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X-ray Photoelectron Spectroscopy (XPS)

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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 performed by excitation with monochromatic ultraviolet light (He-I: 21.2 eV, He-II: 40.8 eV) for the spectroscopy of atoms and molecules in the gas phase, and later by excitation with soft X-rays (Al- K_α : 1486.7 eV, Mg- K_α : 1253.6 eV) for spectroscopic investigations of solids[1]. The latter method was developed by Kai Siegbahn (Nobel Prize in Physics 1981) in ESCA (Electron Spectroscopy for Chemical Analysis). Today normally 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 photoelectrons give direct information of the electronic structure of matter, from which they were raised. With XPS it is possible in a direct manner to measure atomic shell structures as well as the electronic band structure in solid. The latter requires photoelectron emission direction measured relative to a single crystalline solid. This is the so-called ARPES (Angle-Resolved PhotoEmission Spectroscopy) method. For XPS in condensed matter one must note that the method is very surface sensitive, because the photoelectron are emitted losslessly only from a thin surface layer. This so-called depth of escape λ varies from 2 Å to 20 Å, depending on the kinetic energy (E_{kin}) of the photoelectrons. This is described by the so-called universal curve (see Fig. 3) E_{kin} of 40 eV has a minimum λ of about 2 Å (largest surface sensitivity).

In this experiment you have a possibility to go deep in the details of the XPS technology and physics behind this. The technical bases comprise:

- Production of X-rays
- Fundamentals of UHV-technology
- Detection of electrons, monochromatization of electrons
- Sample preparation, e.g. deposition of samarium (Sm) thin films and/or dosing of O₂
- Computer control of the measurement.

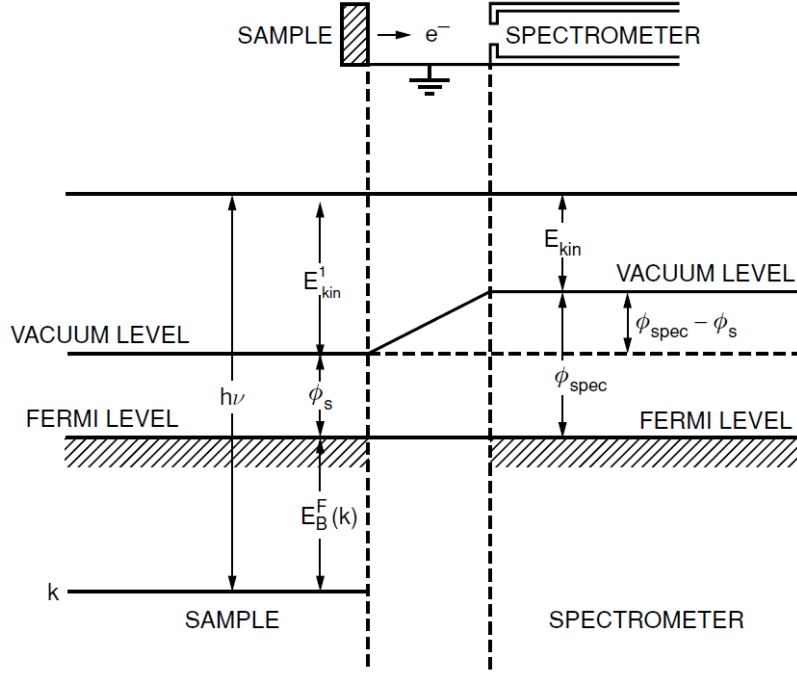


Figure 1: Schematic representation of the photoemission, adopted from [13]

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 has the electron enough energy to overcome the work function (Φ) of the solid, it can leave the solid state (Fig. 1).

