Thickness inhomogeneity and fluorescence effects in EXAFS spectroscopy for powder samples: solution of the inverse problem

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For thin powder samples EXAFS spectra are often suffered from thickness inhomogeneity and for thick samples from fluorescence at energies above edge absorption. As a result EXAFS amplitude is decreased and information about the coordination numbers is distorted. For correction of x-ray absorption spectra on inhomogeneity and fluorescence effects we propose a new method of solving an inverse problem. Model calculations are carried out. This method is applied to preliminary processing EXAFS spectra for Ni-Mn alloys.

Keywords: EXAFS, thickness inhomogeneity, fluorescence, correction of absorption spectra

1. Introduction

The thickness effect, which is caused by inevitable leakage radiation accompanying the absorption process, has been discussed earlier (Rose & Shapiro, 1948; Heald & Stern, 1977; Stern *et al.*, 1979; Rabe *et al.*, 1980; Stern & Kim, 1981; Goulon *et al.*, 1982; Bausk *et al.*, 1999) . It is usually argued on the basis of statistics that the optimum $\Delta\mu_o x$ to measure EXAFS is 2.6 (Rose & Shapiro, 1948), where $\Delta\mu_o$ is the edge step of the x-ray absorption coefficient, x is the sample thickness, but, as Stern and Kim showed in (Stern & Kim, 1981), this value is already thick enough in concentrated samples. They considered that the thickness effect is negligible for $\Delta\mu_o x = 1.5$.

In present paper we adopt the idea to correct XAFS amplitude using pre-edge data (Bausk *et al.*, 1999) and propose the simple models describing influence of thickness inhomogeneity and fluorescence on the edge step, the amplitude of EXAFS oscillations and the asymptotic behaviour of absorption spectra. We use the asymptotic behaviour in order to find some parameters of models and to reconstruct the true absorption coefficient.

2. Apparatus function

Let us denote the incoming flux of x-rays with energy E by $I_0(E)$, the measured by the first detector intensity by $I_0'(E)$, the flux falling on the sample by $(I_0(E) - I_0'(E))$ and the transmitted intensity by $I(E)$. In order to obtain the true absorption coefficient $\mu(E)$ for homogeneous thin sample with thickness x it is necessary to measure the apparatus function, i.e., to perform experiment without sample. Then we have

$$\mu(E)x = \mu_r(E) - \mu_{gr}(E) \equiv$$

$$\equiv ln\left(\frac{I_0'(E)}{I(E)}\right) - ln\left(\frac{I_0'(E)}{I_0(E)-I_0'(E)}\right) = ln\left(\frac{I_0(E)-I_0'(E)}{I(E)}\right). \tag{1}$$

Here $\mu_r(E)$ is the raw absorption data, μ_{bg} is the apparatus function or the background.

3. Thickness inhomogeneity effect

3.1 Model

We consider a discrete model describing thickness inhomogeneity effect. It is usually assumed that there is a continuous distribution of thicknesses. But it is practically impossible to determine this distribution.

Let we have an inhomogeneious sample with three values of thickness: $x_1 = x - \Delta x$; $x_2 = x + \Delta x$; $x_3 = x$; where x is the average value, Δx is the deviation from x. Then

$$e^{-\mu'(E,x)} = \alpha_1 e^{-\mu(E)x_1} + \alpha_2 e^{-\mu(E)x_2} + \alpha_3 e^{-\mu(E)x_3},$$
$$\alpha_1 + \alpha_2 + \alpha_3 = 1. \tag{2}$$

Here α_i is a ratio of the sample area with thickness x_i to the full area of the sample. $\mu'(E, x)$ is the measured absorption coefficient of the edge. All primed quantities are measured ones and unprimed are true ones.

From numerical simulations of the thickness inhomogeneity it was shown that due to this effect the asymptotic behaviour of the absorption spectrum is distorted, the absorption edge step and the amplitude of EXAFS oscillations are reduced. Applying the discrete model it is possible to reconstruct the true absorption coefficient. Quantities α_i and x_i are regarded as the model parameters. This is done because it is mathematically useful.

