Disappearance of correlations in the atom motion upon hydrogen intercalation into ReO₃ lattice

Janis Timoshenko, Alexei Kuzmin and Juris Purans
Institute of Solid State Physics, University of Latvia, Kengaraga street 8, Riga, LV-1063, Latvia
E-mail: janis.timoshenko@gmail.com

Abstract. The influence of hydrogen intercalation on the local structure of rhenium trioxide is studied in-situ by the Re L₃-edge EXAFS spectroscopy and analysed using a novel approach, based on the use of evolutionary algorithm and wavelet transform. The proposed method allows us to perform accurate EXAFS analysis within the multiple-scattering approach taking into account contributions from outer coordination shells and to access the information on correlations in atomic thermal motion.

1. Introduction
The analysis of extended X-ray absorption fine structure (EXAFS) data from the first coordination shell around the absorbing atom is nowadays a common tool to study the local structure of materials [1]. At the same time, EXAFS spectra, acquired at modern brilliant X-ray sources, often contain much more information, especially for crystalline materials, where a contribution of distant coordination shells (up to 10 Å and more) is frequently present in the total EXAFS spectrum. The precise analysis of EXAFS spectra beyond the first coordination shell using conventional methods is, however, often impossible since the contributions of outer shells overlap, and the total number of parameters, required to describe the local structure, grows exponentially with the increase of the number of coordination shells, included in the analysis [2]. Moreover, conventional EXAFS analysis even for the first coordination shell can be imprecise for significantly distorted or disordered systems, where the distributions of interatomic distances are often far from the Gaussian one [3].

This problem may be treated by applying simulation-based techniques as molecular dynamics (MD) [3, 4] and reverse Monte Carlo (RMC) method [5]. For our purposes the latter is especially interesting, since the RMC method does not require the knowledge and calculation of interatomic forces and relies solely on the available experimental EXAFS data. In RMC approach a 3D structure model of the material is constructed using an iterative random process, aimed to minimize the difference between experimental EXAFS and configuration-averaged EXAFS spectra, calculated for the given structure model. Once a good agreement between simulated and experimental spectra is obtained, one may expect that also the constructed model provides a good approximation of the material structure. The existing RMC implementations for EXAFS analysis, however, usually neglect the influence of multiple-scattering (MS) effects or treat them in an approximate way due to concomitant significant computational costs. As a consequence, the information amount, obtainable from EXAFS spectrum, again, is rather limited.
Figure 1. Comparison of the EXAFS spectra (MD model for ReO$_3$, experimental data for pure ReO$_3$ and H$_x$ReO$_3$) with the results of RMC/EA-EXAFS calculations. Left column - Re L$_3$ edge EXAFS, two right columns - corresponding Morlet wavelet transforms (WT).

In the presented study we treat this problem and complement the conventional RMC scheme with (i) a powerful evolutionary algorithm (EA) for efficient structure model optimization [6] and (ii) the use of wavelet transform (WT) [7], which allows us to represent EXAFS spectra in real and frequency spaces simultaneously and, hence, to obtain more information from the same experimental data [8]. This advanced approach allows us to probe more distant coordination shells and to reveal the anisotropy and correlations of atom thermal motion and static displacements.

2. Experimental and simulation details
The experimental Re L$_3$-edge EXAFS spectra of pure polycrystalline rhenium trioxide (ReO$_3$) and of rhenium trioxide after in-situ intercalation with hydrogen ions (H$_x$ReO$_3$) were taken from [9], and for both spectra RMC/EA simulations were performed. Additionally, to validate the proposed approach, RMC/EA simulations were performed also for the model EXAFS spectrum, obtained in MD simulations of cubic ReO$_3$ in [10] (MD-ReO$_3$).

Detailed description of our RMC/EA scheme is given in [6]. RMC/EA calculations were performed using a 4×4×4 supercell (256 atoms). Positions of atoms were optimized by minimizing the mismatch between WTs for experimental EXAFS (or MD-EXAFS) and configuration-averaged EXAFS, obtained in ab-initio FEFF8 calculations within multiple-scattering approach [11]. As a result, a reasonable agreement was obtained for the final atomic configuration for all three cases (Fig. 1). These final structure models are analyzed below.

3. Results and discussion
Radial distribution function (RDF) around absorbing rhenium atom can be obtained straightforwardly from the results of RMC/EA calculations. To demonstrate the accuracy of the
Figure 2. Original and reconstructed by RMC/EA approach RDFs around Re atom for MD model (left panel) and RDFs obtained by RMC/EA calculations for experimental EXAFS for crystalline ReO$_3$ and H$_x$ReO$_3$ (right panel).

