Variable angle XAFS study of multilayer nanostructure: Determination of selective concentration profile and depth-dependent partial atomic distributions

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Abstract. We propose a new method for studying multilayer structure using angle resolved extended x-ray absorption fine structure (EXAFS) measurements. The linear integral equation describing a connection between the fluorescence intensity for spectrum of element C, the incident beam energy $E$, the incident angle $\phi$ and the concentration profile $p(z,C)$ has been derived. It is a Fredholm integral equation of the first kind, it belongs to the class of ill-posed problems and for solution it needs special methods. We use the regularization method. For determining the depth-dependent partial interatomic distances we use angle resolved EXAFS data. The effectiveness of the method has been tested during numerical simulation on the model crystalline three-layer with BCC structure: Cr/Fe/Cr.

1. Introduction
The discovery of oscillations of interlayer exchange coupling (IEC) with the thickness of the spacer layer in metallic magnetic superlattices opens a new field in low dimensional magnetism. Non-commensurability of the lattice constants and de Broglie wave-length for electrons in the multilayers leads to the "aliasing" effect and suppression of short range oscillations of the IEC. It is essential to extract layer and interface information to clarify the mechanism of the IEC. However, it is difficult to directly obtain the depth resolved atomic structure with conventional EXAFS, because this technique observes only the average over the whole multilayer.

The ability to characterize multilayer nanostructures with depth is of great interest in the field of material science. We propose a non-destructive method, where EXAFS measurement performed at the varied incidence angle. Many current approaches to modelling used for describing the magnetic and structural experimental data are as follows: 1) all layers consisting of the $C$ atom have the equal thickness; 2) the interfaces are described by the equal interatomic mixing, thickness, and roughness [1]. It allows to use the parametrized model for the least-square fitting. But, this method is a very unstable. There exists an infinite amount of solutions for one set of experimental data.
2. Integral equation for fluorescence intensity of multilayer

Let us define a concentration profile $p(z, C)$ as a probability to find atom C at a depth $z$ from a sample surface $p(z, C) = n(z, C) / n_0(C)$, where $n(z, C)$ – an atomic density of element C at a depth $z$, $n_0(C)$ – atomic density of element C for pure layer without mixing. Then we can derive the equation for fluorescence intensity $I_f^C(\phi, E)$ for spectrum of C, using the approach describing in [2].

$$I_f^C(\phi, E) = \frac{I_0}{\sin \varphi} \mu_a n_0(C) \int_0^D p(z, C) \mu_a(z, E) \exp \left[- \left( \frac{\mu_I}{\sin \varphi} + \frac{\mu_f}{\sin \theta} \right) z \right] \, dz.$$  

(1)

Here $E$ is the incident beam $I_0$ energy, $\varphi$ is the incident angle, depth $z = a \sin \varphi = b \sin \theta$ (see figure 1), $\mu_a(z, E)$ is the absorption coefficient at a depth $z$, $\varepsilon_a$ is the fluorescence efficiency per unit solid angle. If $p(z, C) \equiv 1$, we obtain the formula from [2].

3. Determination of selective concentration profile

The integral equation (1) can be used for determination of a concentration profile $p(z, C)$ performing experiment at the fixed energy $E_{\text{fix}}$ (for example, $E_{\text{fix}}$ near the absorbing edge Fe, figure 2; for more information about x-ray lines used see appendix A) and with changing the incident angle $\varphi$ at the range $0.1 – 1$ deg., step 0.01 deg.

In this case the equation (1) can be rewritten as

$$I_f^C(\phi, E_{\text{fix}}) = \frac{A}{\sin \varphi} \int_0^D p(z, C) \exp \left[- \left( \frac{\mu_I}{\sin \varphi} + \frac{\mu_f}{\sin \theta} \right) z \right] \, dz,$$

(2)

where $A = I_0 \varepsilon_a n_0(C) n(E_{\text{fix}})$. In order to test the algorithm for determination of depth-dependent $p(z, C)$, we simulated a sample such as three–layer Cr/Fe/Cr (figure 3). The corresponding intensities are represented in figure 4. Solution of inverse problem (2) for Cr depth profile compares with model curve in figure 5. As can be seen, model and solution curves are in a good agreement.
Figure 3. Depth profiles of Cr and Fe concentrations in multilayer structure Cr/Fe/Cr – model for numerical simulation.