3.2. Correction on thickness inhomogeneity effect

Let us rewrite Eq. (2) with new notations

$$Z_i = \alpha_1 b_{1i} + \alpha_2 b_{2i}, \tag{3}$$

where i is the number of point in asymptotic E space, α_1, α_2 are the unknown quantities.

$$Z_i = e^{-\mu'(E_i,x)+\mu(E_i)x} - 1,$$
$$b_{1i} = e^{\mu(E_i)\Delta x} - 1, \qquad b_{2i} = e^{-\mu(E_i)\Delta x} - 1. \tag{4}$$

Here $\mu(E_i)$ is the Victoreen function of an alloy.
Assuming α_1 and α_2 to be unknown parameters we find its formally from the system of the two linear algebraic equations (3)

$$\alpha_1 = \frac{b_{22}Z_1 - b_{21}Z_2}{b_{11}b_{22} - b_{12}b_{21}}, \qquad \alpha_2 = \frac{b_{12}Z_1 - b_{11}Z_2}{b_{21}b_{12} - b_{11}b_{22}}. \tag{5}$$

An asymptotic behaviour of the true spectrum $\mu(E)$ is described by the Victoreen function (International Tables, 1962). The Victoreen function of an alloy $\mu_V(E)$ is calculated according (International Tables, 1962) as

$$\mu_V(E) = \rho_0 \frac{\sum_i c_i m_i \left(\mu/\rho \right)_i}{\sum_i c_i m_i}, \qquad (6)$$

where ρ_0 is the mass density (g/cm^3), c_i is the atomic concentration of i-element in the alloy, m_i is the atomic weight of i -element in the alloy, the mass absorption coefficient of i-element $(\mu/\rho)_i = P_i\lambda^3 - Q_i\lambda^4$, P_i, Q_i are the Victoreen coefficients (International Tables, 1962).

The parameters α_1 and α_2 are constant in the asymptotic range for any pairs of points E_1, E_2 and E_1,E_3. Then we obtain a transcendental equation for an unknown parameter x, assuming Δx to be a free parameter,

$$\frac{b_{22}z_1 - b_{21}z_2}{b_{11}b_{22} - b_{12}b_{21}} = \frac{b_{23}z_1 - b_{21}z_3}{b_{11}b_{23} - b_{13}b_{21}}. \qquad (7)$$

To determine the parameters x and Δx Eq. (7) is solved by the bisection method.

For correction of absorption spectra on the thickness inhomogeneity effect we use the following iteration scheme using Eq.2

$$\mu_n(E)x = \mu'(E,x) + \\ + \ln\left[1 + \alpha_1\left(e^{\mu_{n-1}(E)\Delta x} - 1\right) + \alpha_2\left(e^{-\mu_{n-1}(E)\Delta x} - 1\right)\right], \qquad (8)$$

where n is the iteration number, $\mu'(E,x)$ is the measured experimental spectrum, parameters x, Δx, α_1 and α_2 are determined above. At $n = 1$ we use the Victoreen function for an alloy: $\mu_{n-1}(E) \equiv \mu_0(E) = \mu_V(E)$.

The numerical simulations have been carried out for the different models. For example, we assumed the continuous Gauss distribution with average thickness $x_{av} = 12.9\times10^{-4} cm$ and average deviation $\sigma = 2.5\times10^{-4}\ cm$. We have obtained the true spectrum $\mu(E)$ with very high accuracy (the residual norm between the model spectrum and the reconstructed one $\delta = 7.2\times10^{-8}$) at the following parameters of solution: $x = 12.9\times10^{-4}\ cm$, $\Delta x = 4.4\times10^{-4} cm$, $\alpha_1 = 0.15$; $\alpha_2 = 0.16$; $\alpha_3 = 0.69$.

