XAS a new computer package program for X-ray absorption spectroscopy data analysis

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A new version of Fourier analysis of XANES and EXAFS data obtained using synchrotron radiation, a self-contained Fortran program-package and Gnuplot with graphical data interface facilities that permits users a simple manipulation is described. By the direct dialog between the user and the Gnuplot supports, based on XANES and EXAFS spectra, there is the possibility to obtain the electronic and structural parameters. An improved procedure is used to extract more information from XANES spectra by second derivative analysis and electronic transitions distribution associated for each edge. Another purpose of the program package is based on EXAFS measurements analysis, to obtain the structural parameters: R_j - distance from the central absorbing atom to atoms in the jth coordination shell, N_j - number of atoms in the jth shell, σ_j - root mean square deviation of the interatomic distance about R_j, λ_j - mean free path for inelastic scattering, A_j – backscattering amplitude envelope function and $\delta_j(k)$ - phase shift. Additional the principal component analysis allows determining the number of primary components in a set of experimental XANES or EXAFS spectra. The new computer package program was tested on different systems: supported metal catalysts, oxides and other materials.

1. Introduction

X ray absorption spectroscopy (XAS) is a useful method for probing the electronic and local structure of nanostructred materials using X ray absorption near and extended edges data analysis (XANES, EXAFS) [1]. The new version of computer package developed by us was tested on different kind of materials; its physical parameters obtained are reliable. It is based on interactive modules of XAS containing all necessary numerical algorithms and procedures for standard XAS data analysis [2]. Gnuplot portable supports for many techniques of graphical analysis, different types of input-output and data calculus [3] are used. A complete analysis of XANES is realized in order to obtain the chemical shift, one and multi-electron transitions probabilities, for K and L edges respectively [4]. For information related to binding energy of K or L edges position we adopted the computing of XANES function and its first and second derivatives by cubic splines in the least squares sense. Beside XANES analysis the new computer package program can furnish

the atoms number and shell radius associated to each coordination sphere, thermal disorder parameters and electron mean free paths ejected from central atom. Additionally methods were implemented that exceed standard data redaction such as principal component analysis (PCA) and XANES data fitting by linear combinations have been implemented.

2. Program description

XAS pack is divided into five modules written in Fortran language and Gnuplot portable command-line, each performing a specific activity in the data redaction. The definition interval of different signals during data redaction is determined by command *Click the left and right limits*. The main results for Co_3O_4 spectrum measured at room temperature are graphically illustrated. Table 1 shows manipulation mode of the data for obtaining the local structural parameters of investigated samples.

Table 1. Manipulation mode of the data for all five modules.

Sample Cr$_3$O$_4$	Language	Content Suffix of input files	Content Suffix of output files
Background determination	**Module 1** gnuplot	XAFS - signal (energy [eV], μ (energy) xxxxxxx.**abs**	Polynomial approximation
XASF determination	**Module 2** Fortran gnuplot	XANES - experimental signal(energy, μ(energy)) xxxxxxX.**abs**	XANES signal approximated (i) xxxxxxX.**out** - approximated (ii) xxxxxxX.**d1** – first derivative (iii) xxxxxxX.**d2** – second derivatives
		EXAFS - experimental signal(energy, μ (energy)) xxxxxxx.**abs**	EXAFS - signal approximated xxxxxxx.**chi**
Atomic radial distribution function determination	**Module 3** Fortran gnuplot	EXAFS - signal approximated (k, χ) xxxxxxx.**chi**	Radial distribution function(r, Φ) (i) xxxxxxx.**ft1** – FT[wf*χ*k] (ii) xxxxxxx.**ft2** – FT[wf*χ*k^2] (iii) xxxxxxx.**ft3** – FT[wf*χ*k^3]
Inverse Fourier Transform determination and its application	**Module 4** Fortran gnuplot	Radial distribution function (r, Φ) (i) xxxxxxx.**ft1** (ii) xxxxxxx.**ft2** (iii) xxxxxxx.**ft3**	EXAFS – a portion of χ signal (i) xxxxxxx.**if1** – IFT[wf*χ*k] (ii) xxxxxxx.**if2** – IFT[wf*χ*k^2] (iii) xxxxxxx.**if3** – IFT[wf*χ*k^3]
EXAFS data fitting	**Module 5** gnuplot	EXAFS – a portion of χ signal ((k, χ) (i) xxxxxxx.**if1** (ii) xxxxxxx.**if2** (iii) xxxxxxx.**if3**	EXAFS - χ calculated in k and r spaces xxxxxxx.**fit** all information **history.inf**

