

Part I
Chapter 2

**Quantitative Analysis of the Plasmon Loss Intensities
in X-ray Photoelectron Spectra of Magnesium**

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Abstract

X-ray photoelectron spectra of free-electron metals like magnesium and aluminium contain pronounced electron energy loss peaks due to plasmon excitations. Part of the intensity contained in these plasmon peaks is of intrinsic nature. In this work a procedure is presented, which allows the determination of the intrinsic and extrinsic contributions to the plasmon loss structure and accounts for possibly different electronic properties at the surface. It is based on the reconstruction of a spectrum by convolution of physically realistic functions for the X-ray energy distribution, the core-level main peak, the cross sections for plasmon excitation and instrumental broadening. The procedure has been applied to a Mg 2p spectrum, giving a total intrinsic plasmon contribution of 46 % relative to the main peak intensity.

Keywords: X-ray photoelectron spectroscopy (XPS), intrinsic plasmon excitation, inelastic electron scattering cross section, surface effects, magnesium

2.1. Introduction

The shape of a spectrum obtained with X-ray photoelectron spectroscopy (XPS) is determined by the X-ray energy distribution, the intrinsic core-level excitations, the extrinsic energy losses, and the instrumental response. Usually, one obtains the intrinsic part of the spectrum by subtracting a background, representing the extrinsic contribution of inelastically scattered electrons, from the main peak region. Further analysis is then performed with the remaining background-corrected main peak. Thereby, intrinsic intensity not contained in the main peak is ignored. Besides an asymmetric tail, an additional intrinsic contribution can arise at the high binding energy side of a peak due to coupling of the core hole with collective electron oscillations (plasmons). Particularly, XPS spectra of free-electron metals, like Be, Na, Mg and Al, have a significant intrinsic contribution within the plasmon peaks [52-56]. Neglecting this contribution falsifies results, e.g. for composition or layer thickness, obtained from the spectra. Unfortunately, determining the intrinsic part of plasmon peaks is difficult, because of the overlap with the extrinsic part, which results from coupling of the moving photoelectron with the collective electron oscillations.

A correct separation of the intrinsic and extrinsic contributions to an XPS spectrum can be made with the background-calculation formalism of Tougaard [47], which takes the cross section for inelastic electron scattering into account. Since the cross section is generally not known, Tougaard proposed a universal cross section [57], which gives a good description of the extrinsic background in XPS spectra for most materials, but not for free-electron metals [58]. Furthermore, possibly different electron emission and scattering within the bulk and surface region of a material is usually not considered.

In this paper the intrinsic and extrinsic surface and bulk contributions to the 2p spectrum of Mg have been separated, by fitting the spectrum with physically realistic functions for the different contributions. The material is thereby considered as a substrate covered with a thin film of the same material, but with possibly different electronic properties. Results have been compared with literature data.

2.2. Experimental

From a polycrystalline magnesium rod (99.95 wt %) a disc has been cut, which has been ground with SiC paper and polished with diamond paste (down to 1 μm grains) using a mixture of distilled water, ethanol and liquid soap as a lubricant. Subsequent etching with a

mixture of ethanol (98 %), HCl (1.2 %) and HNO₃ (0.8 %) for 130 s removed the mechanically distorted surface due to grinding and polishing and made the grain boundaries just visible with a light-optical microscope, indicating a grain size of ~ 25 μm. Final sputter cleaning with 3 kV Ar⁺ ions in the UHV XPS chamber resulted in survey XPS spectra with no peaks due to other elements than Mg.

