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Correction of XAFS amplitude distortions caused by the thickness effect

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Absorption data measured using transmission mode in many cases are reduced due to a sample inhomogeneity. If the sample composition is known XAFS amplitude can be restored by comparing of pre-edge absorption in a wide region with tabulated values or with experimental data for a uniform sample. In some cases the sample thickness distribution can be restored and used to calculate true absorption. We propose to correct XAFS amplitude by constructing correcting function using pre-edge data without the restoring of the thickness distribution. The comparison of the pre-edge absorption for inhomogeneous samples with the same composition can be used for relative scaling of damped XAFS amplitudes or to check the samples homogeneity only.

Keywords: X-ray absorption; thickness effect

1. Introduction

XAFS amplitude measured using transmission detection mode can be distorted because of the thickness effect first discussed by Parratt, Hempsted & Jossem (1957). Detailed analysis of the distortions originating from a sample inhomogeneity, radiation scattering around the sample, a sample fluorescence and harmonics was done later in many papers (Goulon, Goulon-Ginet, Cortes & Dubois (1982); Heald & Stern (1977); Heald (1988); Stern & Kim (1981)). In present paper we will discuss a possibility to correct XAFS amplitudes distortions caused by a sample inhomogeneity only using pre-edge or far above the edge experimental or tabulated data.

2. Restoring of a thickness distribution profile

For a homogeneous sample transmitted X-ray beam intensity I is determined as $I = I_0 exp(-\mu\rho x_0)$, where I_0 - incident X-ray beam intensity, μ - mass absorption coefficient, ρ - the sample density, x_0 - the sample thickness. The $\mu\rho x_0$ value is calculated in this case simply as $ln(I_0/I)$. In practice a sample is always inhomogeneous and I value should be calculated by integrating over the sample area along y and z coordinates:

$$I = \frac{I_0}{S} \int e^{-\mu\rho x(y,z)} dydz \qquad (1)$$

where S is the sample area and $x(y,z)$ is the sample X-ray thickness at y, z coordinates. The sample area can be separated on a number of areas S_i with thickness x_i when $S = \sum S_i$. In this case:

$$I = \frac{I_0}{S} \sum_i \oint_{S_i} e^{-\mu\rho x_i} dydz = \frac{I_0}{S} \sum_i e^{-\mu\rho x_i} \oint_{S_i} dydz$$

(2)

As far as $dydz$ integral over S_i is simply equal to S_i value then:

$$I = I_0 \sum_i \frac{S_i}{S} e^{-\mu\rho x_i} = I_0 \sum_i F_i e^{-\mu\rho x_i} \qquad (3)$$

where $F_i = S_i/S$ as relative parts of the sample with the X-ray thickness x_i are introduced. For a sample with arbitrary thickness distribution the sets x_i and F_i should be replaced by x variable and $F(x)$ function, respectively. In this case sum over i should be replaced by an integral over x and transmitted X-ray beam intensity can be expressed as:

$$I = I_0 \int F(x) e^{-\mu\rho x} dx \qquad (4)$$

It is not important to know localization of cracks and holes and a sample inhomogeneity can be characterized by the introduced thickness distribution function $F(x)$ when $F(x)dx$ is equal overall part of the sample area with the X-ray thickness x with small variation dx. As far as $F_i = S_i/S$ and $S = \sum S_i$ the $F(x)$ function is normalized

$$\int F(x)dx = 1 \qquad (5)$$

For example, for a uniform sample $F(x)$ is simply the delta function $\delta(x - x_0)$ and for a sample with holes it can be expressed as $C\delta(0) + (1 - C)\delta(x - x_0)$ where C is the holes portion. In practice $F(x)$ can be more complex.

Experimental value $(\mu\rho x)_{exp}$ calculated as $ln(I_0/I)$ can be expressed as:

$$(\mu\rho x)_{\exp} = \mu\rho x_0 - \ln \int F(x) e^{-\mu\rho(x - x_0)} dx \qquad (6)$$

Where average thickness x_0 is introduced:

$$x_0 = \langle x \rangle = \int xF(x)dx \qquad (7)$$

If the sample thickness or its variations are small then $\mu\rho(x-x_0) \ll 1$ and $(\mu\rho x)_{exp} \approx \mu\rho x_0$. It should be emphasized that XAFS amplitude determined using the $ln(I_0/I)$ experimental values and normalized to the edge jump for inhomogeneous sample are damped by a nonlinear way. Figure 1 illustrates calculated relative damping of a near edge feature of varying amplitude A on a spectra with the edge jump equal to 1 depend on pre-edge absorption when X-ray leakage through the sample is equal to 1%.

