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LMM Auger primary excitation spectra of copper

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ABSTRACT

The shape and intensity of measured Auger peaks are strongly affected by extrinsic excitations due to electron transport out of the surface and to intrinsic excitations induced by the sudden creation of the two static core holes. Following a method developed for XPS in a previous work [N. Pauly, S. Tougaard, F. Yubero, Surf. Sci. 620 (2014) 17], we have calculated the effective energy-differential inelastic electron scattering cross-sections, including the effects of the surface and of the two core holes, within the dielectric response theory by means of the QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS). The Auger spectra are then modeled by convoluting this energy loss cross section with the primary excitation spectrum that accounts for all effects which are part of the initial Auger process, i.e. L–S coupling and vacancy satellite effects. The shape of this primary excitation spectrum is fitted to get close agreement between the theoretical and the experimental spectra obtained from X-ray excited Auger electron spectroscopy (XAES). We have performed these calculations of XAES spectra for various LMM Auger transitions of pure Cu ($L_3M_{45}M_{45}$, $L_3M_{23}M_{45}$, $L_3M_{23}M_{23}$ and $L_2M_{45}M_{45}$ transitions). We compare the resulting primary excitation spectra with theoretical results published in the literature and obtain reasonable quantitative agreement. In particular, we extract from experimental spectra quantitative intensities due to Coster–Kronig, shake-off and shake-up processes relative to the intensity from the "normal" Auger process.

1. Introduction

Auger electron spectroscopy (AES) is currently a widely used characterization technique for probing the chemical and compositional properties of solid surfaces [1]. To perform practical quantitative AES, it is necessary to know specific parameters as ionization cross sections, electron back-scattering factors and Auger transition probabilities.

As for Auger transition probabilities, calculations have been available for a long time [2–4] but good agreement with experimental data was up to now never achieved. Note that the identification and quantification of Auger transitions is in general a very involved task because, in practice, the "normal" Auger emission after a photoemission process often overlaps with other competing Auger processes as for example the Auger decay in the presence of a spectator vacancy after a Coster–Kronig transition or other Auger processes where shake-up or shake-off states participate in the process [4,5].

Even recently, experimental determinations of Auger transition probabilities from X-ray excited Auger Electron Spectroscopy (XAES) were performed [6,7] but possibly their accuracy is poor due to the procedure, namely Shirley's method [8], used to carry out the background subtraction, i.e. the removal of intensity corresponding to energy losses due to inelastic scattering events experienced by the electrons after their initial excitation.

Indeed, it was previously shown [9] that background subtraction methods not only from Shirley [8] but also from Tougaard [10] (which intends to only correct for extrinsic excitations) do not take into account intrinsic losses, namely excitations due to the sudden creation of the static core-hole and the associated electric field, but only extrinsic excitations that take place during the photoelectron transport process which are due to the time and space varying electric field from the moving photoelectron. This fact blurs attempts to rigorously compare theoretical and XAES experimental results for Auger transition probabilities.

Recently a method was proposed [11,12] to determine the primary excited spectrum $F(E)$ (which accounts for all contributions that are part of the initial photoexcitation process) from a measured experimental XPS spectrum as well as the full simulated XPS spectrum. This method is based on a convolution of the energy-differential inelastic electron scattering cross-section for XPS, K_{sc}^{XPS}, including both extrinsic and intrinsic excitations, with the primary excitation spectrum, $F(E)$, which is considered as an input in the calculations. The energy loss cross section, K_{sc}^{XPS}, was determined with the QUEELS-XPS software (QUantitative

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analysis of Electron Energy Losses at Surfaces for XPS) [13,14] which is based on the semiclassical dielectric response model [15,16].

In the present work, we show that the QUEELS-XPS software can also be used to calculate the energy-differential inelastic electron scattering cross-section, K_{sc}^{Auger}, valid to describe the electron transport related to an Auger emission process by assuming two static core-holes instead of one. Then, using the same procedure as in Refs. [11] and [12], we have modeled several XAES spectra of copper (more specifically the $L_3M_{45}M_{45}$, $L_3M_{23}M_{45}$, $L_3M_{23}M_{23}$ and $L_2M_{45}M_{45}$ transitions) and consequently obtain the full $F(E)$ primary excited spectra including all the terms contributing to each Auger cascade (terms resulting from L–S coupling of 2 or 3 holes) following the photoexcitation process. This analysis allows to quantify the relative Auger transition probabilities of the individual L–S coupling terms and also the relative importance of the relaxation processes contributing to the measured Auger spectra. The obtained results are compared with theoretical calculations published in Refs. [3] and [4].

In the next section we describe the model used in the QUEELS-XPS software as well as the procedure followed to obtain the primary excitation spectra $F(E)$ of the Auger transitions. The resulting contributions to $F(E)$ will then be compared to theoretical calculations for each individual Auger cascade.

2. Theoretical model

2.1. QUEELS formalism

The model implemented in QUEELS-XPS [13–15] is based on the surface reflection model [17] which describes the interactions of electrons with semi-infinite media in terms of the dielectric properties of the bulk material and incorporates the effects of the surface (when the electron travels both in the solid and in the vacuum), of the static core-hole(s) created during the photoionization process, as well as interference between these effects. The QUEELS-XPS formalism has been abundantly described in Ref. [15] and numerous examples of its validity have been reported in the literature [11,16,18,19] when one core-hole is considered, i.e. for XPS applications. To our knowledge, only one study [20] has been carried out for two core-holes, i.e. for Auger spectra with this model, and again a good agreement between theory and experiment was found. We only describe here the basic elements of the model.