XPS spectra have been recorded in a PHI 5400 ESCA system using non-monochromatic Al K α radiation. The energy scale of the hemispherical analyser has been calibrated using the Ag 3d_{5/2} peak set at 368.3 eV. The intensity scale has been corrected for the analyser transmission function provided by the manufacturer. The Mg 2p spectrum has been measured in the binding energy range from 43 to 93 eV with a pass energy of 17.9 eV and a step size of 0.05 eV at a detection angle of 45°. To determine the instrumental broadening at these settings, the Mg KLL peak has been measured in the binding energy range from 295 to 305 eV at different pass energies. The full width at half maximum (FWHM) of those peaks has been plotted against pass energy. Extrapolation to zero pass energy gives the intrinsic line width of the Mg KLL line (0.751 eV). Subsequently a Lorentz function with this width convoluted with a Gauss function to account for instrumental broadening has been fitted to the Mg KLL line measured at a pass energy of 17.9 eV, with the FWHM of the Gauss function as fit parameter. The resulting value for the instrumental broadening at this pass energy is 0.358 eV.

2.3. Calculation of the Mg 2p spectrum

The complete Mg 2p spectrum, including intrinsic and extrinsic plasmon peaks, of a clean Mg sample has been calculated as described below. The bulk and surface regions have been treated separately by considering the sample as a bulk substrate covered with a thin surface layer of the same material but with different electronic properties.

The spectral broadening due to the X-rays is described by a Lorentz function:

$$I_L(E) = \frac{1}{\pi \cdot (\gamma_X / 2)} \cdot \frac{1}{\left(\frac{E}{(\gamma_X / 2)} \right)^2 + 1} \quad (2.1)$$

where E is the photon energy relative to the energy of the Al K α_1 line and γ_X is the FWHM of the X-ray line. Since in this work non-monochromatic Al radiation has been used, the contributions of both the Al K α_1 and Al K α_2 radiation (the other X-ray satellites have been

subtracted from the experimental spectrum, see chapter 4) have been added to obtain the X-ray energy distribution: $I_X(E) = \frac{2}{3}I_L(E) + \frac{1}{3}I_L(E - E_{X2})$. For E_{X2} , the energy of the $K_{\alpha 2}$ line relative to the $K_{\alpha 1}$ line, a value of - 0.413 eV has been used, i.e. the average of the values cited in Ref. [59]. For both peaks a value of 0.224 eV has been used for γ_X , determined from Ref. [60].

The energy distribution I_M of electrons emitted due to excitation of a metal core level by X-ray photons can be described by a Doniach-Sunjic line shape [61,62]:

$$I_{DS}(E) = \frac{\Gamma(1 - \alpha_M) \cdot \cos\left(\frac{\pi \cdot \alpha_M}{2} + (1 - \alpha_M) \cdot a \tan\left(\frac{E_M - E}{(\gamma_M/2)}\right)\right)}{\left((E_M - E)^2 + (\gamma_M/2)^2\right)^{(1 - \alpha_M)/2}} \quad (2.2)$$

where E is the electron binding energy, Γ is the gamma function, E_M is the core level binding energy, γ_M is the FWHM of the line shape (without asymmetry) and α_M is the singularity index, determining the magnitude of the asymmetric tail towards higher (binding) energies. Since the Mg 2p core level is split into the Mg 2p_{3/2} and Mg 2p_{1/2} levels, the Mg 2p main peak has been calculated as the sum of two Doniach-Sunjic lines: $I_M(E) = H_M \cdot I_{DS}(E) + \frac{1}{2}H_M \cdot I_{DS}(E - E_{2pS})$, where H_M is the height of the Mg 2p_{3/2} peak and E_{2pS} is the core level splitting. A core level splitting of 0.265 eV has been used, which is the average of the values cited in Ref. [59]. The other parameters, H_M , E_M , γ_M and α_M , have been used as fit parameters. Electrons in the surface region have a slightly lower binding energy. Therefore, separate main peaks for the bulk ($I_{M,b}$) and surface ($I_{M,s}$) contributions have been calculated with the surface main peak shifted relative to the bulk main peak: $I_{M,b}(E) = I_M(E)$ and $I_{M,s}(E) = I_M(E - E_{SCS})$. A surface core level shift E_{SCS} of 0.14 eV has been used [63]. All other parameters have been set equal for bulk and surface main peaks.