Figure 4. Fluorescence intensity for Cr and Fe in multilayer structure Cr/Fe/Cr – numerical simulation.

Figure 5. Depth profile of Cr concentration in multilayer structure, model and solution curves.

4. Depth-dependent EXAFS
For known function $p(z, C)$ equation (1) can be regarded as the equation for determining depth-dependent function $\mu_a(z, E_{fix})$:

$$I_f^C(\varphi, E_{fix}) = \int_0^D \mu_a(z, E_{fix})K(z, \varphi)dz$$  \hspace{1cm} (3)

where $K(z, \varphi) = \frac{I_0}{\sin \varphi} n_0(C) p(z, C) \exp \left[ - \left( \frac{\mu_i}{\sin \varphi} + \frac{\mu_f}{\sin \theta} \right) z \right]$. 
The numerical simulations for depth-dependent EXAFS was divided into the following several steps:

1. Generation of a model matrix $\chi(k, z)$ (figure 6).
2. Transition $\chi(k, z) \rightarrow \mu(z, E)$ using a free electron dispersion law and energy dependence of the absorption for isolated Fe atom.

3. Direct problem solving for equation (3) with known $p(z, C)$ and $\mu(z, E)$ at each energy point in the range $7142 – 8092$ eV, step is 5 eV. The result is the matrix $I(E, \varphi)$ (figure 7).
4. Inverse problem solving for equation (3), using $I(E, \varphi)$ as input data. The function $p(z, C)$ is regarded as known function (from the first stage, where it was determined). Thus we reconstruct the matrix $\mu(z, E)$.
5. Transition $\mu(z, E) \rightarrow \chi(k, z)$, this matrix showed at figure 8.

5. Partial interatomic distances for multilayer nanoheterostructures
To obtain information on partial interatomic distances at a given depth $z$ we solve the EXAFS integral equation for 2-component system:
\[
\chi_i(k) = \frac{4\pi \rho_0}{k} R(k) \sum_{j=1}^{\infty} f_j(k, r) e^{-2\lambda(k)} \sin(2kr + \psi_j(k, r)) g_{ij}(r) dr ,
\]

(4)

here \( k \) is the wave number of a photoelectron, \( \rho_0 \) is the mean atomic density, \( R(k) \) is the amplitude reduction factor, \( \lambda(k) \) is the mean free path of photoelectron, \( f_j(k, r) \) is the absolute value of its backscattering amplitude, \( 2\delta_i(k) \) is the phase shift due to scattering on the central atom \( i \), \( \varphi_j(k, r) \) is the backscattering phase shift and \( \psi_j(k, r) = 2\delta_i(k) + \varphi_j(k, r) \) 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. They are involved in the integral operator \( A_{ij} \), which, as it acts on the function \( g_{ij} \), generates a contribution of a specific atomic pair \( i-j \) to the normalized oscillating part \( \chi_i \).

The function \( g_{ij} \) is the partial pair correlation function (pPCF) which, by definition, is the probability to find atom \( j \) at the distance \( r \) from atom \( i \).

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.

In symbolic form (4) becomes as follows:

\[
u_i = \sum_{j=1}^{\infty} A_{ij} g_{ij} ,
\]

(5)

where \( A_{ij} \) is the integral operator, the function \( u_i(k) \) include experimental data \( \chi_i \) and asymptote of \( A_{ij} g_{ij} \). In the numerical simulation we used reconstructed function \( \chi(k, z) \) at a particular depth \( z \). In this way we are going to receive an information about partial interatomic distances at the different depths.

