Method for Extracting of EXAFS Oscillation Function Based on the Variation Principle

© M.D. Sharkov, K.Ju. Pogrebitsky¶, S.G. Konnikov

Ioffe Physico-Technical Institute Russian Academy of Sciences,
194021 St. Petersburg, Russia

A new method to detemine EXAFS smooth component has been suggested. A certain functional minimized by the sought μ_0 has been proposed. The analysis of an amount of spectra has been proceeded. The way for solution optimizing has been pointed out. The suggested method results applied to the experimental spectra in comparison with other techniques are presented.

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1. Introduction

One of the most sensitive methods for determining of atomic structure of a sample is EXAFS (extended x-ray absorption fine structure). EXAFS is observed as oscillations after an absorption edge. These oscillations (χ) contain information on the absorber atom neighboring structure. Thus, we are to determine the χ function from the experimental spectrum. It is necessary to select the oscillation part from the smooth decreasing absorption spectrum. To solve this problem one has to simulate the „smooth“ (non-oscillating) component μ_0 of the spectrum. This is one of the main tasks of evaluation of EXAFS spectra. Several different techniques of obtaining μ_0 are well known [1–5]. All of them have advantages and disadvantages. For instance, a polynomial fit can be used to describe the smooth EXAFS component [1–3]. Besides, one can consider ranges of knots (E_j, μ_j) with a certain width. Average values of the function μ versus those of the argument E then constitute the smooth function μ_0 [4]. It is difficult to choose the appropriate data range in using this method. Narrow ranges lead to solutions with invalid shape. Wide windows give rise to great errors near the edges of the E range. Another approach to obtaining μ_0 deals with spline construction. In this case, one chooses a number of points (E_j, μ_j) to build an approximate function through them (*e.g.*, the cubic spline) [1,5].

The variation principle can also be used to treat EXAFS. This paper is aimed at inventing a reasonable functional convenient for EXAFS data treatment.

2. The suggested method

To solve the problem of extracting EXAFS smooth component, we can assume a functional which is minimized by the sought μ_0. The functional is to depend on the both μ and μ_0. Here μ should be close enough to μ_0 and sufficiently smooth. It is also reasonable to add an extra condition that the definite integral of $(\mu-\mu_0)$ on the interval $[E_1, E_2]$ of μ_0 definition were equal to zero. We introduce therefore

$$\Phi[\mu_0] = \int_{E_1}^{E_2} dE \left[\alpha\big(\mu(E) - \mu_0(E)\big)^2 + (1-\alpha)\left(\frac{d\mu_0}{dE}\right)^2 + \beta\big(\mu(E) - \mu_0(E)\big)\right],$$

where α and β are variable parameters and α is always arranged between 0 and 1.

The searched μ_0 can be obtained by solving the Euler–Lagrange equation for the considered functional with respect to μ_0:

$$\frac{\partial\Phi}{\partial\mu_0} = \frac{d}{dE}\,\frac{\partial\Phi}{\partial(d\mu_0/dE)}.$$

For the introduced functional the Euler–Lagrange equation is

$$\left(\frac{d^2}{dE^2} - C^2\right)\mu_0 = C^2(A-\mu).$$

A and C are here equal to $C = \sqrt{\frac{\alpha}{1-\alpha}}$, $A = \frac{\beta}{2\alpha}$.

These two parameters are to meet also the extra condition

$$\int_{E_1}^{E_2} \big(\mu(E) - \mu_0(E)\big)dE = 0.$$

A pair of boundary conditions complements the problem to one having the only unambiguous solution. It is reasonable in the considered case to introduce the first type boundary conditions

$$\mu_0(E_1) = \mu(E_1),$$

$$\mu_0(E_2) = \mu(E_2).$$

Such a technique for extracting μ_0 appears to:

1. Be easy, rapid, naturally and mathematically conclusive.

2. Give rise to reliable results. The method was applied to three spectra of Cu and Cr and its comparison with literature data showed the technique to be usable.

3. Allow varying two parameters and thereby influence the obtained solution. This means the solution can be fit in the necessary way.