2.1 Background correction

The module executes background subtracting on the whole spectrum based on polynomial fit in the least squares sense defined on pre-edge interval by the user indication. EXAFS background correction is realized by extrapolated to higher energy. The normalization of XAS signal is realized by choosing the lowest and highest values of the ordinates and then scaled it between one and zero, respectively. Fig1. shows the graphical result of the background correction. The glitches of data can be removed from experimental data during approximation of absorption coefficient, $\mu(k)$.
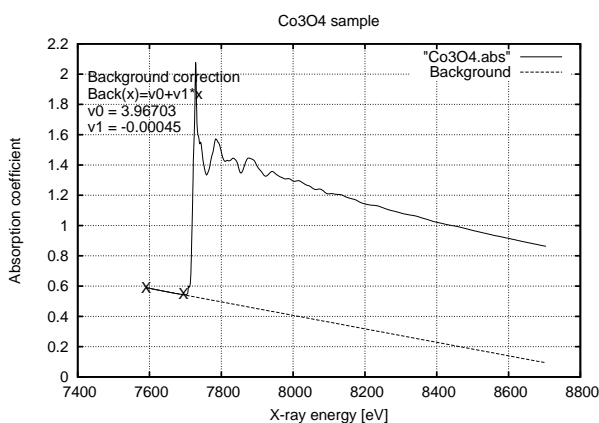

Fig 1. The background correction of XAFS spectrum for Co$_3$O$_4$ system.

2.2 XAFS determination

The procedure for smoothing and interpolation of absorption coefficients $\mu_0(k)$ and $\mu(k)$ is performed with cubic splines in the least squares sense. The spectrum smoothing quality is given by the total number of splines, NSP chosen for portion of interval [A,B] (x_i-x_{i-1}= H const., i=2, 3, N, x_1=A, x_N=B), N is total number of experimental points [5]. The $\mu_0(k)$ and $\mu(k)$ are calculated for different values of NSP parameters in according with Cook-Sayers criterion [6] as well as based on the user experience in data reduction. The binding energy represents necessary energy to excite a core electron into an unoccupied or continuum state within a matrix sample creating a photoelectron. Energy reference used in EXAFS data analysis is not defined relative to electron configuration as defined Fermi level in solid state physics but it is a parameter that is used to align the experimental data to simulated spectrum. Practically binding energy as threshold energy can be determined by the abscissa value of first derivative maximum or more precisely by the zero value of the second derivatives for the XANES signal. Its derivatives are calculated with the same technique of cubic splines in the least squares sense. Other features of XANES analysis consist in principal component analysis (PCA) for determining the primary number of components included in experimental XANES or EXAFS spectrum. Primary components mean to reconstruct each experimental spectrum by a suitable linear combination. Another XANES fitting approach is to model the spectrum in terms

of curves fitting of different line shapes for evaluation the probabilities of the electron transitions associated to K or L edges [7]. Figs 2-4 present the graphical results of this module.
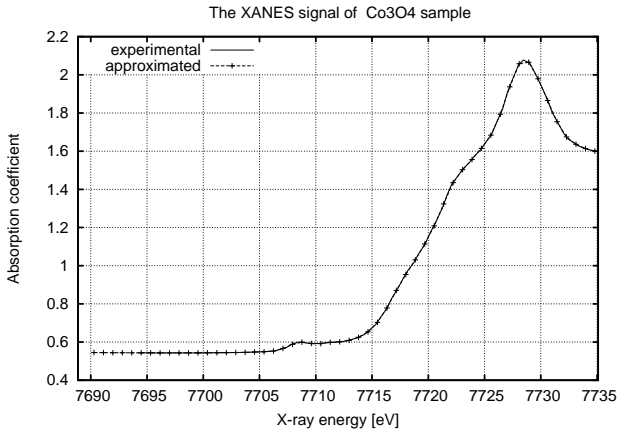

The XANES signal of Co3O4 sample

Fig 2. XANES approximation of K edge for investigated sample.

