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Dielectric description of the angular dependence of the loss structure in core level photoemission

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This is a study on the validity of the previously published semi-classical dielectric response model description of the electron energy losses observed in X-ray photoelectron emission [A. Cohen Simonsen, et al., Phys. Rev. B 56 (1997) 1612]. In particular, we study the loss structure corresponding to Cu 2p and Fe 2p photoelectron emission from pure copper and iron samples for several emission angles. We have chosen these core level emissions because they have different natural width and asymmetrical line shape. It is found that both the total intensity below the main photon excited peaks and the dependence of particular surface loss structures (with respect to both shape and intensity) with the angle of emission is well reproduced by the dielectric model.

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1. Introduction

X-ray photoelectron spectroscopy (XPS) is today the most widely used technique for chemical surface analysis. It is routinely applied to study electronic structures, chemical bonds and the quantitative elemental composition of the surface [1].

To get the full potential of XPS it is necessary to have models that describe the effects which are responsible for the energy distribution of the detected electrons. This is a complex problem because a number of physical phenomena are involved. These include energy loss due to transport of the electrons out of the solid, surface excitations and energy loss processes which take place after the photoelectron has left the surface due to interaction with its image charge, shake up processes that take place due to the interaction of the core hole with the surrounding electrons of the solid, and purely quantum mechanical effects like multiplet splitting and life time broadening. Models have been suggested for routine analysis of the background of inelastic electrons in XPS [2]. These models are based on a physical model of the energy loss processes and they describe with reasonable accuracy the changes in energy distribution of emitted electrons which are caused by differences in the atom depth distribution. This is therefore a rather precise method to determine the depth distribution of atoms and thus to characterize the surface nano-structure and it is widely applied for this. But it is insufficient to get detailed information on the electronic excitations in the photo excitation process.

To be able to describe the effects of the abovementioned energy loss phenomena, it is necessary to apply a more involved model. In the past, several model calculations of energy loss in XPS have been done from first-principles quantum-mechanical descriptions [3–6]. These models have been extremely valuable to enlighten the fundamental mechanisms behind the photo-excitation process. But the complexity of this approach makes it impractical for calculations other than for the free-electron-like solids.

To get a more practical and manageable model for XPS, we proposed a semi-classical dielectric response model [7,8] in which the interaction between the time-varying electric fields from the charges (i.e. the moving photoelectron and the static core hole) and the electronic states of the solid, with the boundary conditions imposed by the surface, are described by the dielectric function of the material. This is a one-step model where the effects along the full trajectory from the point of excitation in the solid to the electron spectrometer are calculated and it thus includes contributions from interference between the effects. With this model, extensions beyond the nearly free-electron-like materials are straightforward because the only input in the calculations is the dielectric function of the material.

Within this semi-classical model, there are two origins to the energy-loss structure. The first is due to the sudden creation of an electric field from the core-hole which appears as a result of photo excitation of the core electron. This field excites valence electrons and the excitation energy is lost by the photoelectron. The
second contribution is due to the time and space varying electric field from the moving photoelectron which also causes excitations and thereby energy loss and such processes occur even after the photoelectron has left the surface due to the interaction of the photoelectron with its image charge. The energy loss processes corresponding to these two contributions are usually called “intrinsic” and “extrinsic” excitations, respectively, although a strict separation is not possible because the effects interfere. Recently this model was used to calculate the combined effects of core-hole and surface excitations [9] on measured XPS peak intensities.

We have previously presented a similar semi-classical one-step model for quantitative interpretation of the energy loss observed in reflection electron energy loss spectroscopy (REELS) [10,11]. This model was found to quantitatively account well for the observed changes in energy loss structure for a wide range of geometries and for energies down to at least 200 eV [12,13]. The model has been widely applied to determine the complex dielectric function ε(k,ω) for several materials as well as for nano-meter thin films from analysis of a REELS spectrum [14].

The validity of the semi-classical XPS model was previously tested by its ability to describe photoelectron spectra from free electron like materials and it was found that it gives a good quantitative description of the dependence of the Al 2p and Si 2p spectra on photon energy and angle of emission [7,8,15–17]. In these previous tests on the accuracy of the XPS model, we focused on the first plasmon excitation loss. The loss structure of Al and Si consists of a distinct plasmon loss peak which however is not typical for most materials which have much wider energy loss structures.

