

Ma 10: Auger- and Electron Energy Loss Spectroscopy

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1 Introduction

In this experiment a aluminium substrate will be analyzed with surface spectroscopial methods. Due to the small penetration depth of the Auger electron spectroscopy (AES) it will be used to detect impurities. After measuring the Auger spectrum of pure Aluminium, the electron energy loss (eel) method will be used to detect plasmons.

1.1 Cylindrical Mirror Analyzer (CMA)

The CMA is an apparatus , which selects electrons within a small range of energy ΔE around a certain energy value E_0 from an electron source of various energies. This is performed by two cylinders, where the inner cylinder of radius r_1 has two ring-slits for the exit and entrance of the electron beam and a negative potential V is applied to the outer cylinder with radius r_2 (Fig. 1.1).

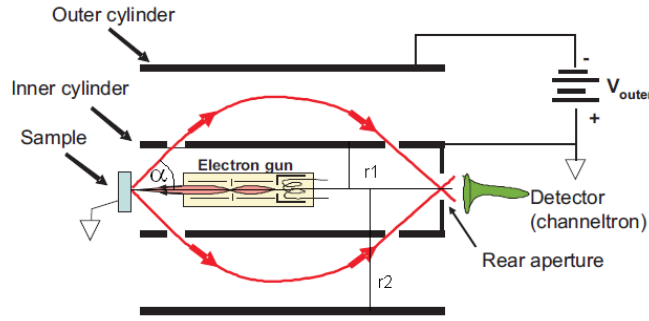


Figure 1.1: Schematic cross section of a CMA. [?]

Therefore, the electrons are bend towards the inner cylinder again. There exist a special emission angle $\alpha = 42^\circ 18, 5'$, where the focusing properties are eminently better (focus of 2nd order). For CMAs operated at this angle the selected energy value is given by

$$E_0 = \frac{1.3099e}{\log r_2/r_1} V , \quad (1.1)$$

where e is the electron charge. The energy resolution is determined by the angular spread of the emission angle $\Delta\alpha$ (Fig. 1.1) and given by

$$\frac{\Delta E}{E_0} = 2.75 \Delta\alpha^3 . \quad (1.2)$$

The current at the detector I is proportional to the number of incoming electrons $N(E)$. By measuring the voltage V , the function $N(E)$ is directly given by (1.1). However, the characteristic Auger-peaks are easier to detect considering the derivative $\frac{dN(E)}{dE}$. This can be achieved by a small sinusoidal modulation of the voltage with amplitude V_ω . The current I can then be expanded in terms of the small perturbation $V_\omega \sin \omega t$ as

$$I = I(V_0) + \frac{dI}{dV} V_\omega \sin \omega t + \dots , \quad (1.3)$$

where the derivative $\frac{dI}{dV}$ represents the amplitude of the oscillating signal and is proportional to $\frac{dN(E)}{dE}$

$$\frac{dI}{dV} = A_\omega \propto \frac{dN(E)}{dE} . \quad (1.4)$$

This amplitude can be selected and amplified using a lock-in amplifier.

1.2 Lock-in Amplifier

In general the term lock-in amplifier refers to an amplifier, which is operated using an external characteristic signal, that is multiplied with the signal to be amplified, instead of an unspecific amplification. This characteristic external signal is related to the incoming signal, mostly via the frequency. E.g. during a measurement process a signal S_I of known frequency ω is created according to

$$S_I = A_0 + A_\omega \sin \omega t . \quad (1.5)$$

Then an amplification signal S_A of the same phase and frequency is used to amplify the incoming signal and afterwards an integration over a complete period is performed. The out-coming signal S_O is then proportional to the amplitude A_ω of the incoming signal S_I

$$S_O \propto A_\omega . \quad (1.6)$$

Therefore, the signal-to-noise relation can be significantly improved, as the constant off-set A_0 is almost completely eliminated from the signal.