¶ E-mail: Kpogr@xiees.ioffe.ru

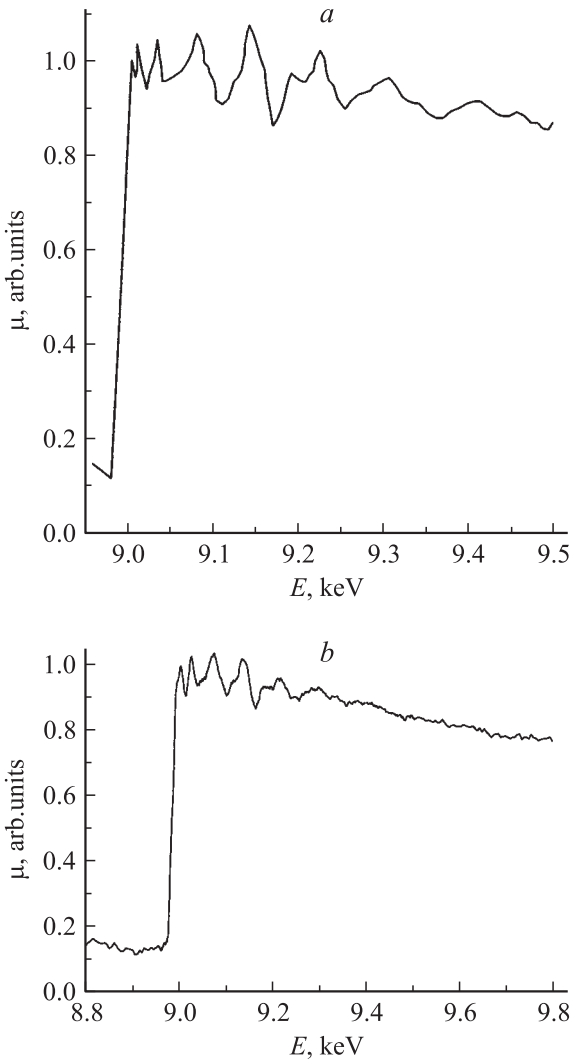

Figure 1. Cu *K*-edge EXAFS taken from literature (top) and measured on „MAXIM“ device located in South Korea (bottom). The latter is the courtesy of Dr. Yu.N. Yuriev and Dr. Y.K. Cho, South Korea.

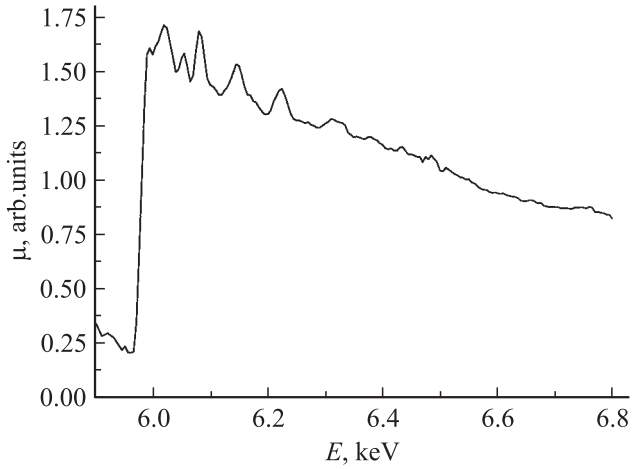

Figure 2. Cu *K*-edge EXAFS $\mu(E)$ measured on „MAXIM“ device located in South Korea (courtesy of Dr. Yu.N. Yuriev and Dr. Y.K. Cho, South Korea).

3. Results

A. Analyzed spectra

The three EXAFS spectra analyzed are shown in Fig. 1 and Fig. 2. These spectra are obtained at Cu and Cr samples, respectively, for their *K*-edges. The photoionization threshold energy magnitudes were chosen to be equal to 8.995 eV for the copper absorption edge and 5.977 for the chromium one. The top plot in Fig. 1 describes the Cu

