X-ray monochromatization from [15, 16].

The emission line of an electron shell that is fully occupied in the ground state spliting into a doublet with $(l + \frac{1}{2})$ and $(l - \frac{1}{2})$. Of course, electrons in the s state a not affected because of thier orbital angular momentum $l = 0$.

— **magnetic spin-spin exchange splitting:** Full inner s-shells are occupied with a spin-up electron and one spin-down electron. Normally, these two spins are equal and therefore have the same energy and wave function. Abragam and Pryce found in 1951 that the exchange coupling between a full s shell and the magnetic spin moment of a partially filled shell, can cause an energy splitting of the s shell [5]. For the first time this magnetic exchange splitting was observed by Fadley et al. [6]. In this experiment, the effect was measured on the 4s electrons of samarium [7].

3 Experimental setup

The experimental setup consists of an UHV chamber (fig. 5), in which, among other things, sample holder is ingerted with the test materials:
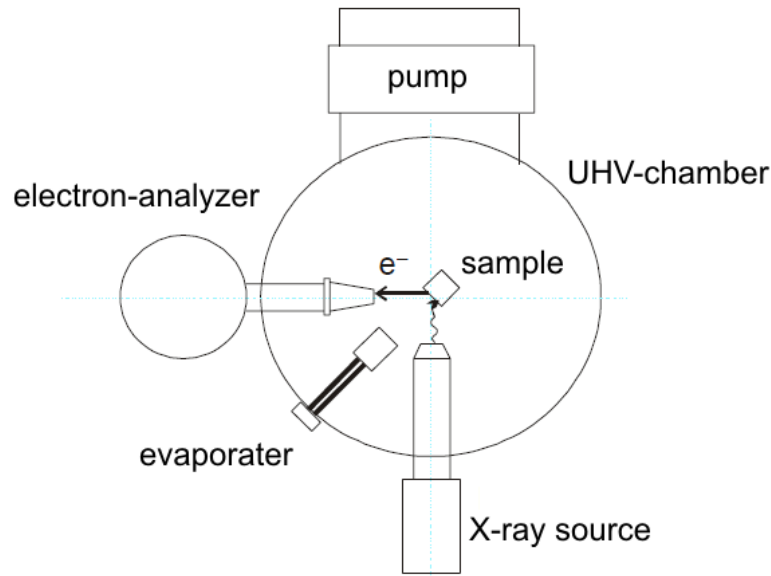— silver sheet
— 2x steel sheet for evaporation of Sm

Figure 5: Scheme of the UHV chamber with a photo emission equipment

— 10 DM coin

3.1 Vacuum System

The UHV system of the experiment is based on a turbo molecular pump with an upstream rotary vane pump. The turbo molecular pump works very efficiently for heavy gases. Light gases, mainly H_2, will be pumped slowly because of high particle speeds. After some time the turbopump reaches a final pressure of about 10^{-9} mbar. As a residual gas in the recipient remains mainly water, that sticks on the steel walls due to its dipole structure. Therefore, the chamber is baked out under UHV conditions for some hours up to days. After cooling a final pressure down to 10^{-11} mbar can be reached.

