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Peak shape analysis of core level photoelectron spectra using UNIFIT for WINDOWS

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Abstract Several approaches used in the peak shape analysis of core level spectra for the purpose of modelling of both peak shapes and background profiles will be discussed. A universal program is presented, which combines options for adequate modelling of the peak shapes and background, implementation of a successful numerical algorithm for an iterative non-linear parameter estimation procedure, and a flexible as well as convenient data handling. The performance of this program code is demonstrated by fitting a synthesized model spectrum. An example for analysis of a complex experimental spectrum is presented, too. An S 2p spectrum recorded from a MBT-treated pyrite surface is successfully analyzed using the presented software and is found to be characterized by five different S 2p contributions.

1 Motivation

The resolution and the sensitivity of photoelectron spectroscopy have been greatly improved since the development of the first electron spectrometers in the sixties [1–3]. While the resolution of the X-ray photoelectron spectra was initially restricted to the order of a few eV by the width of the exciting X-ray lines, nowadays energy resolutions ΔE in the order of a few 10 meV may be obtained in optimum cases by both taking advantage of high-resolution electron spectrometers and employing monochromatized synchrotron radiation. However, an adequate modelling of the experimental spectra by several different spectral components has remained a challenge all the time regardless of the achieved level of energy resolution. This is due to the facts that by far most XPS data still have been recorded with ΔE of about 0.5–0.8 eV and because higher resolution gives access to much more de-

tailed information, which again has to be distracted from the raw data. In particular, binding energies and intensities of spectrum components have to be derived for the identification of chemical species and quantification of chemical composition of investigated samples [1, 2]. In order to obtain the desired information from core level spectra, several computer codes have been developed in the past, which permit the numerical determination of the parameters of the theoretical peak models.

However, for practical applications of such data analysis software there is need for appropriate characterization of the spectra by adequate models, comfortable data handling, excellent numerical performance for fast calculations, and versatile opportunities for data transfer and representation. The typical advantages of commercially available software are comfortable handling and the extensive possibilities of graphics design. However, they often exhibit severe restrictions in data modelling. On the other hand, user-developed program codes are very often tailor-made for single spectrometers and special applications. In many cases they have been written for use by insiders only. In order to fill the above described gap, a program for the peak shape analysis of core level photoelectron spectra has been developed, tested and used by the group of the authors for years [4, 5]. The result is the software UNIFIT FOR WINDOWS presented here, which permits to solve several important problems in the evaluation of electron spectroscopical data and thus contributes to a better utilization of spectral information in XPS.

2 Numerical analysis of XPS core level spectra

2.1 General approach for peak shape analysis

Generally, the analysis of the experimental core level spectra will be performed by comparing the experimentally determined peak shape with a theoretical model curve. The theoretical curve has to be synthesized from contributions of several species as well as a background or baseline curve. The determination of the peak model

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parameters, e.g. peak positions and intensities, proceeds iteratively by a nonlinear parameter estimation routine. The Marquardt-Levenberg algorithm has been chosen very often in order to minimize χ^2 , because it has been well-documented and has been known to be very successful even for a less than optimum guess of the initial peak parameter set [6, 7]. The final set of peak parameters, characterized by the parameter vector p , will be taken from the minimum of $\chi^2(p)$, determined by the expression

$$\chi^2(p) = \frac{1}{N-P} \sum_i \left[\frac{M(i) - S(i;p)}{\sqrt{M(i)}} \right]^2 \quad (1)$$

with the measured spectrum $M(i)$ recorded at N energy values corresponding to channels i and the synthesized model curve $S(i;p)$, sampled at channels i in dependence on P varying parameter values. The term enclosed in brackets corresponds to the normalized residuals $R(i)$, which provide a weighted measure of the difference between fit curve and the data at each data channel or energy value. The normalization by the denominator ensures that every data channel enters with the same statistical weight. Neglecting this normalizing denominator would emphasize the data channels near the intensity maxima.