4. Influence of fluorescence on absorption spectra

4.1. Model

Following (Stern & Kim, 1981), we write an expression for the absorption spectrum of the homogenious thick sample including fluorescence

$$I(E) = \left(I_0(E) - I_0'(E)\right) e^{-\mu'(E,x)} \equiv \\ \equiv \left(I_0(E) - I_0'(E)\right)\left(e^{-\mu(E)x} + d(E,x)\right), \qquad (9)$$

where leakage of the fluorescence described as

$$d(E,x) = \left(a + bE + cE^2\right)x. \qquad (10)$$

For a binary alloy we rewrite Eq.(9) and Eq.(10) as

before the edge of the x-ray absorption spectrum for the first element in an alloy

$$e^{-\mu_1'(E_1,x_1)} = e^{-\mu_1(E_1)x_1}, \qquad (11)$$

after

$$e^{-\mu_1'(E_1,x_1)} = e^{-\mu_1(E_1)x_1} + \left(a_1 + b_1E_1 + c_1E_1^2\right)x_1, \qquad (12)$$

before the edge of the x-ray absorption spectrum of the second element in an alloy

$$e^{-\mu_2'(E_2,x_2)} = e^{-\mu_2(E_2)x_2} + \left(a_1 + b_1E_2 + c_1E_2^2\right)x_2, \qquad (13)$$

after

$$e^{-\mu_2'(E_2,x_2)} = \\ e^{-\mu_2(E_2)x_2} + \left((a_1 + a_2) + (b_1 + b_2)E_2 + (c_1 + c_2)E_2^2\right)x_2, \qquad (14)$$

where the energy E_1 less than the energy E_2, x_1 is the thickness of the first sample for performing experiment on the first edge. Sometimes, for performing experiment on the second edge it is necessary to prepare another sample with thickness x_2.

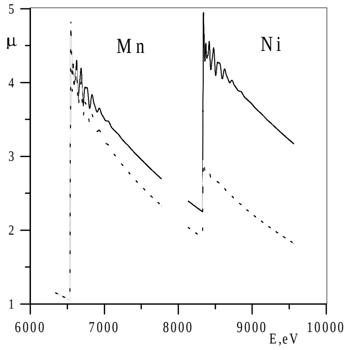

Figure 1
Influence of fluorescence on absorption spectra of the ordered $Ni_{50}Mn_{50}$ alloy: model calculation. Solid line – the true spectrum, dashed line – the spectrum with the fluorescence contribution.

Fig. 1 presents the result of model simulation for the absorption spectra of homogeneious samples for ordered $Ni_{50}Mn_{50}$ (the thickness $x_1 = x_2 = 18\ \mu m$) with and without the fluorescence contribution.

4.2 Correction of absorption spectra on the fluorescence effect

The procedure of correction is rather simple. Using the pre-edge part of the first spectrum (Eq. 11), it is possible to find the thickness

x_1. The parameters a_1, b_1 and c_1 are determined in asymptotic range from Eq. 12 by the least square method. Knowing the values a_1, b_1 and c_1, we repeat this procedure for the second edge and determine the thickness of the second sample x_2 and the parameters a_2, b_2 and c_2. Then the true absorption coefficient $\mu(E)$ is obtained from the equation

$$\mu_i(E)x_i = -ln\left(e^{-\mu'_i(E,x)} - \left(a_i + b_i E + c_i E^2\right)\right), \qquad (i=1,2) \tag{15}$$

It is necessary to note that our procedures of correction on the thickness inhomogeneity and fluorescence effects use the asymptotic behaviour of the experimental quantity $\mu'(E,x)$ and without measuring the apparatus function (background) practically impossible to reconstruct the true x-ray absorption coefficient. But the measurement of the apparatus function is performed separately and often under different conditions then the spectrum and the absolute value of $\mu'(E,x)$ is indefinite. Toward this end, we add some constant c to $\mu'(E,x)$ and calculate the parameters a_i, b_i and c_i (i = 1,2) several times. At the energy $E = E_F$ (Fermi energy) the fluorescence is absent and leakage $d(E) = 0$. Then

$$\tilde{a}_i = -\left(b_i E + c_i E^2\right) \tag{16}$$

If $a_i = \tilde{a}_i$ the value of $\mu'(E,x)$ is definite.