3.2 X-ray source

The X-ray source (fig. 6a) consists of a cathode (filament), which emits thermal electrons through heating (usual emission current of about 30 mA), and an anode to which the electrons are accelerated by appling a high voltage of typically 9 kV to 12 kV. The construction of the X-ray source allows to choose between Mg and Al as the material of the anode, each with a characteristic emission spectrum (fig. 6b,6c). This spectrum includes bremsstrahlung and characteristic radiation.
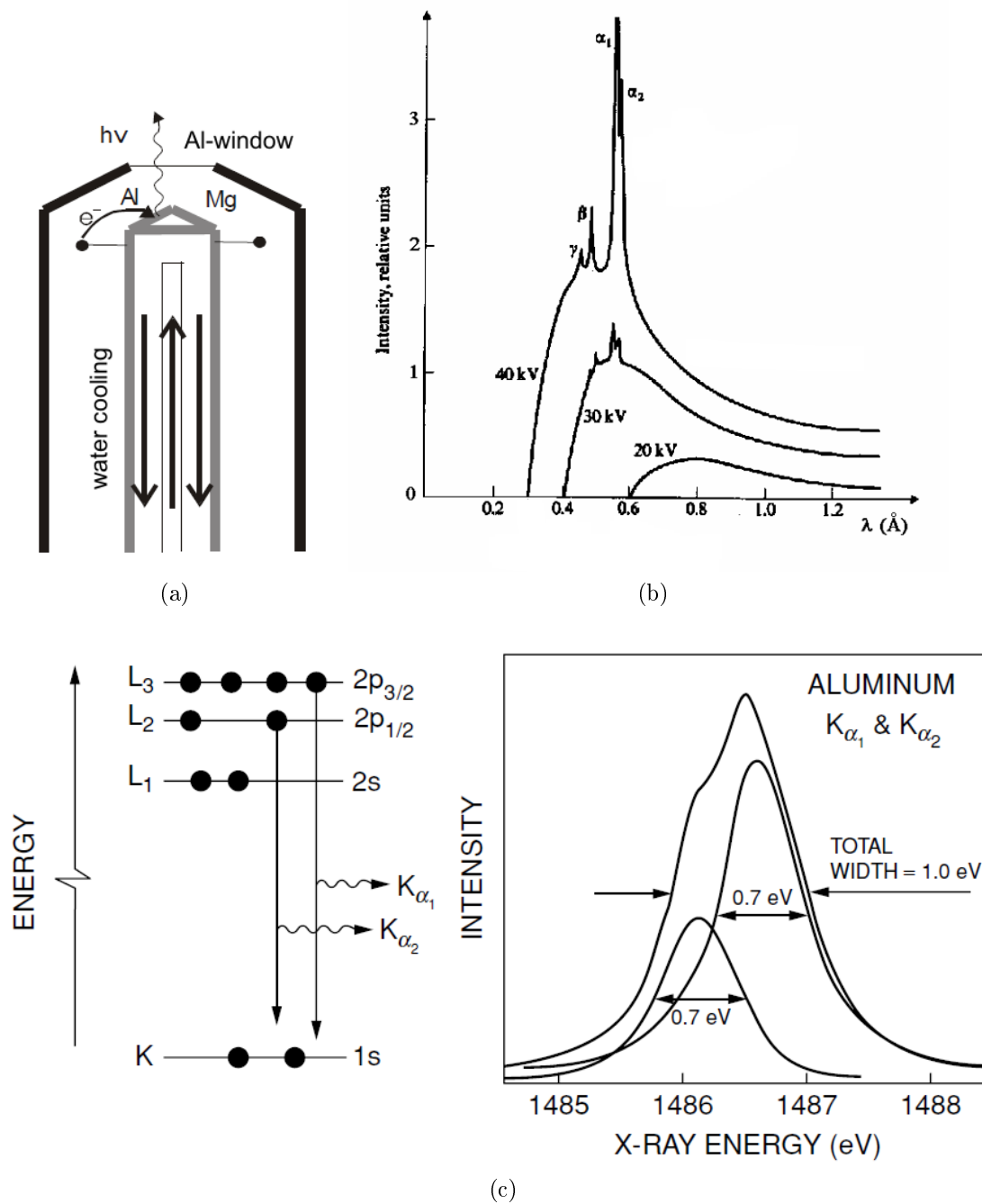
(a)

(b)

(c)