2.2 Modelling the peak shapes

Energy (E) distribution curves in photoelectron spectroscopy may be theoretically characterized by spectral functions, which take into account all the possible excitation processes in the sample of interest. In the majority of cases these spectral functions may be represented by a set of peaks, e.g. main line and satellites, multiplets, doublets or even single lines. The peak shapes are typically determined by a Lorentzian contribution due to the limited lifetime of the core hole state and a Gaussian broadening, mostly due to incoming radiation and the measurement process in the spectrometer. Gaussian contributions may also be related to thermal excitation processes. Chemical, structural, and electronic (by dopants) inhomogeneities in the surroundings of the emitting atoms often also contribute to Gaussian broadening.

Both the height-normalized Lorentzian function $L(E)$ (Fig. 1)

$$L(E) = \left\{ 1 + \left[\frac{E - E_0}{\beta} \right]^2 \right\}^{-1} \quad (2)$$

and the Gaussian function $G(E)$ (Fig. 1)

$$G(E) = \exp \left\{ -\ln 2 \cdot \left[\frac{E - E_0}{\beta} \right]^2 \right\} \quad (3)$$

are completely characterized by the peak parameters β , corresponding to 1/2 of the full width at half maximum (FWHM), and E_0 , the peak position.

Due to a more complex photoexcitation process most metal signals exhibit inherently asymmetric peak shapes, which may appropriately taken into account by substitut-

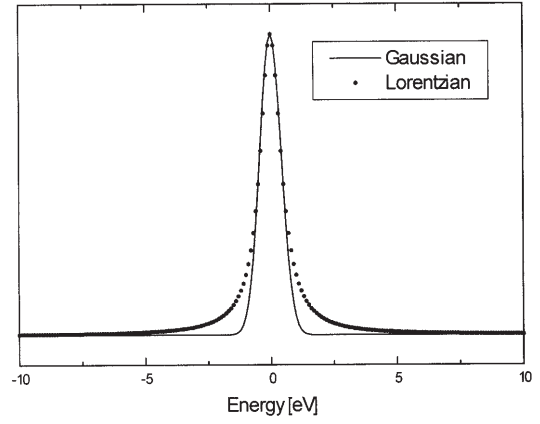


Fig. 1 Comparison of Gaussian and Lorentzian functions (line width = 1 eV)

ing the Lorentzian by the Doniach-Sunjc (DS) peak shape [8]. It may describe low-energy tails of the peaks, which are determined by the values of the so-called asymmetry parameter α . DS(E) is given here as

$$DS(E) = \beta \cdot \frac{\cos \left\{ \pi \frac{\alpha}{2} + (1 - \alpha) \arctan \left[\frac{E - E_0}{\beta} \right] \right\}}{[(E - E_0)^2 + \beta^2]^{\frac{1-\alpha}{2}}} \quad (4)$$

Notice that the Doniach-Sunjc peak shape transforms into a Lorentzian in the limit of $\alpha \Rightarrow 0$.

A frequently used approach to describe XPS core level lines has been the presentation of the peaks by a product of Gaussian and Lorentzian of the same width [2, 9]. In order to include asymmetrical lines too, the peak width parameter β may be substituted by $[\beta + \alpha(E - E_0)]$.

$$f(E) = h \cdot \left\{ 1 + M \cdot \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\}^{-1} \cdot \exp \left\{ (-1 - M) \cdot \ln 2 \cdot \left[\frac{E - E_0}{\beta + \alpha(E - E_0)} \right]^2 \right\} \quad (5)$$

Besides E_0 and β , the peak height h , the asymmetry index α , and the Lorentzian-Gaussian mixing ratio M have to be specified in this product function.

