Interpretation of EXAFS in ReO_3 using molecular dynamics simulations

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Abstract. Temperature dependent Re L_3-edge EXAFS signals from perovskite-type cubic ReO_3 have been successfully interpreted using a combination of classical NVT molecular dynamics (MD) and *ab initio* multiple-scattering approach. The force field model, required for MD simulations, has been determined by fitting the Re–O and O–O pairwise interatomic potentials to a set of experimental data (lattice parameter, elastic constants and bulk modulus) and phonon frequencies, theoretically calculated from the first principles at high symmetry points of the Brillouin zone. The MD simulations reproduce well the anisotropy of thermal vibration for oxygen atoms and confirm a deviation of the mean Re–O–Re angle from $180°$. The atomic configurations from the MD simulations have been used to calculate the configuration-averaged EXAFS spectra at several temperatures. The use of the MD results allows a straightforward treatment of thermal disorder in the multiple-scattering contributions to the total EXAFS signal. Good agreement between calculated and experimental EXAFS signals has been found, that additionally supports the accuracy of our force field model.

1. Introduction

Analysis and interpretation of disorder effects in EXAFS signal in the presence of multiple-scattering (MS) contributions is still a challenging task [1, 2, 3, 4]. This problem can be overcome combining the *ab initio* EXAFS theory with classical molecular dynamics (MD) simulation [5]. The key task in such an analysis is developing an appropriate force field (FF) model, which is further used in the MD simulation at required temperature to generate a set of atomic configurations. These configurations are finally used to compute the configuration-averaged EXAFS signal, which is compared to the experimental EXAFS signal, acquired at the same temperature.

Among different compounds, perovskite-type cubic ($Pm\bar{3}m$) rhenium trioxide ReO_3 is well known for years as a nice example of a system whose Re L_3-edge EXAFS signal has very strong MS contributions coming from linear Re–O–Re atomic chains [6, 7, 8, 9, 10, 11, 12, 13]. However, up to now the treatment of this effect was in the best case limited to a fit of the total EXAFS signal by a restricted number of MS contributions treating thermal disorder contributions, given by the Debye-Waller factors σ^2, as free fitting parameters.

In this work, we applied recently developed combined MD-EXAFS approach [5] to the analysis of the temperature dependent Re L_3-edge EXAFS spectra in ReO_3.

2. Simulation details

To perform MD simulations, one needs to obtain the parameters of the force field model, describing pairwise interactions in the compound. This was done in two steps procedure.

First, the first-principles calculations were performed for cubic ReO_3 using the hybrid B3PW exchange-correlation potential with the 2×2×2 supercell by the LCAO (linear combination of atomic orbitals) CRYSTAL06 code [14]. As a result, the Mulliken atomic charges were determined, and the phonon frequencies at high symmetry points (G, R, M, X) of the Brillouin zone were calculated by the frozen phonon method [15].

Next, the force field potential model was chosen in the form of the Buckigham and covalent exponential interatomic potentials to describe Re–O and O–O bonding (table 1). The model parameters, including ions charges, were optimized using simulated annealing method to reproduce a set of experimental data (lattice parameter [16], elastic constants and bulk modulus [17]) and theoretically calculated phonon frequencies.

Thus determined force field potential model was further used in the MD simulations. The NVT MD simulations were performed using GULP code [18, 19] for a supercell 5×5×5, containing 500 atoms, at temperatures 300 K, 423 K and 573 K. For each temperature, a set of 4000 static atomic configurations was obtained during a simulation run of 20 ps with a time step interval of 0.5 fs. These configurations were further used to calculate the Re L_3-edge EXAFS signals by the *ab initio* FEFF8 code [20]. The complex exchange-correlation Hedin-Lundqvist potential and default values of muffin-tin radii, as provided within the FEFF8 code [20], were used. Finally, the configuration-averaged EXAFS signals were calculated using (i) single-scattering (SS) and (ii) multiple-scattering (MS) (with paths up to the 8th order) approximations by averaging over all 4000 configurations and compared with the experimental data from [13]. All calculations were performed at the Latvian SuperCluster facility [21].

Table 1. The parameters of optimized Re–O and O–O pairwise potentials used in the MD simulations. For parameters definition see [18, 19].