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

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

$$E_{kin} = h\nu - [E(A^*) - E(A)] - \Phi = h\nu - E_B - \Phi \quad (1)$$

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 spectrum is given as kinetic energy distribution of photoelectrons, which can be measured with electron analyzer. For a known photon energy ($h\nu$)

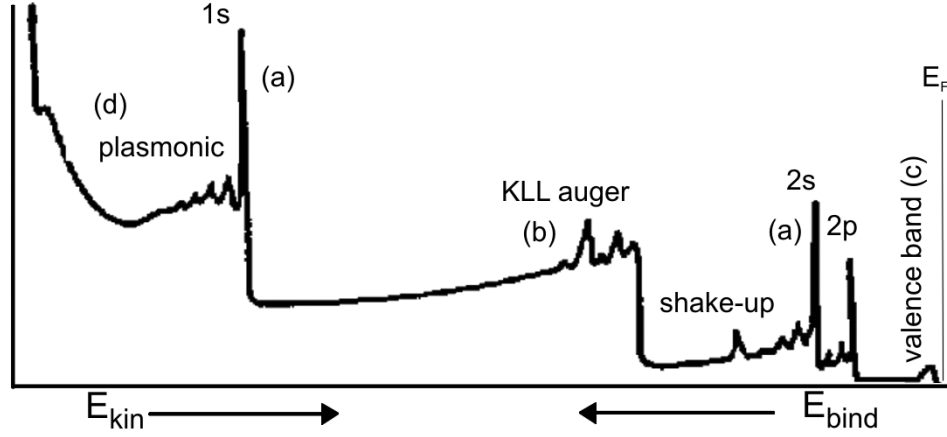


Figure 2: A typical XPS overview spectrum of a solid

the binding energy can be determined in the spectrum for all core electrons with $E_B < h\nu$, see Eq. 1.

2.1 Characteristic excitation processes in solids

Figure 2 shows an overview of XPS spectrum, with the characteristic excitation processes in solids:

- a) emission from core levels,
- b) Auger processes,
- c) emission from the valence band,
- d) secondary electron excitation and energy losses in inelastic scattering with electrons before their withdrawal from the surface.

Furthermore peaks can be observed in a defined distance to a photoemission line, such as shake-up lines from two-electron processes. In this emission process the excited electron stimulates a second electron at a higher shell (mostly at valence band). In metals' spectra a satellite peaks are also observed by plasmon excitation. This presents a 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 of the final state, the width of the exciting X-ray line, the energy resolution of the electron energy analyzer, and thermal broadening 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 that of electron energy analyzer (at $E_{kin} \sim 1000$ eV) is also of about 1 eV (see Section 3.3).

2.3 Surface sensitivity

Electron spectroscopic methods allow surface sensitive measurements up to one monolayer. An important parameter to describe the surface sensitivity is the **mean escape depth** (λ), which is identical with the mean free path of a photoelectron in the solid state. 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 energy range of $20 \text{ eV} < E_{kin} < 100 \text{ eV}$. In this experiment, we can change the kinetic energy of the photoelectron by varying the anode of the X-ray tube from Mg to Al.

2.4 Binding energy

The binding energy E_B depends on different terms:

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

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

- **Spin-orbit coupling:** The spin s of an electron interacts with its orbital moment l . This is described by the Hamiltonian operator

$$H_{sl} = \mathbf{a} \cdot \mathbf{s} \cdot \mathbf{l}$$

The emission line of full electron shell in ground state is split into a doublet with $(l + \frac{1}{2})$ and $(l - \frac{1}{2})$. Of course, electrons in the s-state are not affected because of its null orbital angular momentum $l = 0$.