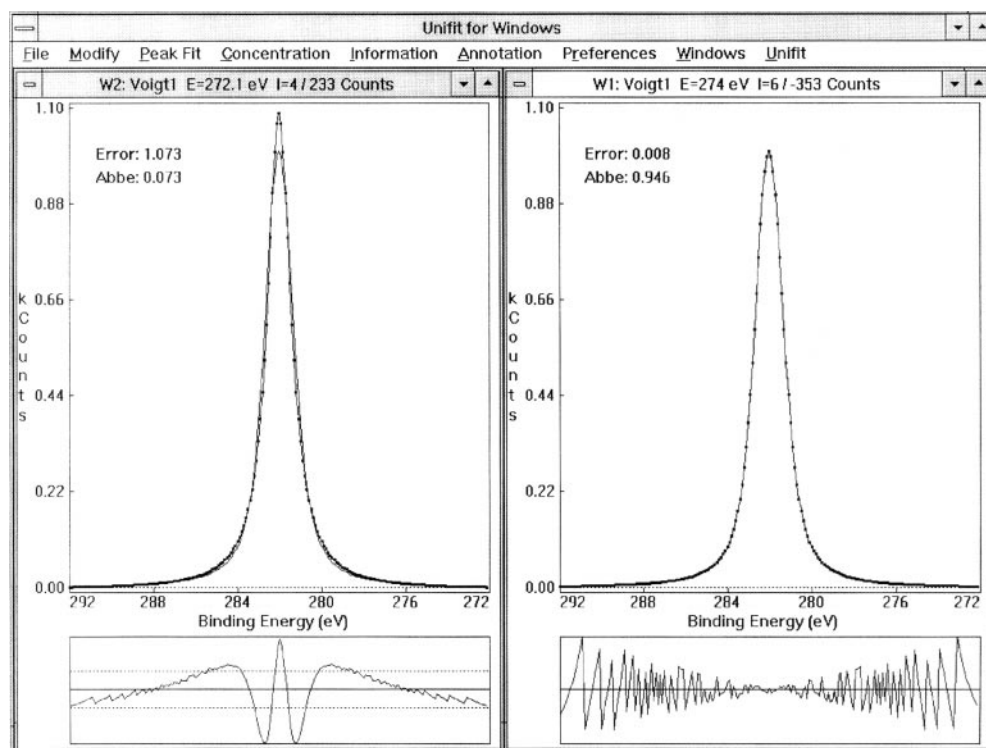
The advantages of application of this product-type peak shape model are the availability of analytical presentations of the partial derivatives of $f(E)$ with respect to the parameters, which are needed in the Marquardt-Levenberg algorithm to establish the Jacobi matrix, the correspondence of experimental FWHM and the analytical value of 2β , and finally a faster convergence of the iterative process as has been observed frequently.

A more adequate description of the core level line shape may be obtained by convoluting independent Gaussian and Lorentzian (or Doniach-Sunjc type) contributions rather than by simple multiplication [2, 3]. This convolution, the so-called Voigt profile, is defined as follows:

$$f(E) = f(L * G) = \int_{-\infty}^{\infty} L(E') G(E - E') dE' \quad (6)$$

Application of this peak shape model is highly recommended if the resolution is sufficient to derive physically meaningful peak shape parameters, e.g. different charac-

Fig. 2 Peak-fit results for a synthetic Voigt function (Gaussian and Lorentzian line width 1 eV each) using different fit procedures: product-type (left) and convolution-type (right) of Gaussian and Lorentzian functions



teristic peak widths of Gaussian and Lorentzian. This profile function and the corresponding derivatives with respect to the parameters have to be evaluated numerically, which makes the minimization process more time-consuming. However, sufficient computer power has not been a serious problem even for PCs, recently.

Notice however, that the peak fit of a Voigt profile by using a product-type model function results in slight but nevertheless significant deviations of systematic origin between fit and Voigt function. These deviations are particularly evident in cases if Gaussian and Lorentzian have comparable widths. This is demonstrated in Fig. 2 (left), which displays a Voigt profile, independently created using the commercial software MICROCAL ORIGIN¹, in comparison to a fit by a product-type model function. The systematic deviations become clearly evident in the presentation of the residuals. On the other hand, the generated profile has been excellently modelled by applying the convolution-type model shape for the fit to this Voigt profile (Fig. 2, right). The scatter in the corresponding residuals is clearly of non-systematic nature and essentially of numerical origin (due to the use of integer intensities).