Figure 6: a) Schematic structure of the used double-anode X-ray source b) typical emmision spectra of X-Ray source with Cu anode c) characteristic radiation of Al [13].
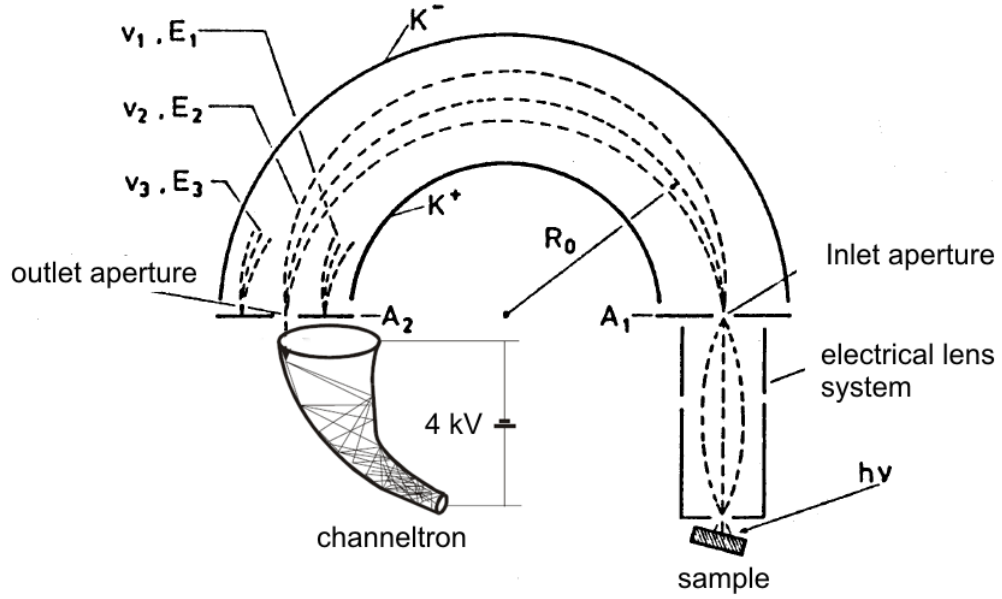
Figure 7: Schematic design of a hemispherical analyzer with channeltron [4].

The short-wave radiation of the bremsstrahlung will be largely absorbed by an approximately 1 micron thick Al window.

3.3 Electron energy analyzer

The analyzer measures the kinetic energy of the photoelectrons by a hemispherical capacitor. It consists of an electrical lens system and two metallic hemispheres, see fig.7. One crucial parameter of such a setup is the pass energy E_{pas}. It have influence on the resolution and the background noise. The highest contribution to the noise in the spectrum stems from electrons excited by **secondary processes** which have low kinetic energy. To reduce the background we select out the electrons with low kinetic energy by applying a pass voltage. This can be realized in many ways for example: slowing down the electrons before they enter the electrical lens. Such that only electrons with $E_{kin} > E_{pas}$ can pass. In our setup the selection is realized through a voltage difference $(K^+ - K^-)$ between the hemispherical plates see fig 7[3]. In this experiment a channeltron is used as a detector consisting of a glass tube which is covered with a conducting material as high electrical resistance. This works on the principle of a secondary electron multiplier. The multiplication level is typically 10^6 to 10^8 With the corresponding electronics the detector amplifies pulses and recorded them.

3.4 Evaporater

The Sm evaporator is firmly installed on an electrical feedthrough the chamber. It consist of a tantalum crucible (high melting point) that contains the samarium and a filament which is wrapped around he cricible (fig. 8). The filament can be heated by a current and heats up the crucible.

3.5 Dosing

One of the exercises is to observe the chemical shift of the Sm surface component. For this task a bottle with oxygen O_2 (approx. pressure 12 Bar) is connected to the chamber trough a leaking valve. This setup allows to dose the oxygen in defined quantities. The unit for the dose is Langmuir L [8]. In case that the sticking coefficient is 1, 1L corresponds to surface which is covered with one monolayer of the adsorbate.

Figure 8: Evaporater

$$1L = 1torr \cdot 1\mu s = 1.33 \cdot 10^{-6} mbar \cdot s$$

4 Exercises

With this setup you have the possibility to go really deep in the physics. In principle its possible to compile and adapt the exercises to your interests together with the tutor (for this contact the tutor one weak in advance). The main topic of the experiment is to investigate and explain the core levels ans the band structure of different materials. Alternatively select 4 of the exercises listed below (one of them must be a "long" exercise)