The first and second derivatives of Co3O4 XANES signal
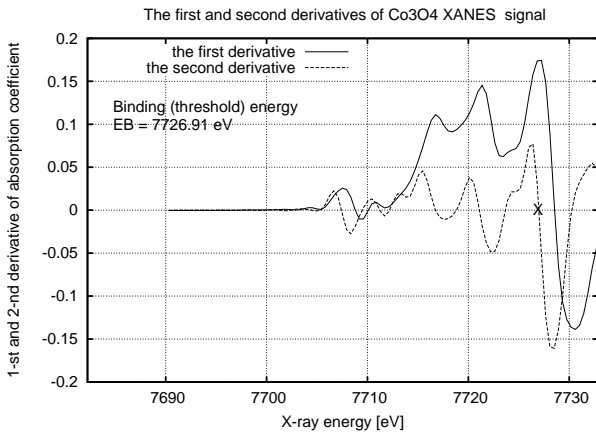
Fig 3. The first and the second derivatives of XANES signal.
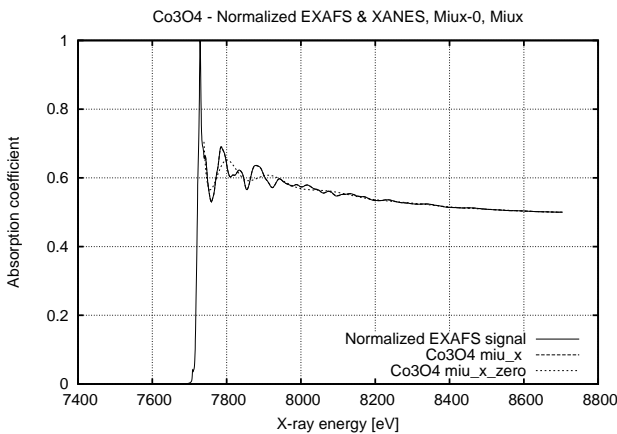

Co3O4 - Normalized EXAFS & XANES, Miux-0, Miux

Fig 4. Normalized XANES, EXAFS spectra and the absorption coefficients μ and μ_0 approximated by the cubic bell splines technique.

2.3 Atomic radial distribution function determination

The Fourier transform of any real signal is a complex function with real argument containing even real and odd imaginary parts defined on the whole real axis. The magnitude of the Fourier transform is like an envelope of the both parts. This module performs the calculation of the real, imaginary and magnitude of Fourier transform function $\Phi(r)$ using Filon quadrature formulae [8] as well as discrete fast Fourier transform algorithm (DFFT) of the EXAFS signal [9]. Important modifications in X ray absorption signal before or after absorption edges cannot be included in final spectrum for analysis due to experimental reasons. These features can produce the errors in background removal procedure with large implications in the shape of radial distribution function evaluation. This involves a harder interpretation when we have to deal with a limited data range. The correction due to the termination error can be made with various filter functions indicated by user [10]. Beside EXAFS signal and filter function must introduce a factor as a power of wave vector that compensates the EXAFS oscillation in high k-region diminishes the effect of the edge jump and the eventuality ambiguity due to the energy threshold evaluation. The power one often can give rough information to the type of coordination atoms. Because heavier atoms have a large oscillation in high k region, the large power of k weighing emphasizes the contribution of higher atoms. One or two power can be used in order to enhance the contribution of lighter atoms. Fig 5 illustrates the EXAFS signal multiplied by Gauss or Hanning filters and k^3.
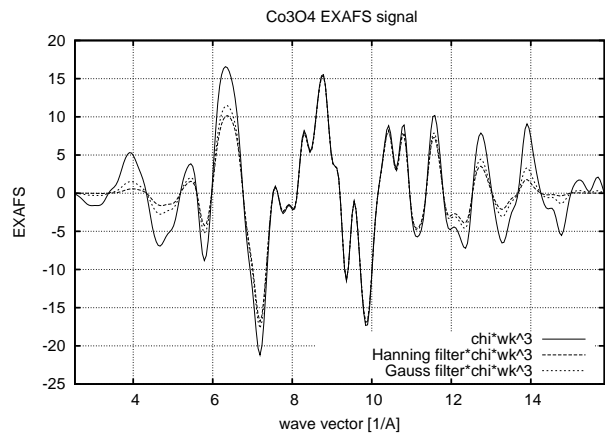