In the present paper, we therefore study the validity of the XPS model for materials with a more complex loss structure than those with free electron like behavior. In particular we present the interpretation of the loss structure in the XPS spectra of Cu 2p and Fe 2p from pure copper and iron samples. We have chosen these materials because they do not have distinct loss features, and because the Cu 2p and Fe 2p peaks have different natural width and asymmetrical line shape emission. Cu has a filled 3d shell while Fe has a partially filled 3d shell. It is therefore expected that the exchange interaction gives rise to a strong multiplet splitting for Fe 2p while this will be absent for Cu 2p. The shape of the spectra will depend strongly on the angle of emission and we will in particular study the ability of the XPS model to accurately describe this variation.

We have recently developed a user-friendly software package named QUEELS-XPS which provides facilities to do the calculations in the present paper [18]. The software is free for non-commercial use.

### 2. Experiments

High purity, mirror-like polished polycrystalline Cu and Fe samples were studied after 3–5 keV Ar⁺ sputter cleaning. The base pressure of the apparatus was 3 × 10⁻¹⁰ mbar. Angle resolved Cu 2p and Fe 2p spectra of these samples were acquired with a VG-ESCALAB200 electron energy analyzer for 0°, 60°, 75°, and 82° emission angles. Unmonochromatized Al-Kα radiation was used to excite the Cu 2p and Fe 2p electrons which end up with kinetic energy of about 550 eV and 770 eV, respectively. More detailed description of the experiments can be found in [19].

### 3. Dielectric description of energy losses of electrons traveling nearby a surface

Details of the semi-classical dielectric response model for XPS and REELS can be found in [7,8,11,18] and will only be described briefly here.

In the XPS model it is assumed that an electron–hole pair (both considered as point charges) is created at a given depth x₀ inside a semi-infinite medium, characterized by a dielectric function ε. The core-hole is assumed to be static with infinite lifetime, i.e. it remains at a fixed position forever after being created at time t=0. The photoelectron escapes from the semi-infinite medium with a velocity v along a rectilinear trajectory. Within this model, one defines an effective inelastic scattering cross section Kₑₑₑₐ(E₀,hν;ω,θ,x₀) in terms of the induced potential, Kₑₑₑₐ(E₀,hν;ω,θ,x₀) is defined as the average probability that a photoelectron excited at depth x₀ with energy E₀ shall lose energy hν per unit energy loss and per unit path length while traveling in the specified geometry. The energy loss includes processes that take place after the electron has left the surface but the average is taken over the path length traveled inside the solid, i.e. x=x₀/cos θ, where θ is the angle to the surface normal. Neglecting angular electron deflection one gets [7]

\[
K_{\text{eff}}(E_0, h\nu; \varepsilon, \theta, x_0) = \frac{2}{(2\pi)^3 h^2 \omega x_0} \times \Im \left\{ \int dt \int d^3r \rho_e(r, t) \left[ \int d^3k \begin{pmatrix} -2r & \epsilon(\omega) \end{pmatrix} \Phi_{\text{ind}}(k, \omega; \varepsilon, \theta, x_0) e^{i[k \cdot (r - v t)]} \right] \right\}
\]

where \(\rho_e(r,t)\) is the charge density of the escaping photoelectron, and \(\Phi_{\text{ind}}(k, \omega; \varepsilon, \theta, x_0)\) the Fourier transform of the potential induced by the escaping photoelectron and the static core-hole in the semi-infinite medium. The expression for \(\Phi_{\text{ind}}(k, \omega; \varepsilon, \theta, x_0)\) is quite involved and can be found in [7].

In an experimental XPS measurement, there will be contributions from photoelectrons excited at a range of depths. It is therefore necessary to account for their relative contributions to the spectrum. This is done by introducing an averaged effective cross section \(K_{\text{eff,av}}\) [7,8] with a weighted average over the total path-length \(x\) traveled by the electron inside the medium which takes into account the path-length distribution of the electrons having suffered only a single inelastic scattering event.

It should be noted that this model, of course, does not include any effects which are part of the initial photo-excitation process. It only evaluates those energy loss processes which are due to the static core-hole, the moving photoelectron, and the surface. It can therefore be used to isolate those contributions to the spectrum as is done below.

### Table 1

<table>
<thead>
<tr>
<th>j</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(h\omega_j) (eV)</td>
<td>(A_j) (eV²)</td>
</tr>
<tr>
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<td>4.7</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>7.6</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>11.0</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>18.5</td>
<td>56</td>
</tr>
<tr>
<td>5</td>
<td>27</td>
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<td>60</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>130</td>
</tr>
</tbody>
</table>

where the contributions, strength, width, dispersion strength, and energy position of the jth oscillator. The parameters shown in Table 1 for Cu and Fe [20] were determined by analysis of experimental REELS spectra using the QUEELS-\(\varepsilon(k,\omega)\)–REELS software package [21].
3.1. Electron inelastic scattering cross section for electrons traveling in REELS geometry

Although in this work we are dealing with the interpretation of the loss structure in X-ray photoelectron emission, it is worth to first briefly discuss the extrinsic loss structure that is excited for electrons traveling in copper and iron with the same kinetic energy as that considered later in the angle resolved XPS experiments.