Figure 3. MSRD factors obtained by RMC/EA analysis for Re–Re and Re–O atom pairs as a function of interatomic distance for MD model (left panel; MSRDs obtained directly from MD simulations are also shown), pure ReO$_3$ (middle panel) and H$_x$ReO$_3$ (right panel). In-chain and off-chain atoms are shown separately; dashed lines are guides for the eye; vertical lines are estimated error bars of RMC/EA analysis results.

The proposed approach, the RDFs, obtained in RMC/EA simulation for the model EXAFS data and directly from MD simulation, are compared in Fig. 2. The agreement between initial structure model and the results of RMC/EA reconstruction is remarkable both for close and more distant coordination shells up to 8-9 Å. Note that the longest interatomic distance, probed by RMC/EA, is limited by the size of the used supercell.

The RDFs, obtained in RMC/EA simulations of experimental data for ReO$_3$ and H$_x$ReO$_3$ compounds (right panel in Fig. 2), indicate that the intercalation by hydrogen ions leads to the significant broadening of all RDF peaks due to the presence of strong disorder in the system.

The widths of RDF peaks are characterized by mean square relative displacement (MSRD) factors $\sigma^2$ [1]. MSRD for a pair of atoms A and B can be expressed as $\sigma_{AB}^2 = \langle u_A^2 \rangle + \langle u_B^2 \rangle - 2\langle u_A u_B \rangle$, where $\langle u_A^2 \rangle$ and $\langle u_B^2 \rangle$ are mean square displacement factors, related to the amplitudes of atom oscillations in the direction of interatomic bond. The last term $\langle u_A u_B \rangle$ accounts for the correlation in atom motion. The MSRD factors for several Re–Re and Re–O atom pairs are shown in Fig. 3 as a function of interatomic distance. Note that the results of RMC/EA calculations for the model ReO$_3$ system are in a good agreement with the true values of MSRD factors, obtained directly from the atom coordinates, which suggests a good reliability of the method.

The results, obtained from the experimental EXAFS of pure ReO$_3$, are shown in the middle panel of Fig. 3. Here the values of the MSRD factors for Re–Re and Re–O atom pairs suggest the difference in the correlations of atom motion along linear –Re–O–Re– chains (see the inset in the right panel of Fig. 2) with respect to the correlations in the off-chain directions.
The MSRD factors for atom pairs along the chains are small, reflecting strong interatomic interactions, and grow slowly with the increase of interatomic distance. Such behaviour can be explained by the presence of strong correlation in the atom motion, which naturally decreases at large distances. Nevertheless, our result suggests that correlations in the atom motion for the in-chain atoms are important even for atoms that are located as far as 9 Å from the absorbing rhenium atom. Note also that such behaviour of the MSRD factors for crystalline ReO$_3$ is in a qualitative agreement with the results, obtained from the MD simulations in [10], which are able to reproduce the dynamics of ReO$_3$ lattice.

The values of the MSRD factors for the off-chain directions are significantly larger, suggesting weaker interactions, and show almost no distance dependence, thus indicating that a correlation in the atom motion is negligible. Note that fluctuations in the values of MSRD factors for Re–O pairs for the off-chain atoms are a consequence of the anisotropy of oxygen thermal motion in the ReO$_3$ lattice, hence the MSRD factors depend on the angle between corresponding interatomic bond and lattice vectors.

The intercalation of ReO$_3$ by hydrogen ions affects the correlations in the atom motion dramatically (right panel in Fig. 3). First, the values of the Re–Re and Re–O MSRD factors in H$_x$ReO$_3$ are several times larger than those in pure ReO$_3$. Moreover, our results suggest complete disappearance of interatomic correlations beyond the first coordination shell, since there is almost no difference in the MSRD factors for in-chain and off-chain atom pairs in H$_x$ReO$_3$. Thus one may conclude that the intercalation of hydrogen ions leads not only to tilting and distortion of the ReO$_6$ octahedra, evidenced by diffraction studies [12], but also to significant changes in the atomic bonding, hence – electronic structure of the material, observed previously at the Re L$_{1,3}$-edge XANES as a shift of the absorption edges to smaller energies and attributed to the lowering of the valence state of rhenium ions [9].

4. Conclusions
The ability to accurately analyze contributions to EXAFS spectra from atoms located at distances up to 8 Å from absorbing atom is demonstrated for the first time in ReO$_3$ and H$_x$ReO$_3$. For this purpose we employed a complex approach, based on the use of reverse Monte Carlo method, evolutionary algorithm and wavelet transform. This approach allowed us to reveal the presence of very strong and relatively long-range correlations in the motion of Re and O atoms within linear –Re–O–Re– chains in pure ReO$_3$. It was also demonstrated that these correlations are destroyed by the intercalation of hydrogen ions into crystalline ReO$_3$ lattice.

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