The Eqs. (11) – (16) is easily rewritten for the inhomogenious sample.

5. Correction of experimental data

This method was applied to preliminary processing of Ni-Mn samples: one of them was a powder sample, the other was a thick foil.

The K-edge absorption spectra of Ni and Mn for the ordered $Ni_{0.75}Mn_{0.25}$ alloy was recorded in transmission mode at BL7C at Photon Factory in Tsukuba [8]. A Si(111) double crystal monochromator was used. The storage ring was operated at 2.5 *GeV* and the ring current was 200-300 *mA*. All samples were ground at fine powder (the grain size is smaller than 38μm).

The sample of the ordered $Ni_{0.50}Mn_{0.50}$ alloy was prepared by a shear under high pressure. The average thickness of the foil was 20 μm. The K-edge absorption spectra of $Ni_{0.50}Mn_{0.50}$ for Ni and Mn were recorded in transmission mode at BL20ID–B at the APS, Argonne National Laboratory. A Si(111) double crystal monochromator was used. The storage ring was operated at 7.0 GeV and ring current was 65-100 *mA* (Ryazhkin *et al*., this volume).

Our procedure of preliminary processing includes the next steps: a) removing the apparatus function (background); b) correction on thickness inhomogeneity or (and) fluorescence effects; c) removing the pre-edge absorption function; d) removing a smooth background (μ_0') using a cubic spline function; e) obtaining the EXAFS-spectrum in E – space; f) a transition from E – space to k – space using a theoretical EXAFS–spectrum calculated by the code FEFF 8 (Ankudinov et al., 1998) for the crystalline sample as a reference.

The proposed method was applied to the XAFS spectra for Ni-Mn alloys (Ryazhkin *et al*., this volume). As an example of correction on the thickness inhomogeneity, Fig.2 presents EXAFS Ni spectrum for the powder sample of the ordered $Ni_{0.75}Mn_{0.25}$ alloy and Fig.3 shows the fluorescence effect for the thick sample of the ordered $Ni_{0.50}Mn_{0.50}$ alloy on EXAFS Ni spectrum. Amplitude EXAFS oscillations becomes more than two times for of the ordered $Ni_{0.75}Mn_{0.25}$ alloy. Then in this case we obtain (after correction) 1NN coordination number $N_{Ni\text{-}Ni}$ = 7.97, rather close to 8 (a known value for FCC structure). We evaluated also the same parameter for the original data. It was $N_{Ni\text{-}Ni}$ = 3.64. The other local structure parameters evaluated from the corrected XAFS data are presented in (Ryazhkin *et al*., this volume). So, the proposed method may be useful in EXAFS data analysis.

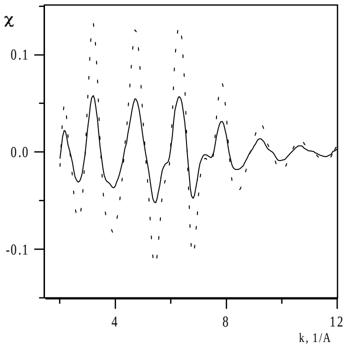

Figure 2
Experimental EXAFS–spectra for ordered $Ni_{0.75}Mn_{0.25}$ alloy before (solid line) and after (dashed line) correction on the inhomogeneity (Ni edge).

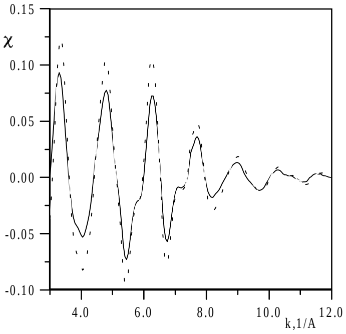

Figure 3
Experimental EXAFS–spectra for ordered $Ni_{050}Mn_{0.50}$ before (solid line) and after (dashed line) correction on the thickness inhomogeneity and fluorescence effects (Ni edge).

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