1.3 Nomenclature

The most commonly used nomenclature for the Auger electron spectroscopy is based on the quantum number n (K for $n = 1$, L for $n = 2...$), followed by an index to denote the different possible states for this n (in the order of increasing energy). To fully describe the Auger electron, all three participating states have to be mentioned in this way.

Alternatively it is possible to simply note the electron configuration at the end of the Auger process. In this way $2s^0 2p^6$ corresponds to KL_1L_1 and so on.

1.4 Expected Transitions

For aluminum the ionization energy of the K-level is about 1.6 keV. Therefore, the typical energy of exciting electrons up to 3 keV is sufficient to excite the Auger KLL-transitions, which are the transitions of highest energy. These have an energy range from approximately 1.3 keV to 1.4 keV and are listed in table 1.1. The LMM transition is also possible and its energy is around 70 eV with again a multiplet splitting.

Auger line	Theoretical Energy (eV)
$KL_{2,3}L_{2,3}$ (3P)	(1398.1) ^α
$KL_{2,3}L_{2,3}$ (1D)	1393.5
$KL_{2,3}L_{2,3}$ (1S)	1386.6
$KL_1L_{2,3}$ (3P)	1358.5
$KL_1L_{2,3}$ (1P)	1342.3
KL_1L_1 (1S)	1304.0

Table 1.1: Theoretical energies [?] of KLL Auger-Transitions for Aluminum. ^α: Forbidden due to parity conservation.

1.5 Energy of Auger-Electrons

The energy balance of the Auger-transition reads

$$E(KLL') = E(K) - E(L) - E^*(L') , \quad (1.7)$$

where $E(KLL')$ is the energy of the Auger electron stemming from a transition KLL' , $E(K)/E(L)$ are the binding energies of the electrons in K/L-level and $E^*(L')$ is the binding energy of the electron in the L' state, where the asterisk denotes, that this energy is altered through the absence of the K and L electron towards.

$$E^*(L') = E(L') + C(LL', T) - R , \quad (1.8)$$

where $C(LL', T)$ stems from the coupling of the two holes in LL' , T represents the final state and R is the relaxation energy arising from the reduction of repelling electronic force.

These formulas hold for free atoms. For an electron, that is emitted from the valence band of a solid the work-function, which gives the minimum energy needed to remove an electron from a solid to the solid surface, has to be taken into account.

1.6 Plasmons

The pseudo particle of fermi-gas oscillation is called a plasmon. These plasmons have characteristic energies, depending on the conduction electron density n .

$$E_p = \hbar \underbrace{\sqrt{\frac{ne^2}{m\epsilon_0}}}_{\omega_p}$$

Apart from the more obvious bulk plasmons (three dimensional oscillations in the sample) there are also surface plasmons when a material with positive dielectric constant (vacuum) interface with a material of negative dielectric constant (Al). For Aluminium the bulk and surface plasmons have energies of approximately 15.3eV and 10.8eV respectively.

An electron that excites a plasmon loses one of these characteristic energies and is said to have suffered plasmon loss. It is possible, that one electron suffers plasmon loss several times, leading to a series of equally spaced losses with decreasing intensity.

1.7 Electron Mean Free Path

As the mean free path of electrons depends characteristically on the energy of the electrons for a broad range of different materials, the so called universal curve (Fig. 1.2) is very useful in order to analyze the surface sensibility of spectroscopic methods. The minimal mean free path exists between 40 eV and 100 eV. Within this energy range the average penetration depth is below 10 Å. Towards higher electron energies the mean free path increases only slowly and for 1 keV is still below 20 Å. Therefore, any electron spectroscopic measurements within this energy range analyses surface properties rather than those of the bulk-solid.