2.3 Background modelling and treatment

The shape of the spectrum background or the baseline may be affected by inelastic energy loss processes, secondary electrons and nearby peaks [2, 3]. A polynomial of

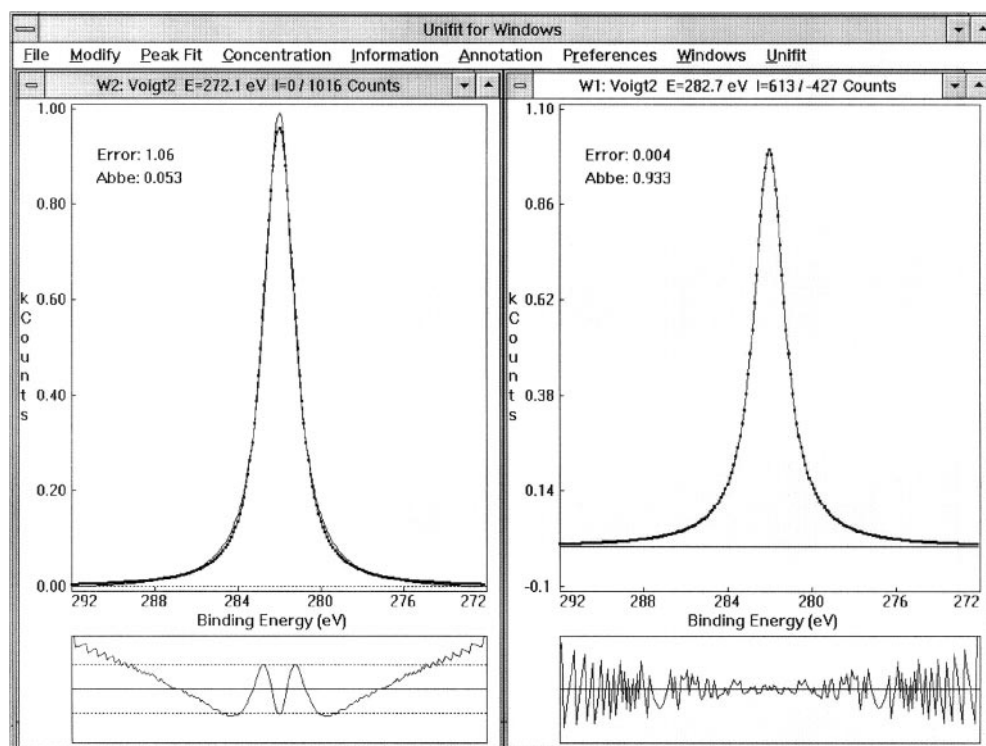
¹MICROCAL ORIGIN is a commercial software by Microcal Corporation.

low order has very often turned out to model the secondary electron background or the tails of closely neighbored peaks reasonably well. The Shirley-type step function $S(E)$ or the more advanced Tougaard background model $T(E)$ have been successfully used to characterize the inelastic loss processes of the photoelectrons within the sample [2]. The choice of an adequate model of the spectrum background will be determined by the physical and chemical conditions of the measurements and the significance of the related background to the information to be obtained [2, 3]. In brief, the rather simple linear background may be reasonably applied for spectra exhibiting small intensity differences between low energy and high energy sides of the peaks, e.g. of peaks derived from surface species, which are hardly affected by inelastic losses. The Shirley model assumes a constant energy loss function (Shirley step function). It has in many cases turned out to be a successful approximation for the inelastic background of core level peaks of buried species, which suffered significantly from inelastic losses of the emitted photoelectrons [2, 3]. The Tougaard background model has originally been developed for transition metals, and it includes a model shape of the energy loss function. The registration of a larger energy window towards lower kinetic energies or larger energy losses is recommended in case of the intended application of this background model [3].