4.1 Commissioning of the apparatus

Turn on the electronics of the analyzer directly after you enter the room. They need at least half an hour to warm up and to run stable. Turn on the X-ray
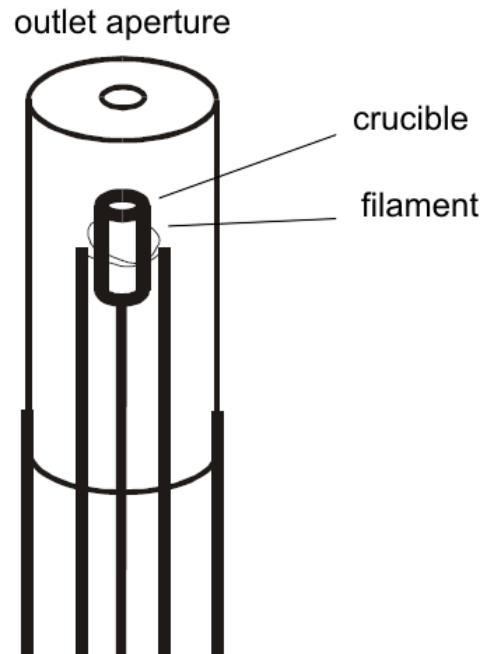
source. Make sure that a high voltage of 12 kV is not exceeded, otherwise it comes to sparkovers in the X-ray tube. More detailed instructions are at the place. The measurement program and communication between the computer and analyzer electronics will be explained to you by the tutor.

4.2 Overview spectrum of a silver sample (midle)

— Turn the sample holder such that the Ag metal sheet is in the focus of the analyzer. The optimum setting is an empirical value and will be given to you by the tutor.
— Set a pass energy to $E_{pas} = 50$ eV, and take an overview spectrum of silver (E_{kin} = 100 eV - 1300 eV) with the Al- and Mg- anode, roughly locate the Fermi level and identify the emission peaks. Make sure that the binding energies are given relative to the Fermi level.
— How can you distinguish between Auger- and photoemission- electron peaks?
— What can you say about the X-ray energy?
— What limits the resolution of the full details of the peak structure?

4.3 Spectra of Sm metal (short-long)

Now set the Sm evaporation into operation. For the Sm metal a low current trough the filament is sufficient. A value for an appropiate current can be found at the place. CHECK EVERY TIME BEFORE EVAPORATION THAT THE SAMPLE HOLDER IS IN THE RIGHT ORIENTATION. ALSO MAKE SURE BEFORE THE EVAPORATION THAT THE **CHANNELTRON HV** IS SWITCHED OFF.

4.3.1 Overview spectrum of Sm (short)

— Take an overview spectrum.
— Try to identify the peaks.

4.3.2 Fermi level and Sm 4f-spectrum (short-midle)

— Now take a spectra with a much better energy resolution at the Fermi level and the 4f-state.
— Set a pass-energy of 25 eV and scan a suitable energy interval.
— Measure the exact location of the multiplets and the Fermi energy, calculate the corresponding binding energies and compare them with theory and literature [9].
— What do you need to ensure to get a resolution better and decrease the statistical fluctuations ?

4.3.3 Sm 4s-spectrum (midle)

— Where do you expect the 4s band?
— Take an accurate spectrum (possibly it is better to prepare a fresh film of Sm).
— What kind of splitting do you expect? [10]
— Try to measure the corresponding multiplet.
— Consider the electronic configuration and deduce from the intensity ratio.

4.3.4 Sm 3d-spectrum (midle)

— Which anode (Al or Mg) is better suited to observe the surface component of Sm.
— Take a spectrum of the samarium 3d spin-orbit multiplets with different pass energes and measure their distances.
— How important is the pass energy for XPS.
— What ratio do you expect on the basis of the given electronic configuration?
— Calculate the spin-orbit coupling constant from the measured splitting.
— Try to extract information about the surfaces prevalence of samarium from the spectrum?
— Justify the direction and intensity of amount of the satellite peaks representing the surface contribution. How do you explain the surface valence transition in Sm metal [10, 11].

4.3.5 Sm 3d-spectra of samariumoxide and chemical shift (midle)

— Dose at least 1L oxygen on the sample.
— Take an overview spectrum and identify all interesting peaks.
— Locate the Sm 3d-multiplet and take an accurate spectrum.
— Examine this spectrum and make statements about the chemical composition of the oxide.
— Compare the peak splitting especially with the spectrum of freshly evaporated Sm metal.
— Now measure the chemical shift the between oxide and the metal.

4.4 ESCA on 10DM coin (long)

— Think about the resolution and number of integrated spectra to get best result in "short" time.
— Take a spectrum of the 10DM coin.
— Try to determine the unknown components of the coin with the help of the literature [9, 12].

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