Calculation of the contribution of intrinsic and extrinsic plasmon excitations to the Mg 2p spectrum requires cross sections for these excitations. The cross section for extrinsic excitations K_e , i.e. the probability that an electron moving in the solid with energy E will lose the energy $\hbar\omega$, is given by [58,64].

$$K_e(\hbar\omega) = \frac{1}{\pi \cdot E \cdot a_0} \int_{k^-}^{k^+} \text{Im} \left[-\frac{1}{\varepsilon(k, \omega)} \right] \cdot \frac{1}{k} \cdot dk \quad (2.3)$$

where $\varepsilon(\mathbf{k},\omega)$ is the complex dielectric function, $a_0 = 0.053$ nm is the Bohr radius and $\mathbf{k} = \sqrt{2m_e/\hbar^2} \sqrt{E \pm \sqrt{E - \hbar\omega}}$ is the wave vector. For a free-electron metal like Mg, the dielectric loss function $\text{Im}(-1/\varepsilon)$ can be described by one Drude-Lindhard term:

$$\text{Im}\left(-\frac{1}{\varepsilon(\mathbf{k},\omega)}\right) = \frac{A_p \cdot \gamma_p \cdot \hbar\omega}{\left[\left(\hbar\omega_p + (\hbar^2\mathbf{k}^2/2m)\right)^2 - (\hbar\omega)^2\right]^2 + (\gamma_p \cdot \hbar\omega)^2} \quad (2.4)$$

where A_p , $\hbar\omega_p$ and γ_p represent the magnitude, position and width of the loss function, respectively, and m is the electron mass. The same parameters have been used for intrinsic and extrinsic plasmon excitations, but different parameters have been allowed for plasmon excitations in the bulk and surface region. The cross sections for bulk and surface have been calculated using $\gamma_{p,b}$, $\gamma_{p,s}$, $\hbar\omega_{p,b}$ and $\hbar\omega_{p,s}$ as fit parameters. A_p has always been chosen such that the area of the cross section equalled one. To calculate the cross sections the analytical solution of Eqs. (2.3) and (2.4) from Ref. [64] has been used.

To obtain the contribution due to intrinsic plasmon excitations, I_{pi} , to the Mg 2p spectrum, the Mg 2p main peaks obtained above have been convoluted with the cross sections for intrinsic plasmon excitation:

$$I_{pi,b}(E) = I_{M,b}(E) * \sum_{n=1}^3 b_n \cdot K_{in,b}(\hbar\omega) \quad \text{and} \quad I_{pi,s}(E) = I_{M,s}(E) * \sum_{n=1}^3 b_n \cdot K_{in,s}(\hbar\omega) \quad (2.5)$$

for bulk and surface region, respectively. The * symbol represents a convolution, b_n is the intensity ratio of the n^{th} intrinsic plasmon peak to the main peak and K_{in} is the cross section for the n^{th} intrinsic plasmon excitation. The intensity ratios b_n have been assumed to follow the Poisson distribution [53], i.e. $b_n = b^n/n!$, where b has been used as fit parameter. Only the 1st to 3rd intrinsic plasmon losses have been considered; higher orders of intrinsic plasmon excitations can be neglected [53]. The cross sections K_{in} have been calculated as described above using the same parameters except the values for $\hbar\omega_p$, which have been set n times the values used for the calculation of K_{i1} . The total intrinsic Mg 2p excitation spectrum, I_i , has then been calculated as the sum of the main peak and the intrinsic plasmon peaks convoluted with the X-ray energy distribution: $I_{i,b}(E) = I_X(E) * (I_{M,b}(E) + I_{pi,b}(E))$ and $I_{i,s}(E) = I_X(E) * (I_{M,s}(E) + I_{pi,s}(E))$ for the bulk and surface regions, respectively.

