



Comparative study of the modelling of the spectral background of photoelectron spectra with the Shirley and improved Tougaard methods

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ABSTRACT

A comparative study for the fitting of x-ray photoelectron spectra using different background model functions is presented. Synthetically generated test spectra and measured spectra from an SrTiO₃ (STO) sample are fitted with the traditionally used Shirley background and the so-called improved Tougaard background calculated with four fit parameters of the inelastic electron scattering cross section. It was found that the results obtained with both methods are strongly different. In many cases the use of the Shirley background resulted in completely wrong component areas in spite of sometimes rather satisfying residual functions and *Abbe* criteria. In contrast, the improved Tougaard background gave excellent results for all wide range spectra including pronounced loss structures. The new source code of the current UNIFIT software (Version 2011 or higher) to calculate the Tougaard-background parameters was verified.

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1. Introduction

X-ray photoelectron spectroscopy (XPS) is a well established tool for quantitative surface analysis. Any data analysis procedure or software use for the modelling of spectra a superposition of a set of synthetically generated functions to describe the photoelectron lines of different components and a model function to approximate the spectral background.

While possible model functions for the photoemission lines are very well established [1], the treatment of the inelastically scattered electrons and the secondary electrons forming the background of the spectra is subjected to a continuous debate [2]. The most universal description of the spectral background in an analysis software would be a combination of all three major options, a polynomial of 3rd order, the Shirley background and the Tougaard background, in which an exclusive choice between the latter two has to be made [3].

The polynomial background is applied to model the general shape of the background function without the energy loss structures close to the primary photoelectron peaks, thus describing mainly the secondary electrons [3–6].

The so-called Shirley background was introduced to simulate loss processes generated from the photoelectrons by means of a constant loss function (Shirley step function) [7]

disregarding the special profile of the inelastic electron scattering cross section (IESCS) of the studied material. This approximation gives always increasing background intensity for increasing loss energies, thus distorting the real form of the energy loss function. As a consequence, only narrow scans can be simulated successfully.

The Tougaard background [2,8,9] was originally developed for transition metals, and includes the energy loss function based on the IESCS. This IESCS might be directly measured with electron energy loss spectroscopy (EELS) and then inserted into the data analysis. The first model to describe the energy loss processes was the two-parameter inelastic electron scattering cross section (2-PIESCS) available for most metals, their oxides, and alloys, also called universal cross section [10]. The introduction of a third parameter [11] allows the application of the Tougaard background also for polymers, semiconductors and free-electron-like solids (3-PIESCS). Tougaard derives the parameters of the IESCS models from comparison to experimental electron excited energy loss spectra.

But for most cases a perfect fit of photoelectron spectra with these fixed IESCS parameters recommended by Tougaard is not possible. It was shown recently [6] that the introduction of a four parameter IESCS (4-PIESCS) which is optimized during the fitting process gives more satisfying results for both the photoelectron peaks and the background including the IESCS. The significant differences of Tougaard background calculations with fixed or adjustable parameters and with the 2-PIESCS, the 3-PIESCS or the 4-PIESCS have been demonstrated already using real spectra of Au, PMMA and SiO₂ [6].

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In the present paper possible errors in the quantitative data analysis due to the application of the commonly used Shirley-type background will be shown using nine synthetic test spectra representing certain not uncommon scenarios. Only the usage of test spectra with well defined peak areas and peak positions can give correct results of the uncertainties of the spectrum fit [12,13]. A critical discussion of the deviations between the parameters of the fitted and the original synthetic spectra is given. The advantage of the improved Tougaard background using the 4-PIESCS with fitable parameters [6] in comparison to the Shirley-type background for these examples will be shown. Finally, the different background approaches are tested on SrTiO₃ (STO).

2. Theoretical details

2.1. Quantities for peak-fit evaluation and optimization

Generally, the analysis of XP spectra will be performed by comparing the experimentally determined peak shape with a theoretical model curve. The determination of the peak model parameters, e.g. peak position and intensity, proceeds iteratively by a nonlinear parameter estimation routine. As in most data analysis routines, also in the spectrum processing, analysis, and presentation software for XPS UNIFIT [14], the Marquardt-Levenberg algorithm [15] has been chosen in order to minimize the reduced chi-square $\chi^{2*}(\vec{p})$ [16] with the final set of peak parameters, characterized by the parameter vector \vec{p} :

$$\chi^{2*}(\vec{p}) = \frac{1}{N-P} \sum_{i=1}^N \frac{[M(i) - S(i, \vec{p})]^2}{M(i)} \quad (1)$$

with the measured spectrum $M(i)$ recorded at N distinct energy values corresponding to channel i , the synthesized model curve $S(i, \vec{p})$ and P independent parameters of the model function. In case of a calculation of the spectral background simultaneously to the peak fit, the model curve S can be described by