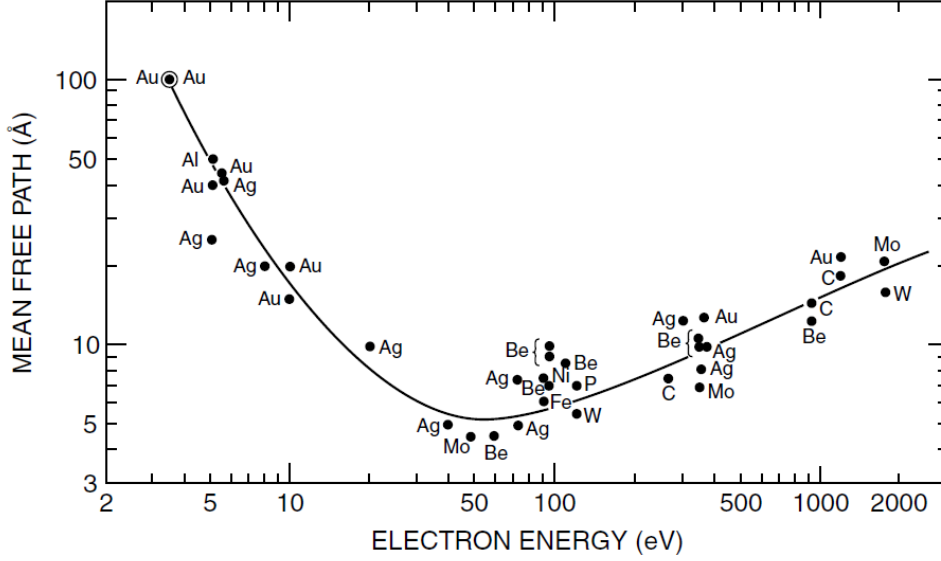


Figure 3: Universal curve of escape depth as a function of E_{kin} , adopted from [14]

- **Magnetic spin-spin exchange splitting:** Full inner s-shells are occupied by 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 arouse 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, this effect can be measured on 4s-electron of samarium [7].

3 Experimental Setup

The experimental setup consists of a UHV chamber (Fig. 5), in which, among other things is a sample holder with the tested materials:

- sheet silver
- 2 sheets of steel for vapor deposition of Sm

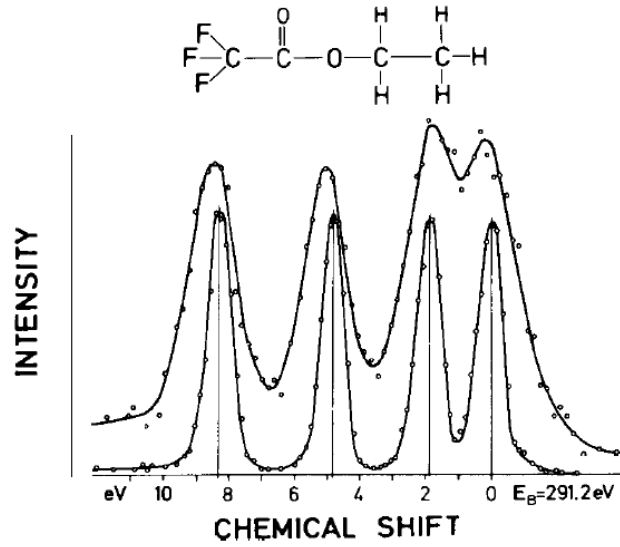


Figure 4: The ESCA shifts of the Cls in ethyl trifluoroacetate. Upper spectrum without and lower with X-ray monochromatization, adopted from [15, 16].