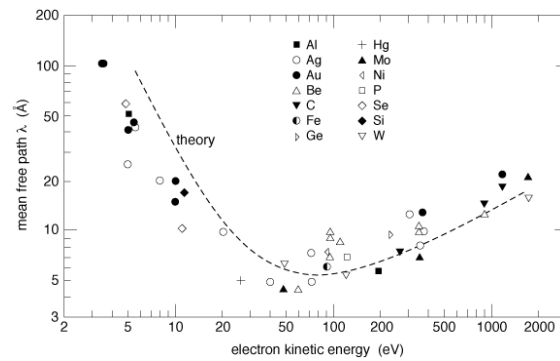


Figure 1.2: Mean free path of electrons in solids (logarithmic scale). Dots: Measurements. Dashed Line: Calculation. For Aluminium the mean-free path is even smaller than predicted by calculation. [?]

2 Analysis

2.1 Oxidization

Due to the imperfect vacuum in the experimentation chamber, the Al is exposed to oxygen all the time. At the beginning of the measurements this shows as a significant buildup of oxygen atoms at the surface of the sample (see Figure 2.1a). Even though it can be removed very easily mechanically (Fig 2.1b), the constant presence of oxygen causes new oxidation. In the time of about 2 hours at $4.3 \cdot 10^{-8}$ mbar \approx 230L the contamination had already reached more than 50% of the equilibrium level (Fig2.1c).

2.2 KLL Auger spectrum of Al

With the cleaned sample, the differential spectrum of aluminium has its most notable activity near 1400eV. The qualitative form of this region (Fig 2.2) is in very well agreement with the literature (cf. handbook of aes) but quantitatively all values seem to be shifted towards higher energies.

This shift is expected, considering the poor alignment of the sample. A deviation from the perfect position Δx will cause a stretching of the form

$$E' = \lambda(\Delta x) \cdot E, \quad (2.1)$$

where E' is the measured and E the actual energy of the electrons (\rightarrow SOURCE). Assuming the deviation does not change significantly over the time of measurement, we can try to recalibrate our measurements with the known minima in the oxygen spectrum.

The resulting values are (or close to) consistent with the literature, but have a rather large margin of error. Using the last minimum of the Al spectrum to calibrate the spectroscope instead gives better values. While this does not allow to compare the absolute values, the relative spacing between the minima can still be compared and confirmed. Due to the significant improvement in accuracy this last calibration will be used throughout the rest of this work.

The integrated version of this spectrum shows peaks corresponding to KLL auger effects in aluminium. The resolution is far too bad to allow the identification of all five expected transitions, but with a reference spectrum from [?] it is possible to identify the 5 most significant peaks. See Table ?? for more details.

2.3 Plasmons

The most significant peaks in section 2.2 already contained electrons that suffered plasmon loss. These characteristic losses can be measured with electron energy loss spectroscopy. A measurement with higher energy electrons (1keV) shows mainly the bulk plasmons, while a second measurement with weaker electrons (170eV) promises to show surface plasmons more clearly, due to the lower penetration depth.

The first measurement (see Fig 2.3b) resulted in a (weighted) mean energy for the bulk plasmons of $B_1 = (15.31 \pm 0.54)$ eV. This result is consistent with the two bulk