The contribution of extrinsic plasmon excitations to the Mg 2p spectrum has been calculated with Tougaard's formalism. A spectrum I_T comprising intrinsic and extrinsic contributions is given by [47,49]:

$$I_T(E) = P(\infty) \cdot I_1(E) + \frac{1}{2\pi} \int_E^\infty dE' \cdot I_T(E') \int_{-\infty}^\infty d\tau \cdot \exp(-i \cdot \tau \cdot (E - E')) \cdot \left(1 - \frac{P(\infty)}{P(\tau)} \right) \quad (2.6)$$

For calculation of the spectrum $I_{T,b}$ originating from the bulk region, $P(\tau)$ is given by:

$$P_b(\tau) = \frac{1}{\Xi_b(\tau)} \cdot \exp\left(-\frac{\Xi_s(\tau)}{\cos(\Theta)} D_s\right) \quad (2.7a)$$

and for the spectrum $I_{T,s}$ originating from the surface region:

$$P_s(\tau) = \frac{1}{\Xi_s(\tau)} \cdot \left(1 - \exp\left(-\frac{\Xi_s(\tau)}{\cos(\Theta)} D_s\right) \right) \quad (2.7b)$$

assuming equal concentrations of Mg in the bulk and surface region. In Eqs. (2.7) is Θ the detection angle relative to the surface normal; D_s is the thickness of the surface region and, for normalised cross sections, $\Xi_b(\tau)$ and $\Xi_s(\tau)$ are given by:

$$\Xi(\tau) = \frac{1}{\lambda} \left(1 - \int_0^\infty A_{K_e} \cdot K_e(\hbar\omega) \cdot \exp(-i \cdot \tau \cdot \hbar\omega) \cdot d\hbar\omega \right) \quad (2.8)$$

where λ is the inelastic mean free path (IMFP) of electrons with energy E and A_{K_e} is the area of the cross section K_e . For calculation of $P_b(\infty)$ and $P_s(\infty)$ Eqs. (2.7) apply with $\tau = \infty$, yielding $\Xi(\infty) = 1/\lambda$. Although I_T appears at both sides of Eq. (2.6) it can be calculated by stepwise evaluation of Eq. (2.6) from low to high binding energies [49]. For the calculation of $I_{T,b}$ and $I_{T,s}$ D_s has been used as fit parameter. The cross sections $K_{e,b}$ and $K_{e,s}$ for bulk and surface region, respectively, have been calculated with Eqs. (2.3) and (2.4). The corresponding values for λ_b and λ_s have been calculated according to Ref. [65], yielding 3.43 nm. The area A_{K_e} should theoretically equal one, but a smaller value has been found before in literature, e.g. the universal cross section proposed by Tougaard has an area of 0.87 [57,58]. A_{K_e} has therefore been used as a fit parameter.

Finally, instrumental broadening has been described by a Gauss function:

$$I_G(E) = \frac{1}{\sqrt{\pi} \cdot (\gamma_G/2)} \cdot \exp\left(-\left(\frac{E}{(\gamma_G/2)}\right)^2\right) \quad (2.9)$$

where E is the detected electron energy relative to the true energy and γ_G is the FWHM. For γ_G a value of 0.358 eV has been used (see Section 2.2). Thus, the total spectrum is obtained by convolution of the sum of bulk and surface spectra with the instrumental broadening: $I(E) = (I_{T,b}(E) + I_{T,s}(E)) * I_G(E)$.