Co3O4 EXAFS signal

Fig 5. EXAFS signal multiplied by Gauss, Hanning filters and k^3.

Some times for r less than 1 Å can appear the false peaks due to errors in background correction or a bad evaluation of $\mu_0(k)$ signal. In this case must return to previous step in according with Cook-Sayers criterion. [6]. In case of DFFT method, between sampling steps δk and δr of *EXAFS* and $\Phi(r)$ functions there is an analytical relation [11] and often it is not possible to obtain a reliable resolution for the radial distribution function (RDF) named

as distribution of the atom pairs. In relation with correlation of structural parameters have to pay attention to the maximum freedom, N_{IP} of fitting number of parameters. Nyquist theorem established a precise relation between number of independent points N_{IP}, the whole interval of EXAFS signal Δk and Δr as a definition domain of $\Phi(r)$ [12]. This consideration has a large implication in robustness of fitting model of structural parameters determination technique. To avoid these limitations we also introduced the Filon algorithm for Fourier transform procedure. The main advantage of Filon quadrature consists in its precision that depends only of integration step of EXAFS signal and the radial distribution function can be calculated on any interval having an arbitrary step in r space. The module of Fourier transform is like a radial distribution function of atoms around the absorbing atom because the peak corresponding to the first coordination shell is related to the bond length of atoms belonging to the first shell. From mathematical point of view it is not quite a radial distribution function because: *(i)* each peaks position are shifted from the true distances, due to phase shift functions that are included in the EXAFS signal; *(ii)* multiple scattering paths of photoelectron can produce strong signal in Fourier transform that do not belong to RDF; *(iii)* the interface between two scattering paths of the photoelectron may produce a minimum rather than a peak in the Fourier transform of EXAFS signal. Fig. 6 contains graphical results of this module.
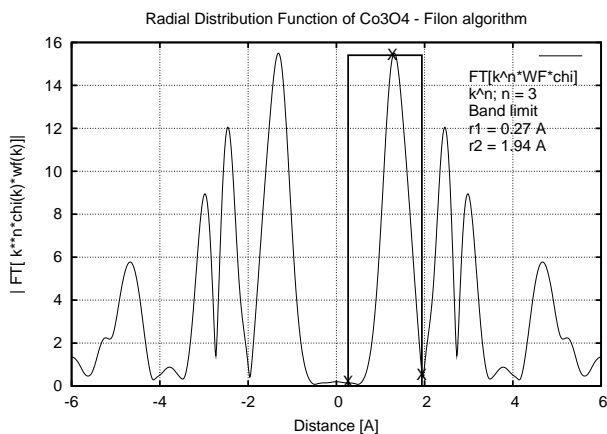

Fig 6. The Fourier transform of EXAFS signal using Filon algorithm. The box illustrates the interval in r space designed for inverse Fourier transform calculation.

2.4 Inverse Fourier Transform determination and its application

From mathematical point of view the inverse Fourier Transform of complex function $\Phi(r)$ is defined on the whole k space of wave vectors and its imaginary part is equal to zero for each k value.

From physical point of view the inverse Fourier transform is useful for determining of some components from original signal that are included to r range from direct Fourier transform. In this case the user must indicate interest interval from r space and signal with complementary frequencies is removed from initial EXAFS spectrum. Also, in order to obtain reliable EXAFS contribution we introduced filtering technique to eliminate the spurious errors due to truncation of interval from r space.