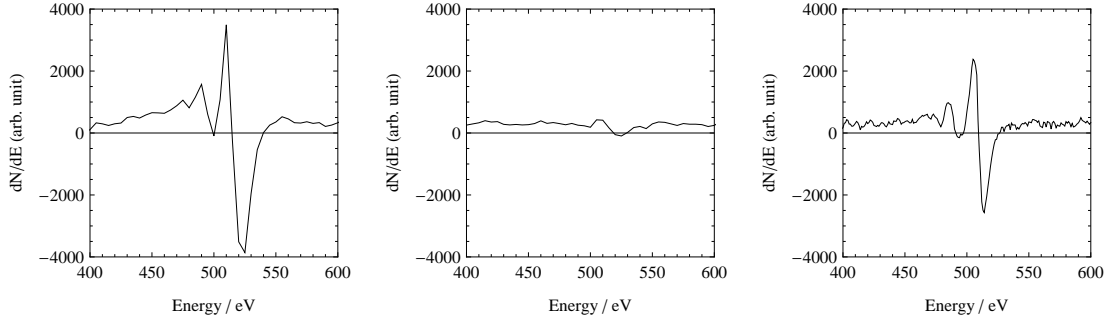


Figure 2.1: Differential detection rate at the oxygen specific energies before cleaning **(a)**, after cleaning **(b)** and after the experiments **(c)**. The characteristic minima are at approximately $(477.8 \pm 1.0)\text{eV}$, $(494.07 \pm 0.30)\text{eV}$ and $(514.12 \pm 0.66)\text{eV}$. Values obtained through the fitting of quadratic functions near the minima.

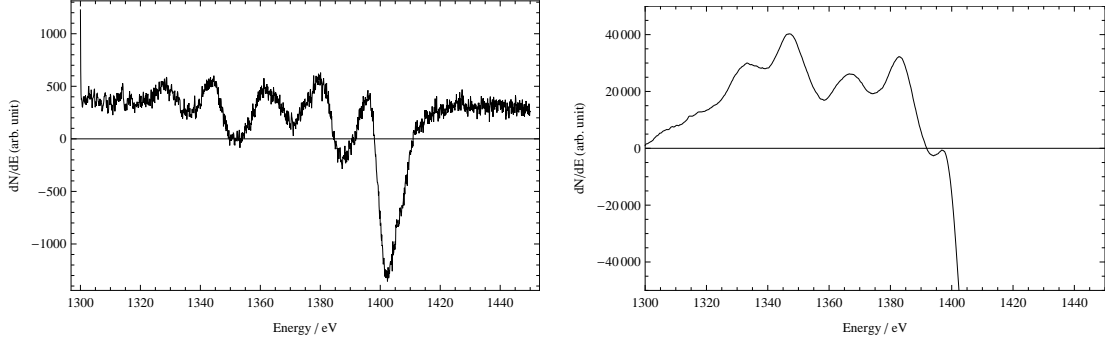


Figure 2.2: All values obtained by fitting quadratic functions near the minima. **(a)** Measured differential detection rate of Al. Minima at $(1336.07 \pm 0.30)\text{eV}$, $(1352.52 \pm 0.20)\text{eV}$, $(1370.73 \pm 0.32)\text{eV}$, $(1388.32 \pm 0.16)\text{eV}$, $(1402.64 \pm 0.14)\text{eV}$. **(b)** Integrated version of (a) after subtracting an estimated noise level of 300. The peaks are at $(1333.64 \pm 0.64)\text{eV}$, $(1346.98 \pm 0.03)\text{eV}$, $(1366.90 \pm 0.05)\text{eV}$, $(1382.81 \pm 0.04)\text{eV}$, $(1396.96 \pm 0.08)\text{eV}$.

O calibration	Al calibration	literature
(1325.1 ± 3.5)	(1329.7 ± 1.2)	1329
(1341.4 ± 3.5)	(1346.1 ± 1.2)	1345
(1359.4 ± 3.6)	(1364.2 ± 1.2)	1364
(1376.9 ± 3.6)	(1381.8 ± 1.2)	1380
(1391.1 ± 3.6)	(1396.0 ± 1.2)	1396

Table 2.1: Positions of the minima in the differential (dN/dE) aluminium auger spectrum. Values corrected with the information of the oxygen minima or the last aluminium minimum compared to the values in the literature. All values in eV.

transition	literature	measurement
$^1P + B_1$	1326.1	(1327.3 ± 1.1)
1P	1341.4	(1340.6 ± 1.1)
3P	1357.2	(1360.4 ± 1.2)
$^1D + B_2$	1362.6	
$^1D + B_1$	1377.9	(1376.3 ± 1.2)
1D	1393.2	(1390.4 ± 1.2)
1S	1387.2	

Table 2.2: Characteristic (corrected) energies of the KLL auger spectrum of aluminium, their according transition and the literature value from [1]. $+B_{1/2}$ denotes the change in energy due to the interaction with bulk plasmons. Whenever two significant peaks are closer than 7eV they merge, resulting in a single, mean value in the measurements due to the very limited resolution of the used apparatus.

plasmons found in the 170eV measurement (see Fig 2.3a). The single peak in the second measurement corresponding to a surface plasmon results in $S_1 = (11.04 \pm 0.20)\text{eV}$.