2.4. Results and Discussion

Before comparison of the calculated and experimental spectra the Al $K_{\alpha 3}$ to $K_{\alpha 6}$ and K_{β} X-ray satellites of the Mg 2p and Mg 2s peaks have been subtracted from the experimental Mg 2p spectrum, using the procedure of Ref. [66]. Furthermore, a constant background intensity equal to the average intensity in the range 43.0 - 43.5 eV has been subtracted from experimental and calculated spectra. Then the calculated spectrum has been fitted to the experimental spectrum in the range 43.0 - 84.0 eV. The following fit parameters have been used: H_M , E_M , γ_M and α_M , describing the Mg 2p main peak; $\hbar\omega_{p,b}$, $\hbar\omega_{p,s}$, $\gamma_{p,b}$ and $\gamma_{p,s}$, describing the cross sections for plasmon excitations; b and A_{Ke} , describing the magnitude of intrinsic and extrinsic plasmon excitations, respectively and D_s , describing the ratio between bulk and surface excitations. For the other parameters the values mentioned in Section 3 have been applied. By minimising the sum of squared intensity differences, χ^2 , between calculated and measured Mg 2p spectrum, using a Nelder-Mead simplex search algorithm, optimum values for the fit parameters have been found. Fig. 2.1 shows a perfect agreement between calculated and measured spectrum. The resulting values of the fit parameters are presented in Table 2.1.

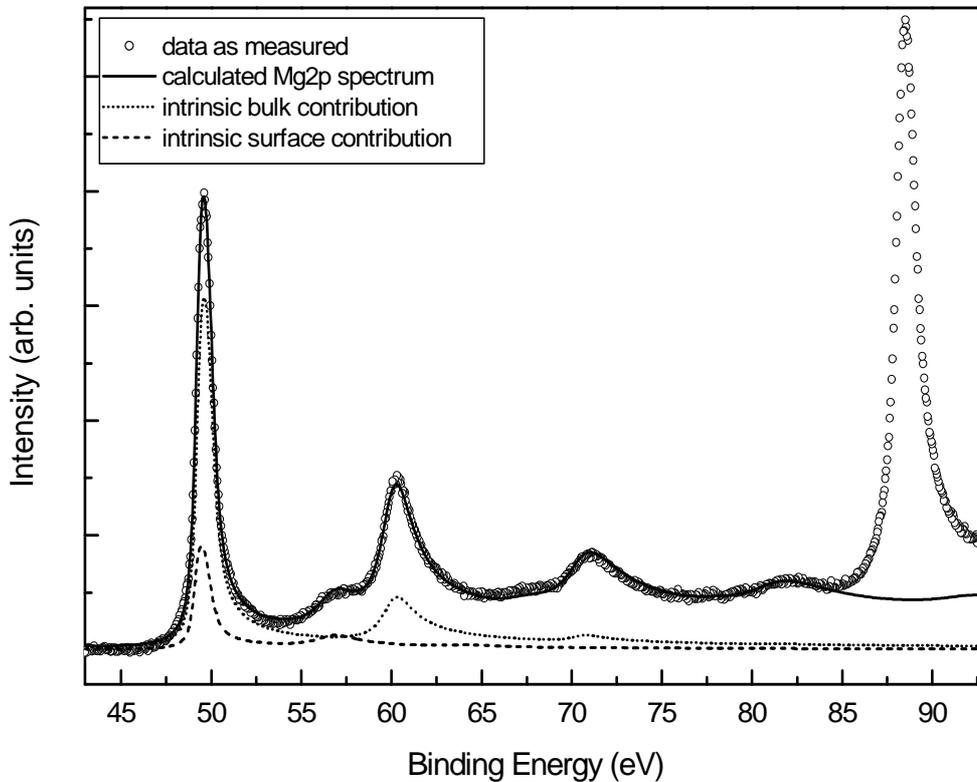


Figure 2.1: The experimental and calculated Mg 2p spectra. Also shown are the calculated intrinsic bulk and surface contributions to the spectrum.