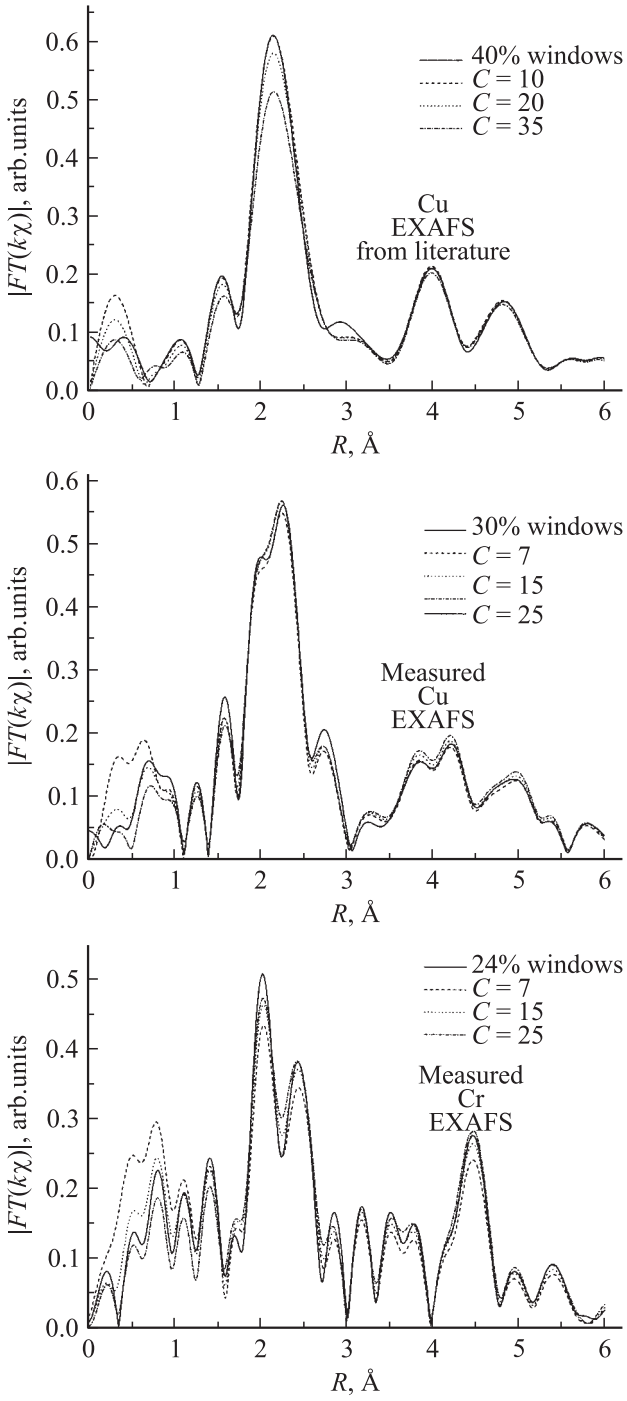

Figure 3. Fourier transforms of EXAFS oscillations.

K-edge EXAFS taken from literature [1]. The bottom one has been measured on laboratory device „MAXIM“ installed at Korea Research Institute of Standards and Science (KRISS, Taejon, South Korea). The Cr *K*-edge spectrum was also measured at this device. These spectra are the courtesy of Dr. Yu.N. Yuriev and Dr. V.K. Cho.

B. Results

The three analyzed EXAFS spectra were treated according to the developed method. The C parameter varied from 0 to values about $25/\Delta E$ where ΔE was the magnitude of the μ_0 definition range. The Fourier transforms of the χ functions for the analyzed spectra are shown in Fig. 3.

The top plot (corresponding to the Cu EXAFS taken from literature) and the middle one (obtained after evaluation of the Cu *K*-edge EXAFS measured on „MAXIM“) are substantially different in spite of the same substance of the samples. That fact might be due to the different origination of the samples. The chromium plot shown in the bottom part of Fig. 3 contains two close main peaks. This situation is a characteristic of substances with *bcc* lattices (like chromium) because two their first coordination shells are very close.

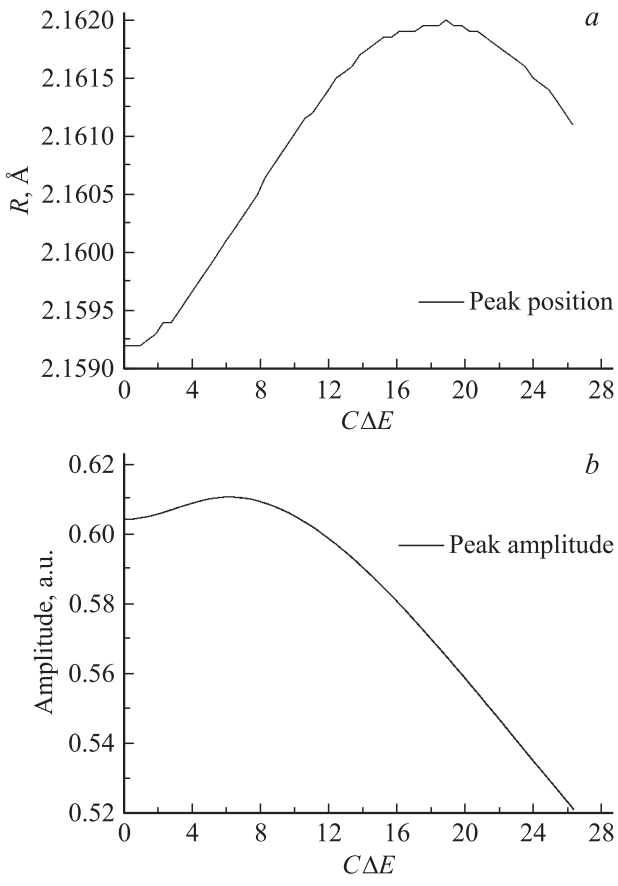

Figure 4. *a*. The main peak position of FT $(k\chi)$ for different C meanings. The considered EXAFS is Cu *K*-edge one taken from literature. *b* The main peak amplitude of FT $(k\chi)$ for different C meanings. The considered EXAFS is Cu *K*-edge one taken from literature.