2.5. EXAFS data fitting

If user would like to estimate the local parameters from the single coordination shell it has two possibilities: *(i)* to estimate the backscattering amplitude and phase shift functions from a standard samples and then to transfer them to investigated sample; *(ii)* to model the EXAFS spectrum using FEFF concepts [13] using a user-friendly interface named IFEFFIT [14]. In the first direction the backscattering amplitude and phase shift functions are parameterized, the thermal Debye-Waller parameters and free main path of the photoelectron can be taken as trial values from literature. The fit of the data is realized by Levenberg–Marquardt algorithm [15] implemented in Gnuplot software. Fig 7-8 illustrate the fit procedures in the both spaces. The second direction is based on software packages IFEFFIT that can be downloaded from link of International XAFS Society http://cars9.uchicago.edu/ifeffit. The theoretical backscattering amplitude and phase shift functions for each scattering path of atom cluster can be obtained by running ARTEMIS code [16]. In the second case coordination shell concept is replaced by scattering paths with their degeneracy. The second direction is not yet implemented in new version of this package programs, but the work is in progress.
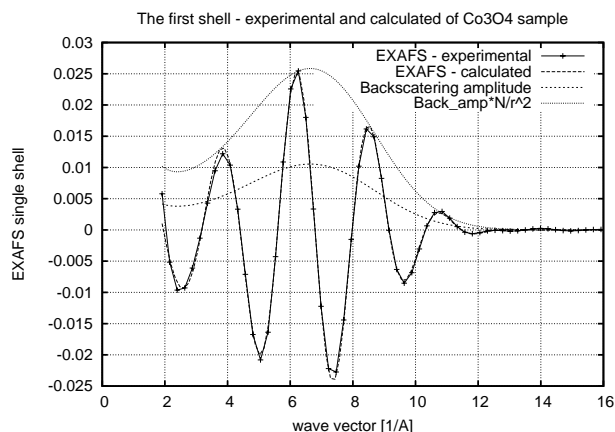

Fig 7. Experimental and calculated in k space of EXAFS spectrum associated to the first coordination shell for investigated system.
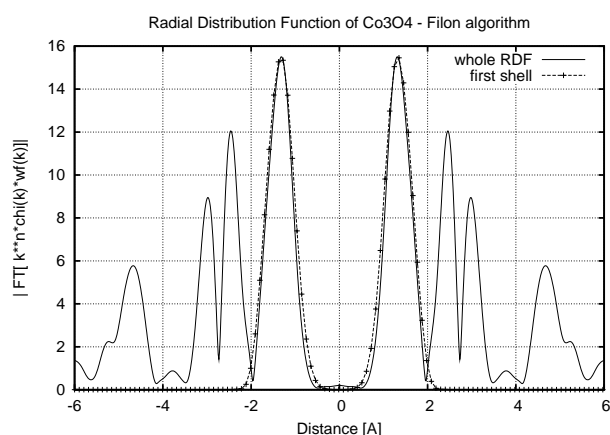
*Fig 8. Experimental and calculated in r space of RDF
signal associated to the first coordination shell for
investigated system.*

3.Conclusions

X-ray absorption spectroscopy is a powerful method for characterizing and understanding the nanostructure of many kind of materials, crystalline and as well as the non crystalline nanomaterials. The electronic and structural results from both XANES and EXAFS data can be consistent if a giving electronic and structural model has a great accuracy. The conclusions that can be drawn from present paper are:
(i) complex analytical and numerical techniques in the new version for analyzing the XANES and EXAFS signal using Gnuplot portable command-line that included executable Fortran codes have been implemented;
(ii) electronic and structural information resulting from data analyzing are reliable and they are similarly as a accuracy with other obtainable from similar codes;
(iii) we preferred Felon quadrature for Fourier transfrom instead of DFT because we are not obliged to consider Nyquist theorem;
(iv) the codes can be installed on any operating system.

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