A rather general approach for the characterization of the background in core level photoelectron spectra takes into account all these contributions, weighted accordingly by background shape parameters a – f :

$$U(E) = a + b \cdot E + c \cdot E^2 + d \cdot E^3 + e \cdot S(E) + f \cdot T(E) \quad (7)$$

Fig. 3 Peak-fit results (convolution-type) for the same synthetic function (Gaussian line width 0.3 eV; Lorentzian line width 1.7 eV) using different procedures for determination of the background: Background subtraction before starting the fit-routine (left) and iterative calculation during the fit (right)



Optionally, one may choose to subtract a baseline before entering the fit iterations or to include the background model into the minimization process. But notice, that systematic deviations of the residuals may occur, as shown in Fig. 3, by fitting photoelectron lines possessing a strong Lorentzian contribution after having performed a formal background subtraction. Therefore, an iterative calculation of the background by including its parameters ($a-f$, or at least part of them) in the fit procedure is recommended especially for this kind of signals. Of course, the background shape and the peak parameters become directly correlated in this manner. This may sometimes turn out to be a problem in case of asymmetric peak shapes in particular, in this manner increasing the uncertainty of the derived parameters. Such problems are inherent to the chosen modelling for the spectral shape and the involved assumptions. They cannot be avoided in principle, but may be reduced by, e.g., constraining parameters in accordance with available knowledge on the system of interest.

3 Characterization of the program UNIFIT

A universal program for XPS core level peak shape analysis, called UNIFIT, which employs the Marquardt algorithm for the minimization of χ^2 , has originally been developed for PCs under DOS. The currently available, advanced versions have been based on Windows 3.1, Windows 95 or Windows NT. This program permits to choose the components of the theoretical model peaks alternatively as functions of the product-type or of the convolution-type. All the peak parameters may be varied completely freely, varied within a chosen interval or fixed

at certain values. Moreover, the parameters may be determined independently of absolute scales or they may be treated as relative parameters, which are related to the leading peak of a doublet model peak or to the first peak of a group of model peaks. Application of the models with relative peak parameters provides the opportunity to include constraints between parameters of the same kind. Choosing relative peak parameters may permit to keep, e.g., energy distances, peak widths or relative intensities of peaks to remain constant during the iterations (exactly fulfilled constraints) by fixing the corresponding relative parameters. In the same manner relaxed conditions (approximately fulfilled constraints) may be imposed by limiting the relative peak parameters to numerical values within an interval, which can be determined by setting adequate upper and lower limits. Additionally, it is possible to include the parameters of the spectrum background in the fit routine. Besides this inclusion in the minimization procedure, the background can be simulated by five different methods and subtracted from the experimental curve before initiating the peak fit.

UNIFIT has been designed to accept data of different formats. The curve-fit results can be printed including fit and acquisition parameters or exported for further treatment. A simultaneous handling of up to 11 windows with spectra is possible, using individual preferences regarding fit procedure, fit parameters, language, colors etc. Several data treatment sub-routines for, e.g., charge correction, satellite subtraction, spike correction, differentiation, integration, and smoothing permit the comprehensive processing of the corresponding spectra.

The next extensions of the program capabilities will include implementations for the estimation of the uncertain-

Table 1 Parameters of model functions before and after peak fit in comparison to those of the test function

Parameter	Function					
	Model function Start parameters		Model function Parameters after fit		Test function	
	Peak 1	Peak 2	Peak 1	Peak 2	Peak 1	Peak 2
Intensity/ counts	8000	40000	10252	49755	10000	50000
Gaussian line width/eV	0.5	0.5	0.37	1.73	0.3	1.7
Peak position/eV	284.50	281.00	284.03	281.99	284.00	282.00
Lorentzian line width/eV	0.5	0.5	1.64	0.25	1.7	0.3
Background function	$33 + 5 \cdot E + 0.25 \cdot E^2$		$28 + 5.2 \cdot E + 0.22 \cdot E^2$		$105 + 1 \cdot E + 0.25 \cdot E^2$	
Error	4809		34			
Abbe criterion	0.013		0.941			

ties and the correlations of the derived peak fit parameters in order to allow a more reliable estimation of the significance of the obtained parameter values. Consideration of more general conditions between fit parameters is also within the scope of further extensions.

