Interatomic distances for overlapping shells in disordered systems: model-less approach

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Abstract. The regularization method of solving ill-posed problem is used to determine five partial interatomic distances from combined two EXAFS spectra without building any model of atomic structure. The mathematical procedure and the experimental results of the EXAFS analysis for Ni\textsubscript{c}Zn\textsubscript{1-c}O (c = 0.0, 0.3, 0.5, 0.7, 1.0) solid solutions with the rock salt (rs) crystal structure synthesized from the binary oxide powders are discussed. The measurements were performed using synchrotron facilities (Russian Research Centre "Kurchatov Institute", Moscow). The Ni and Zn K absorption spectra were recorded in transmission mode at room temperature. It was shown the ideal rock salt lattice is distorted and long-range order exists only at the average (Vegard law).

1. Introduction
A series of the Ni\textsubscript{c}Zn\textsubscript{1-c}O solid solutions with the rock salt (rs) crystal structure belongs to the family of wide-band-gap semiconductors with strong ionic character of chemical bonds. They are of great interest both from a fundamental and an applied point of view. These solutions has been used in wide range of applications such as p-type transparent conducting film, chemical sensors, electro-chromic and high-speed devices. Recent EXAFS studies show that local structure in disordered systems does not coincide with information obtained from X-ray diffraction [1-3]. It has been shown that Vegard's law is locally not obeyed.

In the case of the systems with a disorder, it has been known for some time [1-4] that treating EXAFS data using a standard analysis may cause large errors. There is a serious problem for the systems like Ni\textsubscript{c}Zn\textsubscript{1-c}O solid solutions which is characterized by the coordination spheres, overlapping in r-space. In contrast to the conventional Fourier transformation and fitting we propose a new procedure of obtaining local information for three-component solid oxide solutions. For the first time, the method of combining two EXAFS spectra for two-component system (Ge-Si disordered alloys) was presented in [1]. Later this method was applied for ZnBr\textsubscript{2} aqueous solution [4].

This paper reports the results of EXAFS investigation of the local structure for rs Ni\textsubscript{c}Zn\textsubscript{1-c}O solid solutions. There is some disagreement in the literature concerning the first shell structure of rs Ni\textsubscript{c}Zn\textsubscript{1-c}O solutions; in particular whether or not there is a measurable variation of the nearest-neighbor interatomic distances as a function of alloy composition.
2. Mathematical algorithm

Let us consider a solid solution based on the oxides NiO / ZnO. These solid solutions were prepared by mixing the oxide powders in appropriate proportions: (NiO)_{1-x}(ZnO)_{x} \equiv Ni_{1-x}Zn_{x}O.

Let Ni - 1, Zn - 2, O - 3. The local atomic structure of a homogeneous three-component material can be described by five partial pair correlation functions: \( g_{11}(r) \), \( g_{12}(r) = g_{21}(r) \), \( g_{13}(r) \) and \( g_{21}(r) = g_{12}(r) \), \( g_{22}(r) \), \( g_{23}(r) \). The function \( g_{ij}(r) \) is the probability to find atom \( j \) at the distance \( r \) from atom \( i \), by definition. The integral equations for two EXAFS spectra at Ni and Zn K absorption edges:

\[
\chi_{1}(k) \equiv \chi_{Ni}(k) \quad \text{and} \quad \chi_{2}(k) \equiv \chi_{Zn}(k) - \text{can be written as follows}
\]

\[
\begin{align*}
   k\chi_{1}(k) & = 4\varphi_{0} \int_{0}^{\infty} (1-c) g_{12}(r) f_{2}(k,r) \exp\left[-2r/\lambda_{1}(k)\right] \sin[2kr + \psi_{12}(k,r)]dr + \\
   & + c \int_{0}^{\infty} g_{13}(r) f_{3}(k,r) \exp\left[-2r/\lambda_{1}(k)\right] \sin[2kr + \psi_{13}(k,r)]dr + \\
   & + \int_{0}^{\infty} g_{23}(r) f_{q}(k,r) \exp\left[-2r/\lambda_{q}(k)\right] \sin[2kr + \psi_{23}(k,r)]dr \\
   k\chi_{2}(k) & = 4\varphi_{0} \int_{0}^{\infty} (1-c) g_{22}(r) f_{2}(k,r) \exp\left[-2r/\lambda_{2}(k)\right] \sin[2kr + \psi_{22}(k,r)]dr + \\
   & + \int_{0}^{\infty} g_{23}(r) f_{q}(k,r) \exp\left[-2r/\lambda_{q}(k)\right] \sin[2kr + \psi_{23}(k,r)]dr 
\end{align*}
\]

(1)

Here \( c \) - the atomic concentration of molecules such as NiO, \( f_{i}(k,r) \) - modulus of the amplitude of backscattering, \( \psi_{ij}(k,r) = 2\delta_{i}(k) + \phi_{ij}(k,r) \) - the total phase shift for the ion pair \( i,j \) which is a peculiar "mark" for a specific pair of atoms, \( \lambda_{i}(k) \) - the mean free path of the photoelectron ejected from the ion of type \( i \). All atomic scattering characteristics (amplitude functions, phase functions and mean free paths) were calculated by FEFF-8.1 code [5].