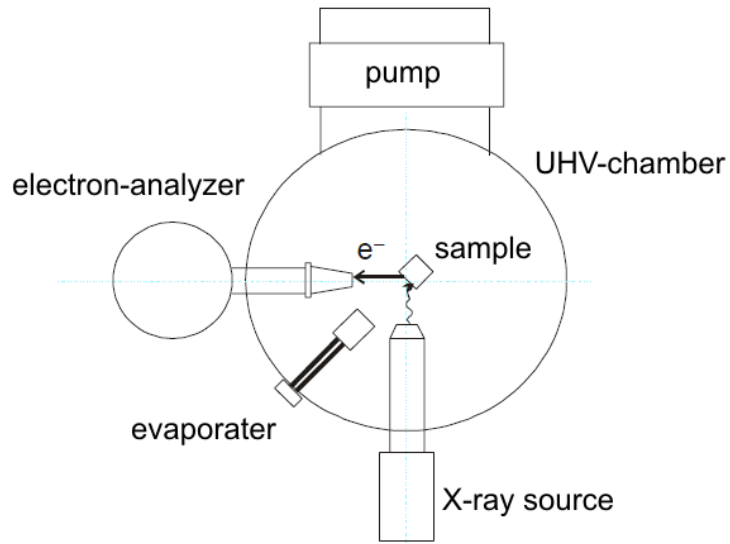


Figure 5: Schematics of the UHV chamber with a photoemission equipment.

X-ray line	Energy [eV]	Line width [eV]
Mg- K_{α}	1253.6	0.7
Al- K_{α}	1486.6	0.86

Table 1: Characteristic X-ray lines for Al and Mg as anode materials.

- 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, but for light gases, mainly H_2 , it will pump slowly because of high particle speeds. After some time the turbo pump reaches a final pressure of about 10^{-9} mbar. As a residual gas in the recipient remains mainly water, which clings on the steel walls because of its dipole structure. Therefore, the chamber is baked out under UHV conditions for some hours up to days. After cooling the final pressure of 10^{-11} mbar can be reached.

3.2 X-ray source

The X-ray source (Fig. 6) consists of a cathode (filament), which emits thermal electrons through heating (usually emission current of 30 mA), and anode to which electrons can be accelerated by applying 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 with each characteristic emission spectrum (Fig. 6(d)). This spectrum includes bremsstrahlung and characteristic radiation. The short-wave radiation of bremsstrahlung will largely be absorbed by an approximately 1 micron thick Al-window.

3.3 Electron energy analyzer

The analyzer measures the kinetic energy of the photo-electrons by a hemispherical capacitor. This consists of electrical lens system and two metallic hemispheres, as in Fig. 7. One of the main point in the setup is the pass energy E_{pas} . This has influence on the resolution and background noise. The highest noise level in the spectrum results from electrons in the **secondary**