4 Adaptation of a test function

In order to demonstrate the adequate performance of the sub-routines for calculation of model peak shapes, the efficiency of the convergence and the reliability of the results, a simple test function $I(E)$ was generated independently using MICROCAL ORIGIN and fitted with UNIFIT. The test function consists of two single lines and a background function. The corresponding model parameters are shown in Table 1. Further, statistical noise has been simulated by the square root of $I(E)$ multiplied by normally distributed random numbers and has been finally included in $I(E)$ (Fig. 4).

Figure 5 presents both the test function and the model functions including background after an initial, crude guess of the parameters. The initial parameters have been chosen deliberately. Symmetrical signals have been assumed (asymmetry = 0) and a second order polynomial has been used to characterize the background. Direct comparison of test profile and first model profile as well as the appearance of the residuals demonstrate the failures of this first approach quite obviously.

The final result obtained from the converged fitting process has been displayed in Fig. 6. A total of 22 iteration steps (successful and unsuccessful) had to be used, applying the convolution-type model and including the background parameters in the iteration process. The derived parameters have been summarized in Table 1. Obviously, the individual parameters are in excellent agreement with the parameters chosen for the peak synthesis of the test function. On the basis of the value for the Abbe criterion near 1 and the residual in Fig. 6 no systematical errors can be detected.

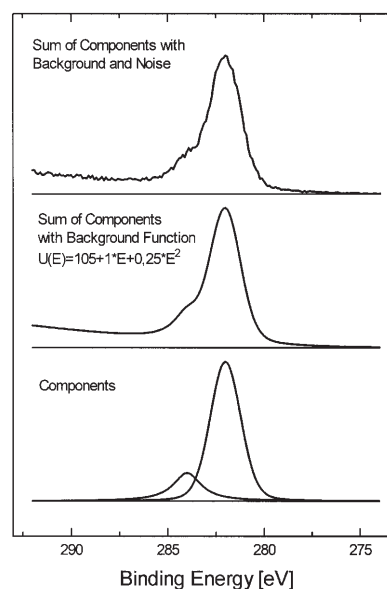


Fig. 4 Synthesis of a test function

5 An example: 2-mercaptobenzothiazol (MBT) on pyrite (FeS_2)

The simulation of complex spectra, e.g. as may be recorded from samples composed of several substrate and adsorbate-related species including the same element, is a special challenge for numerical peak shape analysis programs. An example is presented in Fig. 7a, which shows the S 2p spectrum of a pyrite (FeS_2) sample after treatment with MBT solution. The spectrum has been obtained by exciting with synchrotron radiation ($h\nu = 210$ eV). Note the sloping background towards higher binding energies, which is due to the increasing contribution of secondary electrons at these low kinetic energies below 50 eV, quite typical even for synchrotron radiation excited photoelectron experiments using low excitation energies. Thus, the chosen background model has included a low order polynomial, essentially, in combination with a

Fig.5 Start iteration after manual input of parameters (fit procedure: convolution)