The integral operator \( A_{ij} \) generates a contribution of a specific atomic pair \( ij \) to the normalized oscillating part, as it acts on the partial PCF \( g_{ij} \). We propose to use the dependence of the integral operator \( A_{ij} \) on the atomic scattering characteristics \( \delta_{i}(k) \) and \( \phi_{ij}(k,r) \) for determining partial PCFs in multicomponent systems from EXAFS data.

Let us assume for simplicity: \( g_{1}(r) = g_{13}(r) = g_{NiO}(r) \), \( g_{2}(r) = g_{11}(r) = g_{NNi}(r) \), \( g_{3}(r) = g_{12}(r) = g_{NiZn}(r) \), \( g_{4}(r) = g_{22}(r) = g_{ZnO}(r) \). In operator notation Eq.1 may be rewritten as

\[
\begin{align*}
   u_{1} & = (A_{11}g_{1} + A_{12}g_{2} + A_{13}g_{3}) \\
   u_{2} & = (A_{23}g_{4} + A_{24}g_{4} + A_{25}g_{5})
\end{align*}
\]

(2)

Here vectors \( u_{1}, u_{2} \) - input EXAFS data for both edges.

For the numerical solution of integral equations system (2) can be written as

2
\[
\begin{bmatrix}
  u_1 \\
  u_2
\end{bmatrix} = \begin{bmatrix}
  A_{11} & A_{12} & A_{13} & 0 & 0 \\
  0 & 0 & A_{23} & A_{24} & A_{25}
\end{bmatrix} \times \begin{bmatrix}
  g_1 \\
  g_2 \\
  g_3 \\
  g_4 \\
  g_5
\end{bmatrix}
\text{ or } u = Ag.
\] (3)

where \(A\) is an integral operator, \(g\) is an unknown function describing 5 functions \(g_{ij}\), \(u\) is an input (experimental) data for two EXAFS spectra. The numerical solution of Eq. 3 is an ill-posed problem. In this paper, the Tikhonov’s method of regularization is used [6]. A full description of the mathematical scheme for one EXAFS spectrum and 3 unknown functions can be found in Ref. [7].

3. Experimental

A series of metastable Ni\(_{1-c}\)Zn\(_c\)O solid solutions with the rock salt crystal structure have been synthesized from the binary oxide powders NiO and ZnO by quenching from 7.7 GPa and 1450-1650 K. Phase composition of the samples, as well as structural properties and stoichiometry of synthesized solid solutions have been studied by X-ray powder diffraction, both conventional and with synchrotron radiation [8]. The widest \((c = 0.0, 0.3, 0.5, 0.7, 1.0)\) composition range of the existence of individual rock salt solid solution has been established for the NiO-ZnO system. All samples were prepared at Moscow State University [8].

The measurements were performed using synchrotron facilities (The Structural Materials Science end-station at the Kurchatov Centre for Synchrotron Radiation and Nanotechnology (KCRNT), Moscow, Russia).

The Ni and Zn K edge absorption spectra were recorded in transmission mode at room temperature for rs Ni\(_{1-c}\)Zn\(_c\)O \((c = 0.0, 0.3, 0.5, 0.7, 1.0)\) solid solutions.

4. Results and discussion

Fig. 1 shows EXAFS spectra for two edges: Ni and Zn. These data were used for determination partial pair correlation functions of ternary oxide solutions as a result of solution for inverse ill-posed problem.

The Tikhonov’s solutions for \(rs\) Ni\(_{1/3}\)Zn\(_{2/3}\)O solid solution are depicted on Fig. 2. The maximal values of these curves correspond to interatomic distances. The numerical results obtained for all samples are given in Table 1. It is obvious, that we have a high resolution for the overlapping coordination spheres. The second feature - interatomic distances for pairs NiO and ZnO are almost independent of solution composition of our alloys and are close to the crystallographic distances for NiO \((2.088 \text{ Å})\) and ZnO \((2.140 \text{ Å})\). This suggests that for the \(rs\) NiO/ZnO oxide solid solutions it may be valid Pauling model [9] (see Table 2):

\[
a_c = 2\{c r_O + [c r_{Ni} + (1-c) r_{Zn}]\}.
\] (4)

Here \(r_O, r_{Ni}\) and \(r_{Zn}\) are ionic radii of \(O^{2-}, Ni^{2+}\) and \(Zn^{2+}\).

In order to obtain the lattice parameters for \(rs\)-NiO/ZnO solid solutions from EXAFS data as a function of concentration \(c\) it is necessary to submit the values of bond lengths \(R_{NiO}\) and \(R_{ZnO}\) from Tabl.1 according to formula:

\[
a_c = 2\{c R_{NiO} + (1-c) R_{ZnO}\}.
\] (5)
A method for determining partial interatomic distances from combined two EXAFS spectra for three-component solid oxide solutions has been presented.

We have demonstrated a high resolution for bond lengths of close spacing atoms (Ni, Zn) in the Periodical Table.

These results were obtained without any assumptions concerning interatomic distances for multicomponent systems

Acknowledgments
The authors would like to thank Andrey Baranov and Petr Sokolov (Moscow State University) for a preparation of the samples and also Yan Zubavichus (RRC "Kurchatov Institute") for an assistance in performing the experiment. This work was partially supported by grant № 12-II-2-1032 (the program of the Presidium of the RAS).

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