Fig. 1 shows the cross sections $K_{\text{eff,av}}$ calculated for electrons traveling in Cu with 550 eV (top) and in Fe with 770 eV (bottom) in reflection geometry. The electron is impinging normal to the surface and the cross section is shown for several exit angles $\theta_{\text{out}}$. These calculations are done within the dielectric response model for REELS [11,21]. Also shown in Fig. 1 are the corresponding cross sections evaluated for electrons traveling in an infinite medium. The kinetic energies have been chosen because they correspond to those of the excited Cu 2p and Fe 2p photoelectrons that will be discussed below.

Note that the cross sections evaluated for electrons traveling in reflection geometry depend strongly on the emission angle. In fact, their intensity for energy losses lower than 20 eV are strongly enhanced as the emission gets more glancing. This is due to the larger relative paths that the electron travels close to the surface. Thus, in both cases two main peaks can be associated with surface losses due to electron transport in these materials. For Cu the losses are primarily below 10 eV with peaks at 5 and 7 eV, while for Fe the loss structure is mainly below 20 eV with two main surface losses at 7 and 14 eV. Interpretation of these features in relation to the electronic structure of the corresponding materials has been made in the past [22,23].

Theoretical description of the XPS spectra

A measured XPS spectrum can be considered as the addition of the contribution from electrons that have undergone an increasing number of loss events [26]

$$J(E) \propto F(E) + \lambda \int E' F(E') K_{\text{eff,av}}(E_0, E' - E) dE' + \sum_{n=2}^{\infty} J_n$$

where $F(E)$ is the primary excited spectrum, $K_{\text{eff,av}}(E_0, E' - E)$ is the averaged effective differential inelastic scattering cross section for
energy loss \( E' - E \) evaluated for electrons of \( E_0 \) kinetic energy, and \( \lambda \) is the inelastic electron mean free path. The last term describes the contribution from multiple scattered electrons to the spectrum. Thus, \( J_2(E) \) represent double scattering contribution, \( J_3(E) \) triple scattering contribution, and so on. \( K_{\text{eff},\lambda}(E_0,E' - E) \) is calculated within the XPS dielectric model [7,18] described above and shown in Fig. 2.

The function \( F(E) \) accounts for the complete originally excited spectrum, created at time zero due to the photon excitation process. All quantum mechanical effects related to this event have to be included in \( F(E) \). This includes effects like core-hole lifetime broadening, spin orbit splitting, multiplet splitting and other excitations related to the photoexcitation process, and excitation effects due to the presence of X-ray satellites contributing to the excited spectrum.

A symmetric mixed Gaussian–Lorentzian function described in [27] was used to simulate \( F(E) \) in the case of Cu 2p emission. On the other hand, an asymmetric Gaussian–Lorentzian mixed function described in [27] was used to simulate \( F(E) \) for Fe 2p emission. We have considered one single peak for each spin–orbit contribution (2p_{3/2} and 2p_{1/2}) with intensity ratio of 2 between them. The satellites of the Al-Kα X-ray source are also included as scaled replica of the two peaks (see Figs. 4 and 7). For each of the materials, Cu and Fe, the shape of \( F(E) \) were chosen so the calculated \( J(E) \) match the experimental \( J(E) \) spectrum acquired at normal emission. This \( F(E) \) was then used for all emission angles so no further fitting was made for the remaining calculations.

4. Results and discussion

Fig. 3 (top) shows experimental spectra of Cu 2p photoelectrons for several emission angles. Intensity which is not related to the peaks was removed by subtracting a straight line which was fitted to the intensity on the high energy side of the Cu 2p_{3/2} peak.

Afterwards the peaks were normalized to have the same intensity at the Cu 2p_{3/2} peak energy. Note that the main effect is an increasing inelastic background intensity on the low kinetic energy side of the peaks, as the emission angle is increased from normal emission \((0°)\) to more glancing emission. We observe that the spectra acquired at 60°, 75°, and 82° emission angles have about 15, 45, and 60% more intensity respectively in the background corresponding to the multiple scattered electrons compared to the spectra acquired at normal emission.