We study here the case of an Auger cascade following the photoexcitation process and thus we consider an electron–hole-hole triplet created at a depth x_0 below the surface of a semi-infinite medium characterized by its dielectric function $\epsilon(\mathbf{k}, \omega)$. The electron travels along a straight line with velocity v, energy E and angle θ with respect to the surface normal, while the core holes are stationary with infinite lifetime. Within this model, the effective inelastic electron scattering cross section $K_{eff}^{AES}(E, \hbar\omega, x_0, \theta)$ is defined as the average probability that the electron, excited at depth x_0, loses an energy $\hbar\omega$ per unit energy loss and per unit path length traveled inside the solid (the *AES* in the expression of K_{eff} distinguishes this from the similar expression K_{sc}^{REELS} valid for a REELS experiment where the static core-hole is absent [21] and K_{sc}^{XPS} for XPS calculations with one core-hole).

The effective cross section, $K_{eff}^{AES}(E, \hbar\omega, x_0, \theta)$, is calculated for a single electron trajectory and it therefore depends on the depth x_0 where it is excited, but in XAES experiments electrons that contribute to the measured spectrum originate from a wide range of depths. Thus for comparison to experiments, it is necessary to perform a weighted average of $K_{eff}^{AES}(E, \hbar\omega, x_0, \theta)$ over all path lengths x traveled by the electrons which contribute to the spectrum with a weight function defined as the path-length distribution function for those electrons that have only undergone a single inelastic collision [15]. This results in the inelastic scattering cross-section $K_{sc}^{AES}(E, \hbar\omega, \theta)$ including bulk, surface and core hole effects as well as interferences between these effects.

We emphasize that the only input in the model to determine $K_{eff}^{AES}(E, \hbar\omega, x_0, \theta)$ and thus $K_{sc}^{AES}(E, \hbar\omega, \theta)$ is the dielectric function of the medium $\epsilon(\mathbf{k}, \omega)$ or, more precisely, the energy loss function (ELF) Im $\{-1/\epsilon(\mathbf{k}, \omega)\}$. To evaluate this latter, we consider as a model the expansion in Drude–Lindhard type oscillators [22]

$$\mathrm{Im}\left\{-\frac{1}{\epsilon(\mathbf{k},\omega)}\right\} = \sum_{i=1}^{n} \frac{A_i \hbar\gamma_i \hbar\omega}{\left(\hbar^2\omega_{0ik}^2 - \hbar^2\omega^2\right)^2 + \hbar^2\gamma_i^2\hbar^2\omega^2}\theta(\hbar\omega - E_G) \quad (1)$$

with the dispersion relation:

$$\hbar\omega_{0ik} = \hbar\omega_{0i} + \alpha_i \frac{\hbar^2 k^2}{2m}. \quad (2)$$

A_i, $\hbar\gamma_i$, $\hbar\omega_{0ik}$ and α_i are the strength, width, energy and dispersion of the ith oscillator, respectively and the step function $\theta(\hbar\omega - E_G)$ is included to describe the effect of the energy band gap E_G present in semiconductors and insulators. For the material studied in this work, namely copper, the parameters in the expansion are taken from Ref. [23].

Fig. 1 shows the resulting inelastic scattering cross-section K_{sc}^{AES} for electrons of 920 eV energy emitted from a copper sample at an angle $\theta = 15°$ with respect to the surface normal. This example has been chosen because it corresponds to one of the cases studied in this paper (Cu $L_3M_{45}M_{45}$ Auger electrons). Also shown in Fig. 1 are the inelastic scattering cross sections K_{sc}^{XPS}, K_{sc}^{REELS} and K_{inf} calculated for an electron of 920 eV energy traveling in the presence of one core-hole, in a REELS geometry (with 15° incidence and exit angles with respect to the surface normal) and in an infinite medium, respectively. We note that, for energy losses >30 eV the four spectra are similar, but for smaller energy losses, they deviate strongly. Thus, in comparison with K_{inf}, K_{sc}^{REELS} shows the effect of surface excitations, K_{sc}^{XPS} shows the additional effect of one static core-hole and finally K_{sc}^{AES} shows that two static core-holes further enhance the probability for energy loss.

2.2. Modeling XAES spectra

An XAES spectrum (as well as an XPS spectrum) can be seen as the addition of the contribution from electrons that have undergone an increasing number of energy loss events [24] and can be written

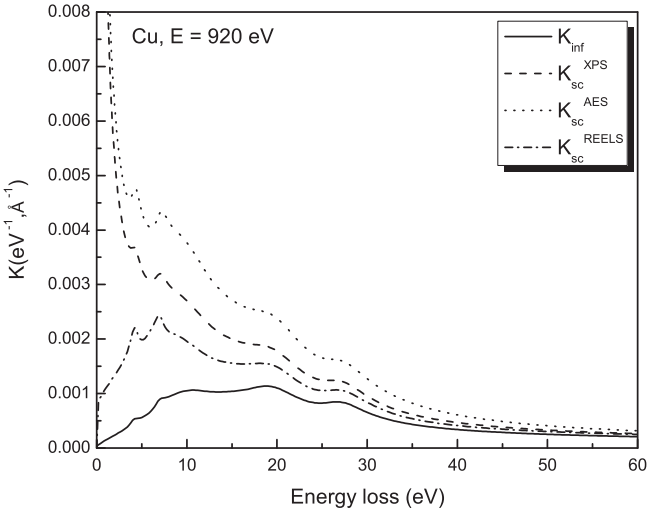

Fig. 1. $K_{inf}(E = 920\ eV, \hbar\omega)$ (solid line), $K_{sc}^{XPS}(E = 920\ eV, \hbar\omega, 15°)$ (dashed line), $K_{sc}^{AES}(E = 920\ eV, \hbar\omega, 15°)$ (dotted line) and $K_{sc}^{R\ EELS}(E = 920\ eV, \hbar\omega, 15°, 15°)$ spectra for Cu.