In case of multilayer Fe/Cr nanostructures for the Fe K edge let us rewrite (5) using the regularization algorithm [3], \( n = 2 \), label for Fe is 1, that for Cr is 2, \( i = 1, \ j = 1, 2 \). We obtain the system of integral equations:

\[
\begin{bmatrix}
A_{11} & A_{11}^* A_{12} \\
A_{12}^* & A_{12}^* A_{12} \\
\end{bmatrix}
\begin{bmatrix}
B_1 \\
B_2 \\
\end{bmatrix}
\begin{bmatrix}
g_{11} \\
g_{12} \\
\end{bmatrix}
= \begin{bmatrix}
A_{11}^* u_1 \\
A_{12}^* u_1 \\
\end{bmatrix} .
\]

(6)

\[
B_i = \begin{bmatrix}
\alpha_i + 2\beta_i & -\beta_i & 0 & \ldots & 0 \\
-\beta_i & \alpha_i + 2\beta_i & -\beta_i & \ldots & 0 \\
0 & -\beta_i & \alpha_i + 2\beta_i & \ldots & 0 \\
\ldots & \ldots & \ldots & \ldots & \ldots \\
0 & 0 & 0 & \ldots & \alpha_i + 2\beta_i \\
\end{bmatrix} .
\]

(7)

Here * denotes transposition, the matrix \( B \) consists of the small, positive regularization parameters \( \alpha_i \) and \( \beta_i \). In the symbolic form:

\[
(A^* A + B) g = A^* u .
\]

(8)

The eigenvalues of matrix \( (A^* A + B) \) are positive. In this case it is possible to use the well-known linear algebra methods to invert the matrix. The so-called Tikhonov solution [3] is obtained as:

\[
g_0 = (A^* A + B)^{-1} A^* u .
\]

(9)

The function \( g_0 \) is an approximate solution of the exact equation (4).

In the Table 1 the results of EXAFS equation solution in points 1 and 2 (see figure 3) are presented (in comparison with model data):
Table 1. Results of numerical simulations for two depth points (see figure 3): 43 Å and 65 Å. All values are given in Å.

|        | Fe-Fe | Fe-Cr |
|--------|-------|-------|
| Depth, z | 43 (p.1) | 65 (p.2) |
| Model   | 2.489 | 2.500 |
| Solution| 2.485 | 2.479 |

6. Conclusion
In this paper, a method for determining selective concentration profile and partial interatomic distances for multilayer nanoheterostructures at specific depths from variable angle XAFS study has been presented. The method was validated by recovering depth profiles from simulated data. Also, we have demonstrated a high resolution for bond lengths of close spacing atoms (Fe, Cr) in the Periodical Table. It is necessary to note that performing experiments at small incident angles is not enough in order to obtain information about the concentration profile and interatomic distances (see figures 4 and 7). The solution of integral equations 2 and 4 needs, using special methods for ill-posed problem. The resolution in sample depth is 2-3 Å has been achieved.

These results were obtained without any assumptions concerning the form of selective concentration profile and interatomic distances for multicomponent systems.

The samples of Cr/Fe/Cr with different thickness of the layer Fe have been grown using MBE on the polished Al₂O₃ substrates in a UHV chamber in Institute of Metal Physics. The measurements were performed using synchrotron facilities (Russian Research Centre "Kurchatov Institute"). The Fe and Cr edge absorption spectra were recorded in fluorescence mode. Experimental results will be published elsewhere.

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Appendix A. Table of x-ray lines energies and absorption

Table A1. Incident and fluorescent x-ray lines used. Each absorption coefficient is given for the pure material, mentioned in the x-ray line description.

| Line                    | Energy (eV) | Absorption coefficient (Å⁻¹) |
|-------------------------|-------------|-----------------------------|
| Incident, near Cr K-edge | 5991,00     | 4.39441×10⁻³               |
| Incident, near Fe K-edge | 7117,00     | 3.20051×10⁻⁵               |
| Fluorescent, Cr Kₙ      | 5411,65     | 5.98815×10⁻⁶               |
| Fluorescent, Fe Kₙ      | 6399,51     | 6.08489×10⁻⁶               |

References
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[2] Booth C and Bridge F *Physica Scripta* 2005 **T115** 202–204.
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