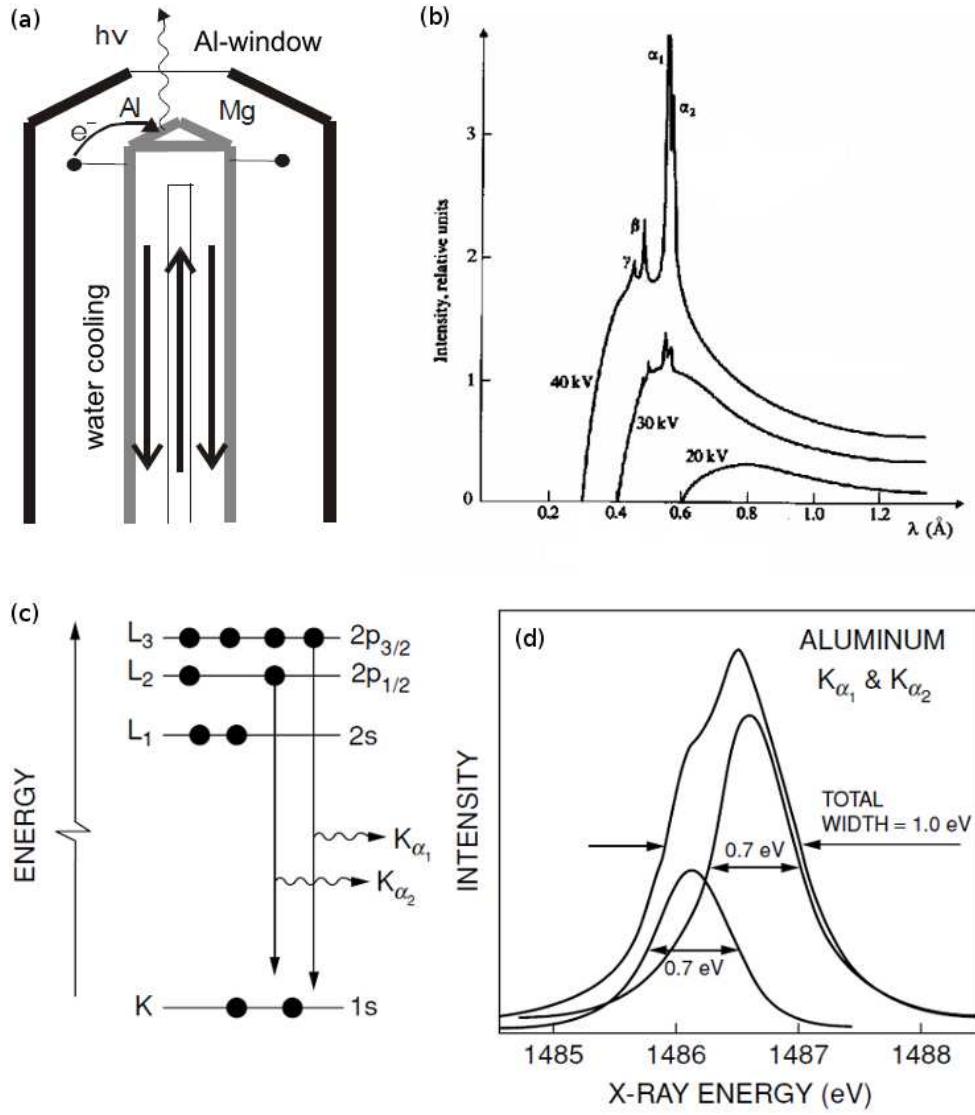


Figure 6: (a) Schematic structure of the used double-anode X-ray source. (b) Typical emission spectra of X-ray source with Cu anode. (c), (d) Characteristic radiation of Al. [13]

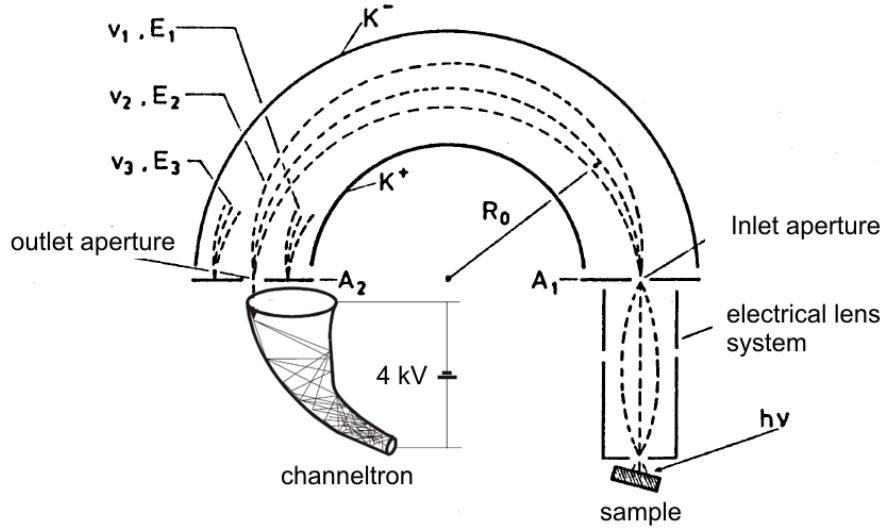


Figure 7: Schematic design of a hemispherical analyzer with channeltron.[4]

processes which have low kinetic energy. To reduce the background we filter out the electrons with low kinetic energy by applying a pass voltage. To realize this there are many possibilities, e.g. slow down the electrons before the electrical lens so the electron with $E_{kin} > E_{pas}$ can pass this. In our setup the selection is realized through voltage difference ($H^+ - H^-$) between the hemispherical plates see Fig. 7[3]. In this experiment, channeltron is used as a detector and consists of a glass tube inside which a material with a high electrical resistance is covered through. This works on the principle of secondary electron multiplier. The multiplication level is typically 10^6 to 10^8 . With the corresponding electronics the detector amplifies pulses and records this.