More detailed information on the angular dependence of the Cu 2p emission can be obtained by subtracting the spectrum acquired at normal emission \((0°)\) from all the rest. Fig. 3 (bottom) shows these difference spectra. This representation stresses the angular effects in an energy region of 10–20 eV below the main Cu 2p emission. A clear loss peak becomes visible in the energy range 4–9 eV below each of the main Cu 2p peaks. The maximum of this loss structure shifts from 5.7 to 7.8 eV as the emission angle increases from 60° to 82°. This is most clearly seen in the loss structure below the Cu 2p_{3/2} peak. Besides, it gets sharper as the emission angle increases. For the spectrum acquired at 82° emission angle, it seems that this loss feature is composed of two peaks at around −4 and −7 eV, respectively.

Note that background subtraction of the angular effects seen in the XPS spectra here was previously achieved [19] by empirically introducing a surface and a bulk cross section and the shape and relative intensities of these were parameterized by fitting to experiments. This gave a good practical method to account for both surface and bulk contributions to the background signals.

As was mentioned in the previous section, we want here to investigate to what extent the dielectric XPS model to evaluate loss structures in XPS is able to predict effects in angular dependent XPS photoemission. Thus, we have simulated Cu 2p emission spectra and compare the results to experiments.

Fig. 4 (top) shows calculated \( J(E) \) spectra corresponding to Cu 2p emission, according to the description presented in the previous section. The primary excitation spectrum \( F(E) \) (shown as a dashed line) is chosen such that the simulated \( J(E) \) matches the experimental Cu 2p spectrum acquired at normal emission. Then, the rest of the spectra corresponding to other emission angles were calculated by Eq. (2) using the same \( F(E) \) spectrum, and the \( K_{\text{eff},\lambda}(E) \) corresponding to the particular emission angle (cf. Fig. 2).

The trend in the simulated spectra in Fig. 4 is similar to that in the experimental results in Fig. 3. We observe (as in the experimental case above) that the inelastic background far from the main Cu 2p peaks increases with the angle of emission. To stress the angular effects predicted by the XPS dielectric model description of the photoemission process Fig. 4 (bottom) shows the corresponding difference spectra. The shape of these is very similar to those in Fig. 3 and even on an absolute scale, the intensity of the difference spectra deviate by only ~20% from the experiment. We observe that in the difference spectra appears a loss peak at 6.4 eV from the main Cu 2p emissions with a shoulder at lower energy losses. Additional broader features develop in the simulated spectra at about 16.0 eV from the main Cu 2p peaks.

The loss features will to some extent be smeared out by the contribution from multiple scattered electrons. Therefore, to clarify the origin of these features Fig. 5 (top) shows simulated spectra including the primary spectrum plus the first loss contribution. This corresponds to the first two terms in Eq. (2). It is observed that the first loss mostly contributes to the total spectra in an energy region of up to ~10 eV below the main Cu 2p peaks. This is more evident in the corresponding difference spectra shown in Fig. 5 (bottom). Note that in this energy range the first loss accounts for about 80% of the difference spectra observed in the total spectra in Fig. 4. Thus, the single scattered electrons account for the main differences in the angular dependence up to ~10 eV below the main Cu 2p peaks. Note
also that the difference spectra in Fig. 5 are 0 at about 10–20 eV from the main Cu 2p peaks, so the feature at about 16 eV (Fig. 4) must be due to multiple scattered electrons.

A similar analysis to that presented for Cu 2p has been performed for the Fe 2p emission from a clean Fe polycrystalline surface. Fig. 6 (top) shows the measured Fe 2p spectra, and Fig. 6 (bottom) the corresponding difference spectra, acquired and treated in a similar way as for the Cu 2p spectra in Fig. 3. Several differences are obvious in comparison to the previous Cu 2p analysis. First, the kinetic energy of the Fe 2p photoelectrons is higher for the Fe 2p than for the Cu 2p emission due to the lower binding energy of the Fe 2p core levels. Second, the widths of the main Fe 2p peaks are larger than in the case of the Cu 2p emission. Besides, the Fe 2p peaks are asymmetric while the peaks in F(E) for Cu 2p are strictly symmetric. This is primarily ascribed to the larger lifetime broadening and the complex multiplet splitting configuration of Fe in comparison to Cu.

The first evident result is that the intensity of the background increases on the lower kinetic energy side of the main Fe 2p peaks, as the emission angle is increased. We observe a 20%, 40%, and 60% increase in the background intensity 80 eV away from the main Fe 2p lines for the spectra acquired at 60°, 75° and 82° with respect to that measured at normal emission, respectively. In this case, no other features are observed in the difference spectra, apart from the increasing background with the emission angle.