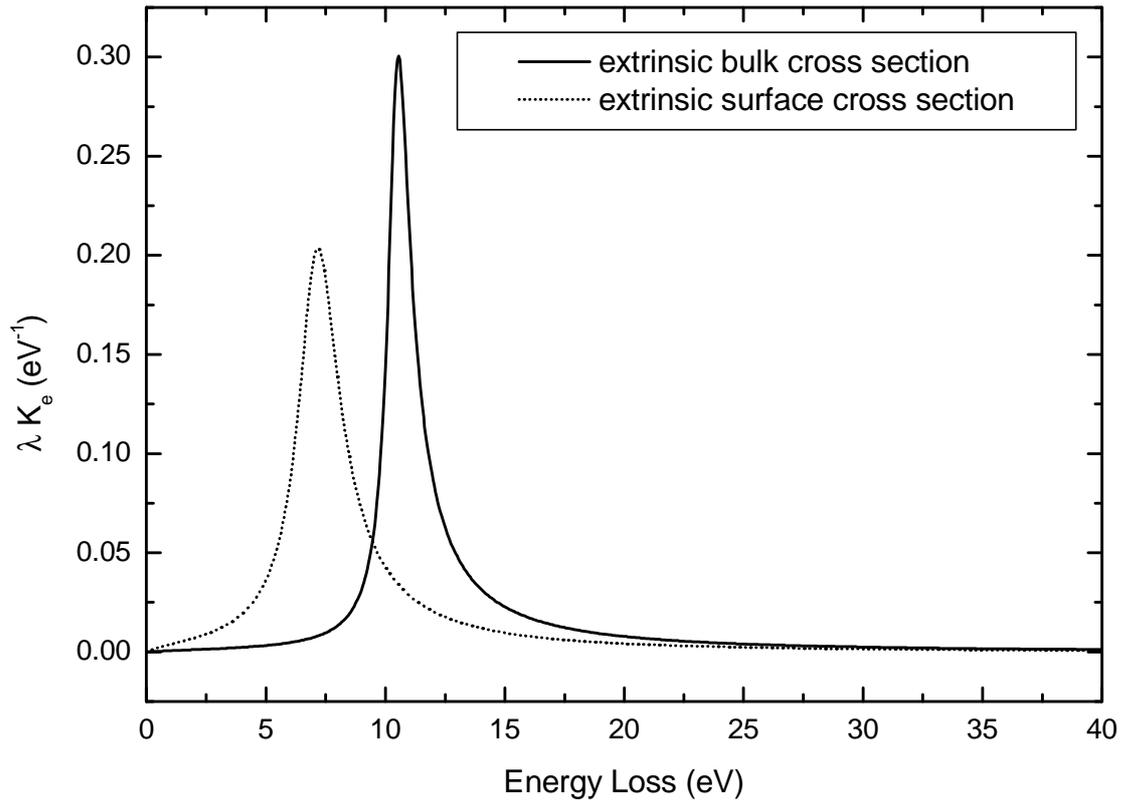


Figure 2.2: The calculated cross sections for extrinsic bulk and surface plasmon excitations multiplied with the IMFP.

fit parameter	value	uncertainty
H_M	$6.01 \cdot 10^5$ (arb. unit)	$\pm 0.09 \cdot 10^5$ (arb. unit)
E_M	49.20 eV	± 0.01 eV
γ_M	0.13 eV	± 0.01 eV
α_M	0.12	± 0.01
$\hbar\omega_{p,b}$	10.41 eV	± 0.05 eV
$\hbar\omega_{p,s}$	7.65 eV	± 0.29 eV
$\gamma_{p,b}$	0.92 eV	± 0.11 eV
$\gamma_{p,s}$	1.81 eV	± 0.53 eV
b	0.38	± 0.02
A_{K_e}	0.77	± 0.02
D_s	0.69 nm	± 0.07 nm

Table 2.1: Resulting values of the fit parameters for the calculation of the Mg 2p.

The uncertainties shown are the values for which χ^2 is at least 10 % larger than the minimum value of χ^2 . Note the relatively poor fit of the small loss peak (successive bulk - surface plasmon energy loss) at ~ 18 eV from the main peak (Fig. 2.1). It was not possible to fit this loss peak without severely decreasing the fit quality of the other loss peaks.