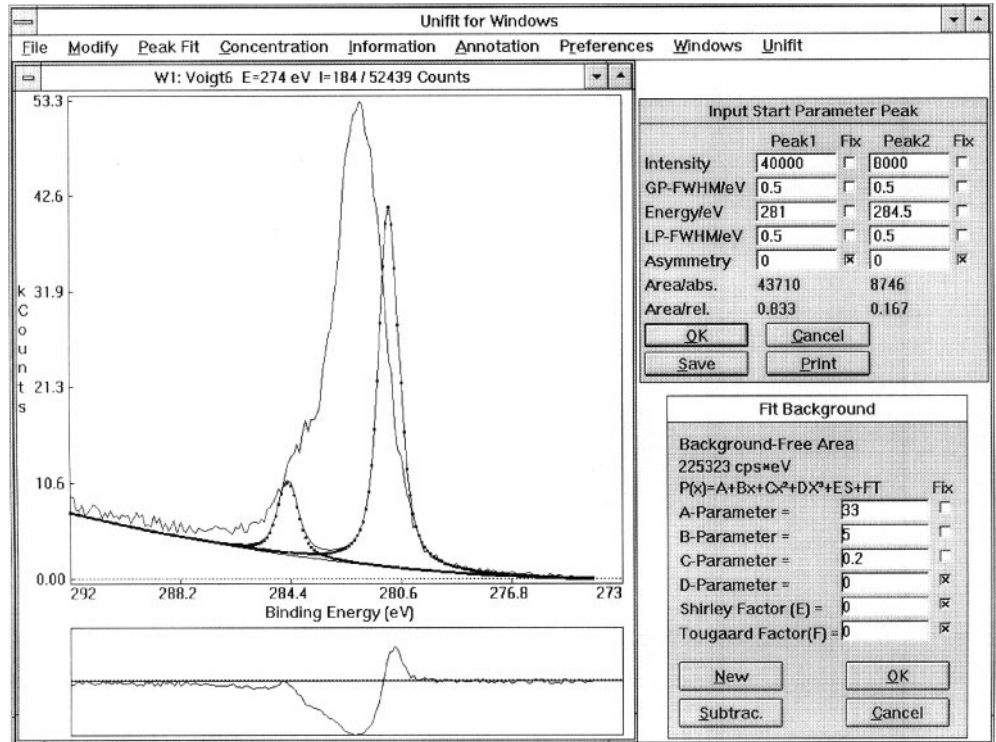
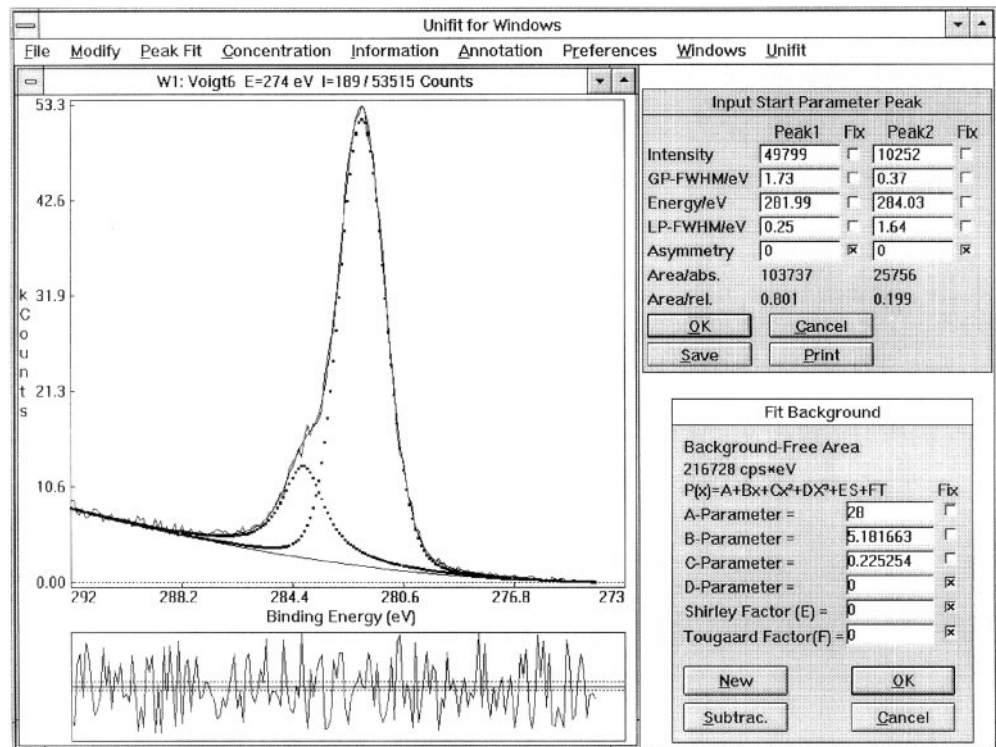