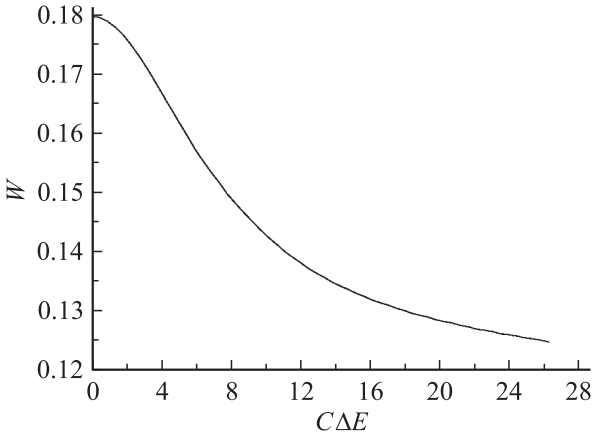

Figure 5. The low frequency contribution W versus C values. The considered EXAFS is Cu *K*-edge one taken from literature.

Let the Cu EXAFS taken from literature be considered. To define the best μ_0 function, some criterion of optimization is required. This criterion may be chosen as the extremum of the FT$(k\chi)$ function peak position or amplitude. Dependences on C of these values are shown in Fig. 4, *a* and Fig. 4, *b*. For each of them the only maximum is observed. Conditions of peak position or amplitude having the utmost value can be selected for optimizing the smooth and oscillating ESAFS parts.

An additional way of defining the best value of the C parameter is to use the low frequency contribution W to the function FT$(k\chi)$. That one is determined to be the definite integral of FT$(k\chi)$ from 0 to the last minimum before the first peak maximum and denoted W in Fig. 5. (Fig. 5 was obtained after evaluation of the Cu *K*-edge EXAFS taken from literature.) The figure shows W to decrease with C increasing. Such a C dependence of W means that higher values of C should be preferred because low frequency harmonics in χ are not due to photoelectron scattering by atoms. On the other hand, the choice of high C values appears to lead to intrinsic μ_0 oscillations. These two limitations confine the region of searching C.

4. Conclusions

1. A physically and mathematically conclusive method for determination of smooth and oscillating EXAFS components has been invented. This method is based on solving a variation problem that is identical to a second-order derivative equation with respect to the smooth EXAFS spectrum component in first type boundary conditions.

2. A comparison of the invented technique with widespread methods for EXAFS oscillations extracting has been carried out.

3. The developed method to treat EXAFS spectra allows results to obtain that are close to the analogical ones

obtained by one of widespread techniques which is to average EXAFS data at a variable array of sorted knots.

4. The technique for EXAFS spectrum proceeding that has been described in this paper can be varied in two parameters. Even though an additional fitting condition for the parameters has been introduced, the method stays sufficiently flexible and allows choosing the model for the smooth and oscillating EXAFS parts which are mostly capable of meeting some optimization criterion.

5. The described method for EXAFS treatment has shown good agreement with experimental data on applying it to the problem of Cu and Cr sample exploration.

References

[1] *X-Ray Absorption: Principles, Applications, Techniques of* EXAFS, SEXAFS, *and* XANES, V. **92**. Ed. by D.C. Koningsberger, R. Prins. — Eindhoven Univ. of Technology, Eindhoven; The Netherlands, John Wiley & Sons Inc., N.Y./Chichester/Brisbane/Toronto/Singapore, 1988.
[2] B. Ravel. EXAFS *Analysis with* FEFF *and* FEFFIT. P. 2: *Commentary*. http://feff.phys.washington.edu $\wedge \sim$ {}ravel/
[3] V.M. Strutinsky, F.A. Ivanjuk. Nucl. Phys. A **255**, 405 (1975).
[4] H.J. Krappe, H.H. Rossner. Phys. Rev. B, **70**, 104 102 (2004).
[5] Р.В. Ведринский. Соросовский образовательный журнал, 1996, № 5, 79 [R.V. Vedrinsky. Sorosovskij Obrazovatel'nyj Zhurnal (in Russian), N 5, 1996, p. 79.]

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