3 Summary and Discussion

An aluminium sample was analyzed in a high vacuum chamber with both AES and EELS. The differential Auger electron spectrum was in good agreement with the literature. As the positional offset of the sample was unknown though, it was necessary to recalibrate the spectroscope using one of the measured peaks itself.

Due to the limited resolution of the used apparatus, the KLL spectrum of Aluminium could not fully be observed. The five peaks that were measureable though agree very well with the literature (see section 2.2).

The EELS to measure the energies of plasmons was a full success. Both the energy of the bulk plasmon ($B_1 = (15.3 \pm 0.6)\text{eV}$) as well as the energy of the surface plasmon ($S_1 = (11.0 \pm 0.2)\text{eV}$) agree with the theory, even though only one surface plasmon was observable.

Despite the good accuracy for the EELS measurements the accuracy for the AES was mediocre at best. While the instruments are precise enough (having neglectible error margins compared to the total error), the experimental setup itself causes a lot of noise and is thus the main reason for all the (high) errors in the performed experiments. A good place to start improving upon the setup probably is the vacuum pump as well as the positioning of the sample.

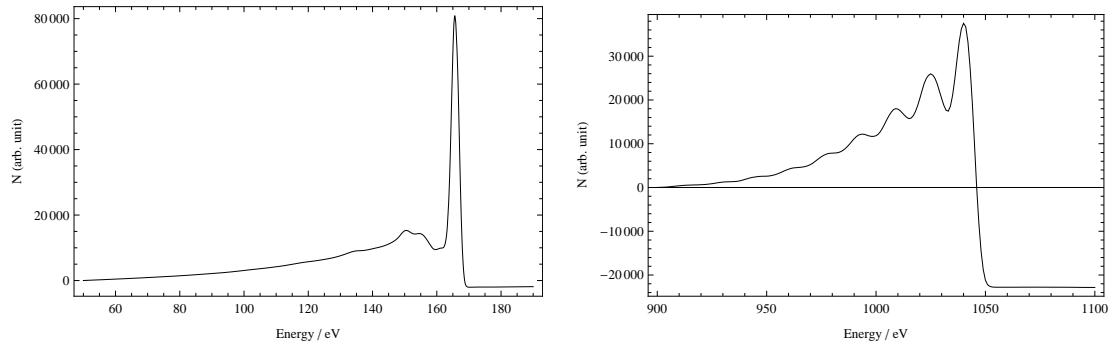


Figure 2.3: Electron backscatter spectra of Al including additional peaks due to plasmon loss. All values obtained by fitting quadratic functions near the maxima. **(a)** Measurement with electrons of about 170eV. Peaks at $(135.84 \pm 0.09)\text{eV}$, $(150.52 \pm 0.03)\text{eV}$, $(154.55 \pm 0.05)\text{eV}$, $(165.65 \pm 0.04)\text{eV}$. **(b)** Measurement with electrons of about 1050eV. Peaks at $(919.6 \pm 6.7)\text{eV}$, $(934.5 \pm 5.4)\text{eV}$, $(948.8 \pm 1.7)\text{eV}$, $(964.7 \pm 1.9)\text{eV}$, $(980.1 \pm 1.2)\text{eV}$, $(994.11 \pm 0.59)\text{eV}$, $(1009.31 \pm 0.26)\text{eV}$, $(1024.96 \pm 0.09)\text{eV}$, $(1039.90 \pm 0.28)\text{eV}$.