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Nuclear Instruments and Methods in Physics Research A 575 (2007) 155–158

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

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Partial pair correlation functions for multicomponent systems by EXAFS: A new approach

Yu. A. Babanov[a,b,*], I. Yu. Kamensky[a], J.-L. Hazemann[c], Y. Calzavara[c], D. Raoux[d]

[a]*Institute of Metal Physics, S. Kovalevskaya Str. 18, Ekaterinburg 620219, Russia*
[b]*Udmurt State University, Izhevsk, Russia*
[c]*CNRS, Laboratoire de Crystallographie, Grenoble, France*
[d]*Synchrotron SOLEIL, Paris, France*

Abstract

A method of determining partial pair correlation functions (pPCFs) for multicomponent systems from EXAFS data is presented. The method is based upon the regularization procedure of solving a Fredholm integral equation of the first kind using special iteration procedure. The effectiveness of the method has been tested on the model crystalline solids $ZnBr_2$. We present the result for $ZnBr_2$ aqueous solution obtained from experimental data at room temperature (303 K) and pressure 250 bar. Experiments were performed using an unique equipment at ESRF (Grenoble, France). Peculiar features of the method are high resolution for closely spaced shells and high accuracy in the determination of pPCFs.

PACS: 61.10.Ht

Keywords: EXAFS; Regularization; Aqueous solution

1. Introduction

EXAFS spectroscopy is used to probe the local atomic arrangement around a specific atomic species in amorphous alloys, catalysis, biological molecules, solutions, etc. The conventional procedure of extracting structural information in real space is based on Fourier transforming the normalized oscillating part of the X-ray absorption coefficient. It is well known that the peaks in Fourier transform are shifted to lower r from the positions of the corresponding peaks in partial pair correlation function (pPCF). Besides, the real space contribution of each shell is long range and sharply oscillatory. The contributions made by two closely spaced shells interfere strongly.

According to theory, the EXAFS can be described as an electron diffraction process where the electron source is the absorbing atom i. The outgoing photoelectron wave and a small part of it, which is backscattered from surrounding atoms j, interfere within the excited atom. This scattering is specified by not only the atomic amplitude f_j, as is the case in X-ray diffraction, but also the phase φ_j. In addition, the scattering on the potential of the central atom i exhibits a phase shift $2\delta_i$. These scattering characteristics are involved in the integral operator A_{ij}, which, as it acts on the pPCF g_{ij}, generates a contribution of a specific atomic pair ij to the normalized oscillating part χ_i.

In this paper, we propose to use the dependence of the integral operator A_{ij} on the atomic scattering characteristics $\delta_i(k)$, $\varphi_j(k,r)$ for determining pPCFs in multicomponent systems from EXAFS data. Earlier, this idea was applied to extract information about bond lengths for multicomponent systems [1]. Now, we introduce a special iteration procedure for obtaining pPCFs.

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[*] Corresponding author. Institute of Metal Physics, S. Kovalevskaya Str. 18, GSP-170, Ekaterinburg 620219, Russia. Tel.: +7 343 3783837; fax: +7 343 3745244.

E-mail address: babanov@imp.uran.ru (Y.A. Babanov).

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doi:10.1016/j.nima.2007.01.048

2. Mathematical

EXAFS equation for n-component system has the form

$$\chi_i(k) = \frac{4\pi\rho_0}{k} R(k) \sum_{j=1}^{n} c_j \int_0^{\infty} f_j(k,r) \mathrm{e}^{-(2r/\lambda(k))} \times \sin(2kr + \psi_{ij}(k,r)) g_{ij}(r)\, \mathrm{d}r \tag{1}$$

where k is the wave number of a photoelectron, ρ_0 is the mean atomic density, $R(k)$ is the amplitude reduction factor, c_j is the concentration, and $\psi_{ij}(k,r) = 2\delta_i(k) + \varphi_j(k,r)$ is the total phase shift, which is a peculiar "mark" for a specific pair of atoms. All atomic scattering characteristics are calculated by FEFF 8.1 [2]. The function $g_{ij}(r)$ is the pPCF, which is the probability to find atom j from atom i at the distance r by definition. In symbolic form we have

$$U_i = \sum_{j=1}^{n} A_{ij} g_{ij} \tag{2}$$

where the function $U_i(k)$ include experimental data χ_i and asymptote A_{ij}. Using the regularization method [3], the solution of Eq. (1) is obtained as

$$C_{ij} A_{ij}^{*} U_i = C_{ij} A_{ij}^{*} A_{i1} g_{i1} + \ldots + g_{ij} + \ldots + C_{ij} A_{ij}^{*} A_{in} g_{in}, \quad (j = 1, 2, \ldots, n). \tag{3}$$

The symbol * denotes transposition, $C_{ij} = (A_{ij}^{*} A_{ij} + B_j)^{-1}$ is the inverse integral operator, and B_j is the regularization matrix. Mathematical details can be found in Refs. [1,4].