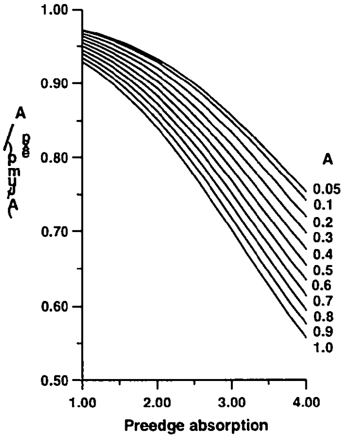

Figure 1
Near-edge feature damping calculated at its various amplitude A when edge jump is equal to 1 and X-ray leakage is equal to 0.01.

Pre-edge absorption is described well by Victoreen's function. If a sample composition is known the following equation can be solved to determine thickness distribution F(x) using pre-edge experimental data:

$$I(\lambda) = I_0(\lambda)\int F(x)e^{-(C\lambda^3 - D\lambda^4)\rho x}dx \qquad (8)$$

Tabulated C and D values as well as experimentally determined $\mu(\lambda)$ function for a homogeneous sample with the same composition can be used in this case. *F(x)* distribution can be used then to construct μ as a function of the I_0/I ratio allowing to determine then its true values instead of damping $ln(I_0/I)$ values. It should be mentioned that this way has got some limitations because $I_0(\lambda)/I(\lambda)$ ratio is always demonstrates smooth behavior and can be approximated well by a function determined by a limited number of independent parameters. So, an *F(x)* function can be restored by solving the equation (7) only if it is determined by a less number of independent parameters. To extend the number of parameters describing $I_0(\lambda)/I(\lambda)$ function and *F(x)* function, respectively, one can use widely extended pre-edge data region or even smooth wide data region far above the edge. Anyway, it seems that these approach will be productive only if some *F(x)* profile limits can be supposed.

2. Simple XAFS amplitude correction

We propose one more way to correct XAFS transmission data distorted by a sample inhomogeneity. Correcting function for $(\mu\rho x)_{exp}$ values can be constructed without restoring of the *F(x)* by comparing of experimental data with those for a uniform sample of the same composition or with tabulated data in a wide pre-edge region. Such a comparison allows to restore dependence of real $\mu\rho x$ on $(\mu\rho x)_{exp}$. The correcting procedure is illustrated in the Fig. 2. For example, experimental μ_1 value measured at the E_{AE} energy should be replaced by the corrected value μ_{cor1} marked on the reference curve at the energy E_1. Experimental μ_2 value measured at the E_{AE} + 1000 eV should be replaced by the corrected one marked on the reference curve at the energy E_2. Each point of the experimental spectrum should be corrected by the same way. The thickness of the uniform or model sample is a free parameter which scales a restored spectrum only. The scaling is eliminated when oscillating part is normalized to the edge jump.

The best way to prepare a uniform sample and to avoid XAFS amplitude damping is to grind starting material preliminary into a very fine powder. At the same time the grinding may cause structural distortions and cracks in fine particles and special attention should be paid to the grinding procedure control as well as to a final particles selection. A very fine fraction of the sample which can be structurally disordered can be used to prepare a uniform reference sample which thickness should not be optimized to measure XAFS but pre-edge absorption only. Pre-edge absorption is a smooth function and data can be measured on the reference sample in several points only and then interpolated. The sample for XAFS measurements can be prepared using appropriate fraction after grinding and respective thickness optimization. The XAFS data measured can be then corrected by pre-edge absorption comparing with those for the reference sample according to the procedure proposed above.