The values for position and shape of the Mg 2p main peak agree well with literature. The Mg 2p binding energy values reported in literature (49.67 eV is the average value obtained from the NIST database [67]) are larger than the value for E_M found here. However, in literature generally the position of maximum intensity of the total Mg 2p peak is reported, whereas in this work spin-orbit splitting and a surface core level shift have been considered, i.e. E_M is the position of the Mg 2p_{3/2} bulk peak. The position of maximum intensity of the Mg 2p peak measured here is at 49.6 eV, which agrees well with literature values. Values for the width (0.18) and singularity index (0.13 eV) of the Mg 2p_{3/2} peak reported in Ref. [62] are larger than those found here, probably because in Ref. [62] the surface core level shift has not been considered.

Values reported for the position of the Mg bulk plasmon loss peak in XPS spectra are generally around 10.7 eV [55,68], which is larger than the value found here for $\hbar\omega_{p,b}$. It should be noted however, that $\hbar\omega_{p,b}$ is not equal to the position of the maximum of the loss function, which depends on the electron kinetic energy. With an electron kinetic energy of 1437 eV (i.e. the kinetic energy of Mg 2p electrons excited with Al K $_{\alpha}$ radiation) and the values of $\hbar\omega_{p,b}$ and $\gamma_{p,b}$ found here the maximum of the loss function is at 10.55 eV (Fig. 2.2). With the same values for $\hbar\omega_{p,b}$ and $\gamma_{p,b}$ and an electron kinetic energy of 184 eV (i.e. the kinetic energy of Mg 1s electrons excited with Al K $_{\alpha}$ radiation) the maximum of the loss function is at 10.81 eV, which is close to the position we found for the 1st bulk plasmon peak of the Mg 1s peak (10.9 eV). The position of the surface plasmon peak agrees well with the theoretical ratio between bulk and surface plasmon energy loss, i.e. $\hbar\omega_{p,s} = \hbar\omega_{p,b} / \sqrt{2}$ [55]. No information about the width of the cross sections for plasmon excitation in magnesium has been found in literature, although some data has been published for other materials [58,69,70]. However, a broader surface plasmon peak width as compared to the bulk plasmon peak width has been observed before [55].

The total intrinsic plasmon contribution, i.e. $b + b^2/2 + b^3/6 = 0.46$ (0.35 due to bulk excitations and 0.11 due to surface excitations at the detection angle applied), is larger than the experimentally found values in Refs. [53,54] (0.36) and [55] (0.21). However, those

authors neglected the contribution of surface plasmons. The intrinsic plasmon contribution is also larger than the value found by the present authors in another work, where a different method has been applied, based on a series of spectra of oxidised Mg samples [71]. However, in that work the results depend on simplifying assumptions made about the oxidation behaviour of Mg. Steiner et al. [53] suggested that a simple power law, $b_n = b^n$, would describe the intensities of subsequent intrinsic plasmon peaks better than the Poisson law. In this work however, fitting the Mg 2p spectrum using the power law instead of the Poisson law yielded a 35 % larger value for χ^2 .

No values of A_{Ke} and D_s for Mg have been found in literature. The value found for D_s implies that the surface region, where physical and chemical properties differ from the bulk properties, extends over ~ 2 atomic layers in (sputter-cleaned) polycrystalline Mg. This value agrees well with the value Kwei et al. reported for Cu and Ni: they calculated that the cross section gradually changes from surface to bulk over a depth of ~ 0.8 nm.

2.5. Conclusions

For the first time the intrinsic and extrinsic as well as surface and bulk contributions to a Mg 2p XPS spectrum including the plasmon peaks have been unravelled completely. This has been achieved by using physically realistic functions to describe the different contributions, by considering the material as a bulk substrate covered with a surface layer of the same material, but with different electronic properties, and by using a suitable background calculation method. A total intrinsic contribution of 46 % relative to the main peak intensity has been found to be contained in the plasmon peaks. The thickness of the surface layer has been found to be ~ 2 atomic layers.