We explain the sense of the procedure by giving an example for binary system AB:

$$C_{AA} A_{AA}^{*} U_A = g_{AA}^{(0)} + C_{AA} A_{AA}^{*} A_{AB}\, g_{AB} \tag{4}$$

$$C_{AB} A_{AB}^{*} U_A = C_{AB} A_{AB}^{*} A_{AA}\, g_{AA} + g_{AB}^{(0)} \tag{5}$$

where $C_{AA} = (A_{AA}^{*} A_{AA} + B_A)^{-1}$ and $C_{AB} = (A_{AB}^{*} A_{AB} + B_B)^{-1}$ are the corresponding inverse operators. The function $g(0)$ is called Tikhonov's solution. In order to make the structure information more exact, we use the following iteration procedure:

$$\begin{aligned} g_{AA}^{(m)} &= C_{AA}(A_{AA}^{*} U_A + B_A\, g_{AA}^{(m-1)} - A_{AA}^{*} A_{AB}\, g_{AB}^{(m-1)}) \\ g_{AB}^{(m)} &= C_{AB}(A_{AB}^{*} U_A + B_B\, g_{AB}^{(m-1)} - A_{AB}^{*} A_{AA}\, g_{AA}^{(m-1)}), \\ & m = 1, 2, 3 \ldots \end{aligned} \tag{6}$$

where m is the iteration number.

After obtaining the Tikhonov's solution ($m = 0$), it is possible to single out the contributions from specific pairs for iteration process. The algorithm of solving this inverse problem is treated in detail [4].

3. Numerical simulation

The effectiveness of the method has been tested on the model crystalline solids $ZnBr_2$ [5]. We calculated pPCFs for Zn–Zn, Zn–Br and Br–Zn, Br–Br pairs with artificial values $\sigma^2 = 0.022$ (Zn–Zn pair), $\sigma^2 = 0.012$ (Zn–Br pair) and $\sigma^2 = 0.023$ (Br–Br pair), $\sigma^2 = 0.013$ (Br–Zn pair). Then Zn and Br EXAFS are calculated with statistical noise. The solutions obtained are shown in Fig. 1 (solid lines). Also we demonstrate Tikhonov's solutions (dashed lines). Numerical values of the structural parameters of obtaining solutions are given in comparison crystalline $ZnBr_2$ data (Table 1). We can see an excellent agreement.

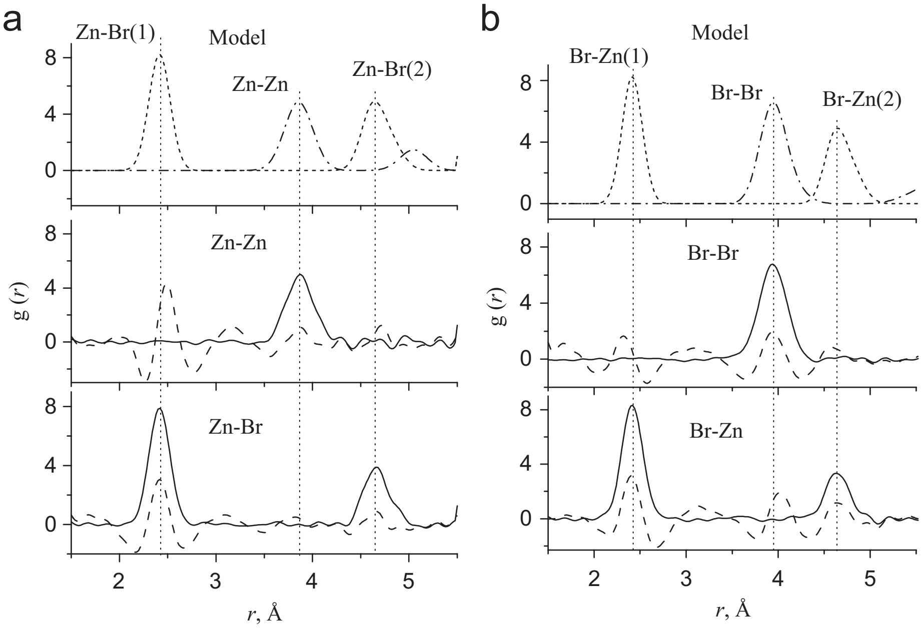

Fig. 1. The pPCFs as a result of solution inverse problem for Zn (a) and Br (b) spectra: the model, Tikhonov's solution (dashed line), the solution obtained after iterations (solid line).