If a XAFS amplitude should be analyzed carefully for a number of samples of the same composition one of them can be chosen as the reference one. XAFS data for all other samples can be corrected using pre-edge data for the reference one. As far as the reference sample can be inhomogeneous in this case the procedure does not allow to restore the true XAFS amplitude but gives the corrected spectra with equivalent amplitude distortions making their following comparison more reasonable. Anyway, careful comparison of experimental absorption in a wide pre-edge region without corrections can be used to test or compare the samples inhomogeneity to be sure that the XAFS data amplitude characteristics are reliable.

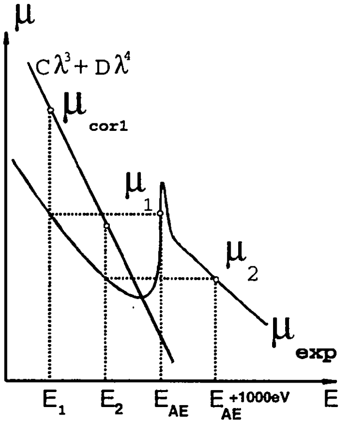

Figure 2
Correction scheme of experimental absorption using pre-edge tabulated or reference experimental data measured on a uniform sample. μ_1 - experimental value, μ_{cor1} - respective corrected value.

There is an experimental problem to use the proposed procedure in some cases. As can bee seen in the Fig. 2 the pre-edge absorption should be measured in the energies interval between E_1 and E_2 energies to correct experimental data in an energy interval about 1000eV starting just above an absorption edge at the energy E_{AE}. Calculated E_1 and E_2 values for some *K* and L_{III} absorption edges are presented in the Table 1 for a number of elements. It seems that it is not possible to measure pre-edge absorption starting from the energy E_1 and *K*-edge EXAFS using the same experimental technique for the elements with Z<32. For samples containing these elements a monitor detector, separation windows and a vacuum scheme could be probably changed to measure absorption at the low energies starting at E_1.

Table 1
Calculated limits E_1 and E_2 for pre-edge absorption data which should be measured to correct XAFS region for various pure materials.

Absorption Edge	E_{AE} (keV)	E_1 (keV)	E_2 (keV)
Mn *K*	6.540	2.979	3.445
Co *K*	7.709	3.567	4.038
Cu *K*	8.981	4.220	4.695
Ga *K*	10.367	4.930	5.409
As *K*	11.868	5.710	6.191
Br *K*	13.474	6.563	7.050
Rb *K*	15.200	7.487	7.977
Y *K*	17.039	8.488	8.980
Nb *K*	18.986	9.551	10.047
Tc *K*	21.045	10.679	11.177
Rh *K*	23.220	11.868	12.386
Ag *K*	25.514	13.168	13.671
In *K*	27.940	14.497	15.002
Ta L_{III}	9.890	6.900	
Re L_{III}	10.545	7.200	
Pt L_{III}	11.570	8.000	
Pb L_{III}	13.040	9.000	

For a sample with a complex composition the absorption of its matrix at the energy E_I may be valuable making the measurements unreliable or even impossible in this region. The situation is more favorable for higher Z elements because E_I value is shifted to higher energies. It seems that for L_{III} edges there is no any experimental difficulty to measure required pre-edge region because E_I values lies much closer to the respective E_{AE} values.

As can bee seen in the Fig. 3 the XAFS amplitude damping is nonlinear and an intensive feature is more sensitive to the sample inhomogeneity than a small one. For, example the leakage variations from 0.25% to 1% cause more than 15% relative changes of normalized near-edge feature intensity A, when A=0.5, edge jump = 1 and pre-edge absorption is about 3. So, the proposed amplitude correction should be done in all cases when sharp intensive near-edge features such as "white lines" are compared.

References

Goulon J., Goulon-Ginet C., Cortes R. & Dubois J. M. (1982) *J. Physique* **43**, 539 - 543.

Heald S. M. & Stern E. A. (1977). *Phys. Rev.* **B16**, 5549-5553.

Heald S. M. (1988) in "*X-ray absorption: Principles, Applications Techniques of EXAFS, SEXAFS and XANES*" Chapter 3, ed. By Koningsberger D.C. & Prins R., Willey

Parratt L. G., Hempsted C. F. & Jossem E.L. (1957). *Phys. Rev.* **105**, 1228-1232

Stern E. A. & Kim K. (1981). *Phys. Rev.* **B23**, 3781-3785

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