$$S(i, \vec{p}) = \sum_{j=1}^k SC_j(i, \vec{p}_j) + B(i, \vec{p}_B) \quad (2)$$

with k different species (peaks or components) SC_j with parameters \vec{p}_j , the spectral background B and the background fit parameters \vec{p}_B . The peak shape of the components SC_j are typically determined by a Lorentzian contribution L and a Gaussian broadening G (using either product, sum or convolution of L and G). In case of purely statistical noise the quantity $\chi^{2*}(\vec{p})$ should approach unity. Another quantitative measure describing correlations in the residuals and thus possible problems with the model function or the data quality is the so-called *Abbe* criterion.

The expectation value of the χ^{2*} should decrease towards or at least approach 1 in case of a good fit to spectra with random noise. The *Abbe* criterion [16] informs on correlation of adjacent residuals and thus on possible errors of the fit. The expectation value of the *Abbe* criterion is 1 in case of a good fit with statistically uncorrelated residuals if the residuals are determined only by random noise of the data. The *Abbe* criterion should approach zero for strong correlations among adjacent residuals and would indicate a poor fit. Anticorrelation of the adjacent residuals, as might be anticipated for mostly numerical errors is indicated by *Abbe* values exceeding 1. This should be considered during the discussion of the following results.

It is strongly recommended to include a normalized plot of the residual function $R(i)$

$$R(i) = \frac{S(i, \vec{p}) - M(i)}{\sqrt{M(i)}} \quad (3)$$

in the presentation of the measured data together with the optimized model curve $S(i, \vec{p})$ and the individual components [16]. A statistically distributed $R(i)$ may already be a strong hint for a successful fit with the chosen fit conditions. But the accuracy of the fitted parameters can only be evaluated by calculating the standard deviation of the fit parameters [16].

2.2. Modelling the spectral background

A polynomial of low order has been used to model the secondary-electron background. This polynomial background P_B describes the general form of the base line without the secondary loss electrons generated by the analyzed photoelectron peaks:

$$P_B(i, a, b, c, d) = a + bi + ci^2 + di^3. \quad (4)$$

The Shirley background $S_B(E)$ assumes a constant energy-loss function (Shirley step function) [7]. The Shirley background is defined by

$$S_B(E, e) = e \int_E^{E_2} S(E') dE', \quad e \geq 0 \quad (5)$$

with the model curve S . In case of a successful spectrum fit the model curve S represents the primary spectrum. The relation between the kinetic energy E and the channel i (used above) is given by $i = 1 + (E_2 - E)/SW$ with the lowest energy E_1 at the last channel of the spectrum, the highest energy E_2 ($E_1 \leq E_2$) at the first channel ($i = 1$) and the step width SW .

The Tougaard background T_B is defined by

$$T_B(E, B, C, C', D) = \lambda(E) \int_E^{E_2} K(E, T) M(E') dE' \quad (6)$$

with the energy loss $T = E' - E$, the inelastic mean free path λ (IMFP), and the probability $K(E, T)$ that an electron of energy E shall loose energy T per unity energy loss and per unit path length travelled in a solid. The product $\lambda(E) \cdot K(E, T)$ gives the inelastic electron scattering cross-section. We apply the 4-PIESCS [6] with the parameters B, C, C' and D :

$$\lambda(E)K(E, T) = \frac{BT}{(C + C'T^2)^2 + DT^2} \quad (7)$$

The presented background fit procedure allows all the parameters to vary freely or to be fixed at certain values.

The sum of the polynomial background P_B , the Shirley-type background S_B and the Tougaard background T_B gives the universal background defined by

$$B(E, i, \vec{p}_B) = P_B(i, a, b, c, d) + S_B(E, e) + T_B(E, B, C, C', D) \quad (8)$$

with the background-parameter vector \vec{p}_B depending on a, b, c, d, e, B, C, C' and D [6]. Of course, in order to describe a particular spectrum a meaningful choice of these parameters has to be selected. In particular, only one of both Shirley-type background S_B ($e \neq 0$) and Tougaard background T_B ($B \neq 0$) should be used in an actual analysis. This procedure has been implemented in UNIFIT 2012 [14] and was tested on both synthetic and real XPS spectra.

3. Generation of synthetic test spectra

In order to demonstrate the validity of the different background models for possible arrangements of overlapping peaks and loss structures, nine test spectra (TS1–TS9) were generated using an iteration procedure (Fig. 1 and Table 1). The test spectra shall simulate realistic photoelectron spectra with peak separations and intensity ratios which can model, e.g. spin-orbit-split core levels or appearance of core levels of different elements in the tail structure of others in combination with a typical loss structure. Because

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