3.4 Evaporater

The Sm evaporator is firmly installed on an electrical implementation of the chamber. It consists of a tantalum crucible (high melting point), in which there is samarium stored, and a filament which is wrapped around the crucible (Fig. 8). The filament can be heated by a current which will heat up the pot.

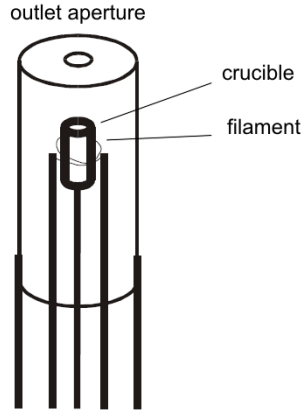


Figure 8: Schematics of Sm evaporator.

3.5 Dosing

One of the exercises is to observe the chemical shift of the Sm surface component. For this you can find on the chamber a bottle of oxygen O_2 (approx. pressure 12 bar) which is connected to the leaking valve. This setup gives you the possibility to dose the oxygen in defined quantities. The unit for the dosage is Langmuir L [8] . In case that a sticking coefficient equals 1, 1 L corresponds to surface which is covered with a monolayer of the adsorbate.

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

4 Exercises

With this setup you have the possibility to go really deep in the physics. In principal it's possible to compile and adapt the exercises on your interests together with tutor (for this contact the tutor one week before). The main topic of this experiment is to observe and explain the near edges and band structure of different materials. Or you select 4 from the below listed Exercises (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 rollovers in the X-ray tube. Keep the emission current around 30 mA. More detailed instructions are on the place. The measurement program and communication between the computer and analyzer electronics will be explained by tutor.

4.2 Overview spectra of a silver sample (middle)

- Turn the sample holder so that the Ag-metal 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 ($E_{kin} = 200$ eV - 1600 eV) with Al- and Mg- anodes. Roughly locate the Fermi level and identify the emission peaks. Make sure that these binding energies are given only as differences to the Fermi level.
- How can you distinguish between the Auger- and photo-emission- electrons' peaks?
- What can you say about the X-ray's 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-evaporator into operation. For the Sm-metal a low current through the filament is sufficient. The corresponding current can be found on the place. CHECK EVERY TIME BEFORE EVAPORATION THAT THE SAMPLE HOLDER IS IN RIGHT ORIENTATION. ALSO MAKE SURE BEFORE THE EVOPARATION THAT THE **CHANNELTRON HV** IS SWITCHED OFF.

4.3.1 Overview spectra of Sm (short)

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

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

- Take now a spectrum with much better resolution of the Fermi level and 4f-state.
- Set the pass-energy to 25 eV and search a suitable energy interval.
- Measure the exact location of the multiplets and the Fermi energy and calculate the corresponding binding energies and compare them with theory and literature [9].
- What do you need to ensure a better resolution and decrease the statistical fluctuations?

4.3.3 Sm-4s-spectrum (middle)

- 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 electron configuration and deduce from it the observed intensity ratio.

4.3.4 Sm-3d-spectrum (middle)

- 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 energy and measure their distances.
- How important is the pass energy for XPS?
- Which ratio do you expect on the basis of the given electron configuration?
- Calculate the spin-orbit coupling constant from the measured splitting.

- Find in this spectrum information about the surface prevalence of samarium?
- Justify the direction and intensity of the satellite peaks representing the surface contribution. How do you explain this surface valence transition in Sm metal [10, 11]?

4.3.5 Sm-3d-spectra of Samariumoxide and chemical shift (middle)

- Dose at least 1 L oxygen on the sample.
- Take the overview spectrum and find all interesting peaks.
- Locate the Sm-3d multiplet in overview 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.
- Measure now the chemical shift between oxide and the metal.

4.4 Coin (long)

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

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