Fig. 7 (top) shows calculated F(E) spectra corresponding to Fe 2p emission, according to the description presented in the previous section, using the XPS cross section shown in Fig. 2 (bottom) in a similar manner as for the Cu analysis described above. The primary
excitation spectrum $F(E)$ (shown as a dashed line) is chosen so the simulated $J(E)$ matches the experimental Fe 2p spectrum acquired at normal emission. Then, the rest of the spectra corresponding to other emission angles were calculated with the same $F(E)$ spectrum and the $K_{\text{eff,}\alpha\nu}$ of the particular emission angle (cf. Fig. 2). Fig. 7 (bottom) shows the corresponding difference spectra. The shape is quite similar to the experiment without any distinct features and the absolute intensity deviates by only $\sim$25% from experiment.

In the following we are going to make a critical discussion of several aspects related to the approximations of the theoretical dielectric model used in this paper to describe the electron energy losses of photoelectrons.

Elastic scattering effects are neglected. It is assumed that the electrons follow straight line trajectories. In a previous work on the elastic scattering description of electrons traveling in a reflection geometry [28] nearby a surface we found that this approach is valid for the majority of the electrons that contribute to a REELS experiment. We expect that elastic scattering effects are weaker in the case of XPS emission than in the case of REELS experiments, so elastic scattering can be neglected to a good approximation.

The assumptions of the dielectric response model used to evaluate inelastic scattering cross sections in a photoemission process were briefly outlined above. The model assumes that at time equal zero a static hole and an electron with a given kinetic energy and momentum are created. Before the electron starts to move (due to its kinetic energy) no losses are produced. As the electron starts to move away from the hole, a field builds up nearby the surroundings of the site where the electron–hole pair was created. The interaction of the time varying field set up by the moving electron and the static hole creates excitations of electrons in the solid. In the present model this interaction is evaluated within a dielectric response description. This description does not take into account local variations on the atomic scale in the electronic structure. Furthermore we should mention that with the chosen expansion in Eq. (1) the dielectric function may not be accurately described for energy loss $<1$–3 eV. This is not a limitation to the model because the finer details in this energy range can in principle be modeled by adding more oscillators in the range of small energy loss than was done here (see Table 1).

Besides, several aspects of the photo-excitation process are also neglected. Thus, the effect of finite core-hole lifetime, spin–orbit and multiplet splitting are purely quantum mechanical effects which are not described within this semi-classical dielectric response model. The latter is clearly seen in the resulting $F(E)$ spectra which are strictly symmetric for Cu but highly asymmetric for Fe. Thus Cu has a filled 3d shell while Fe has a partially filled 3d shell and exchange splitting due to the unpaired d electrons in Fe is expected but this will be absent for Cu.

We should also mention that in Eq. (2) we have assumed that the same inelastic scattering cross section $K_{\text{eff,}\alpha\nu}$ can be used to account not only for the first scattering but also for the multiple inelastic scattered electrons. This is a rough approximation since the multiple scattered electrons are expected to be much less affected by the electron–hole interaction. However, the multiple scattered electrons are convolutions of cross sections and the main effect of these electrons is to smear out any structures and they do not create any new distinct features in the spectra. In fact, its main effect is to contribute to the raising background away from the main Cu 2p and Fe 2p emissions.

Despite all the approximations mentioned above, the agreement between the observed experimental and simulated behavior of the Cu 2p and Fe 2p emissions can be considered as excellent.

The present analysis allows evaluating primary excited spectra, i.e. emission spectra free from effects due to the interaction of the core hole and the transport of the photoelectron out of the solid. Thus, no artificial background subtraction is needed to isolate the primary excited spectrum $F(E)$ of the material under study to interpret its electronic structure [29,19]. This kind of analysis is expected to be helpful for quantitative interpretation of features (shake-ups, multiplet splitting, surface and bulk plasmons) appearing in XPS spectra. The procedure of analysis described in this paper may prove to be particularly useful when used in combination with atomic, crystal field, and charge transfer multiplet calculations characteristic of the material and core level under study [30].

5. Conclusions

It is found that a semi-classical dielectric response description of the energy losses observed in XPS [7,18] is able to reproduce not only the kinetic energy and angular dependence of photoemitted electrons in free electron like materials [8,15] but also that of transition metals. It is found that the shape and absolute intensity on the low energy side of the photoemitted Cu 2p from copper and Fe 2p from iron as well as the dependence of the surface and bulk loss structures on the angle of emission are well reproduced by the dielectric model.

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