Fig.6 Result of the fit procedure (convolution) after 22 iterations with iterative background calculation



smaller Shirley-type contribution. Peak maxima due to three doublet main components are clearly visible at binding energies of 162.0 eV, 162.7 eV, and 164.5 eV. However, the peak fit has turned out to be insufficient using these three doublets only. They are fitted with a fixed branching ratio of the S 2p doublet of 2:1 and a doublet splitting of 1.19 eV. Furthermore, the Lorentzian and

Gaussian line widths obtained from spectral components of the clean vacuum-fractured surface was used. After having adjusted the peak widths in order to describe both low and high energy tails of the experimental spectrum appropriately, the comparison of experiment and simulation as well as of the residuals clearly shows, that two additional signals are required to describe the experimental

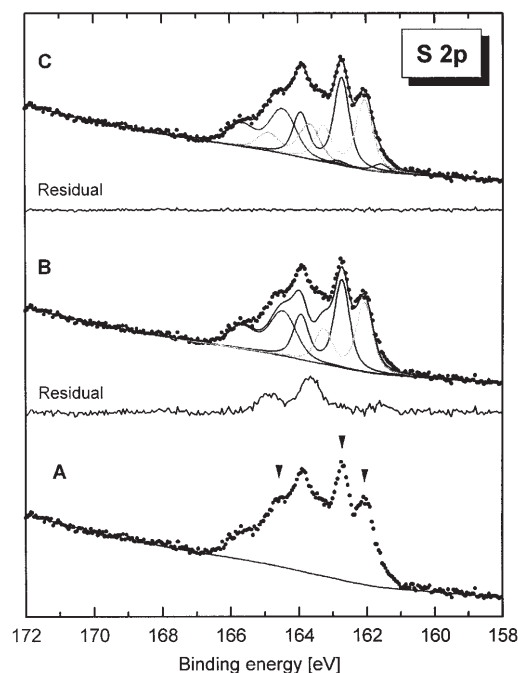


Fig. 7 Peak shape analysis of a complex S 2p spectrum of MBT on pyrite using UNIFIT

curve by the model functions successfully (Fig. 7b). A fit of the experimental spectrum by using 5 doublet components is given in Fig. 7c. These five S 2p doublets may be readily explained. The S 2p signal of the substrate has been shown to consist of three doublets as has been demonstrated by measurements recorded at UHV-cleaved pyrite surfaces [10]. The component at 162.7 eV is due to bulk sulfur whereas the lower-energy signals at 162.0 eV and 161.3 eV have been attributed to emissions from two different kinds of surface atoms [4]. On the other hand, the MBT molecule contains two sulfur atoms with different chemical environments. These are responsible for the two remaining doublets in the observed S 2p spectra. The exocyclic sulfur causes the component at 163.7 eV. The signal at 164.5 eV may be related to the endocyclic sulfur atom.

This example has demonstrated that the peak shape modelling may be a tedious task even if the appropriate software is available. The consideration of as much prior knowledge as possible on the sample and the measurement conditions may be crucial for choosing peak and

background models. It is strongly recommended to check the results of the analysis with respect to available physical and chemical information related to the problem of investigation. On the other hand, we have clearly shown that careful peak shape analysis using suitable software may provide very detailed information on the physical and chemical state of the elements in the samples of interest.

6 Summary

Several approaches used in the peak shape analysis of core level spectra were discussed for the purpose of modelling both peak shapes and background profiles. The program UNIFIT has been presented, which combines options for adequate modelling of the peak shapes and background line, implementation of a successful numerical algorithm for an iterative non-linear parameter estimation procedure, and a flexible as well as convenient data handling. The performance of this program code has been demonstrated by fitting a synthesized model spectrum and a complex experimental spectrum. An S 2p spectrum recorded from an MBT-treated pyrite surface has been successfully characterized by five different S 2p contributions.

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