Coulomb potential	
Atom	Z (e)
Re	3.36
O	-1.12

Buckingham potential, cutoff 20 Å			
Pair of atoms	A (eV)	ρ (Å)	C (eVÅ^6)
Re–O	1194.24	0.342561	98.0988
O–O	3224.54	0.265204	47.39861

| Covalent exponential potential, cutoff 2 Å			
Pair of atoms	D (eV)	a (Å^{-1})	r_0 (Å)
Re–O	4.82827	6.21069	1.875

3. Results and discussion

The perovskite-type ReO_3 structure consists of corner-linked ReO_6 regular octahedra with Re atoms at the centers and linear Re–O–Re chains. The space between eight octahedra forming
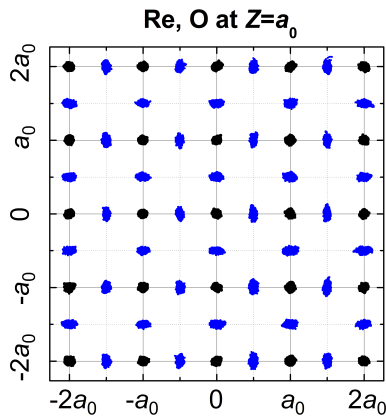
Figure 1. (Color online) Representation of MD trajectories at 573 K for Re (black) and O (blue) atoms located in a plane $Z = a_0$. (a_0 is the lattice parameter.)
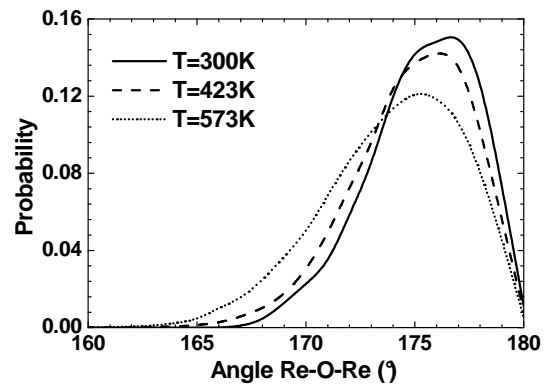
Figure 2. Distribution of the Re–O–Re angles at 300 K, 423 K and 573 K, calculated from MD simulations.
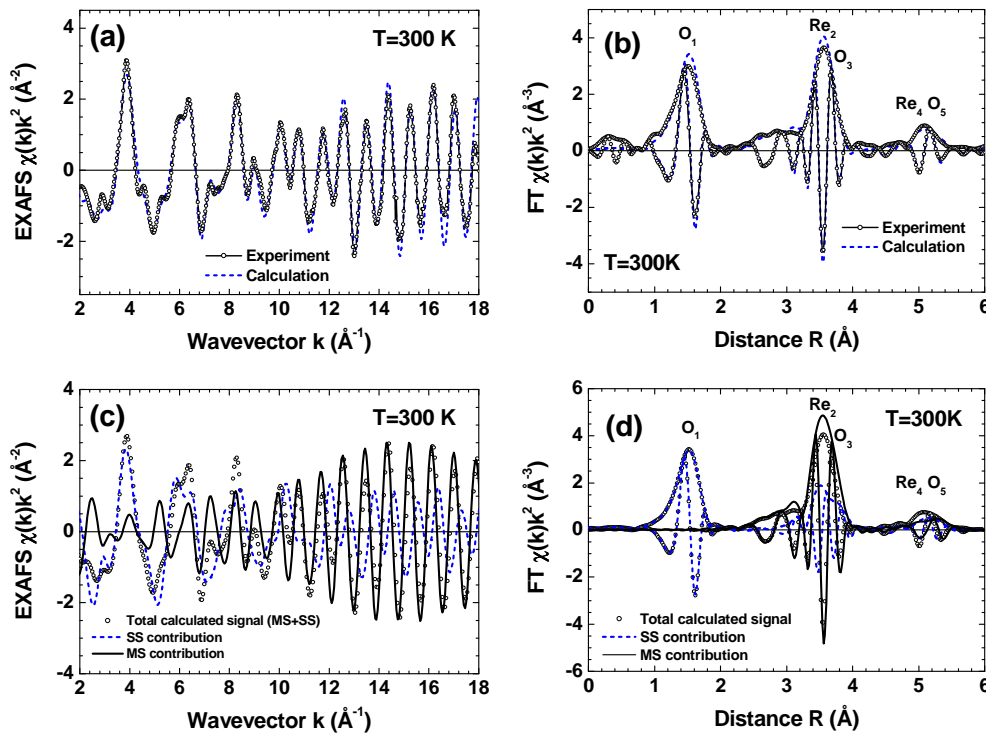
Figure 3. (Color online) Experimental (open circles) and calculated configuration-averaged (dashed line) EXAFS $\chi(k)k^2$ signals (a) and their Fourier transforms (b) at 300 K. Contributions of single-scattering (SS) (dashed line) and multiple-scattering (MS) (solid line) effects into the total calculated signal (open circles) (c,d).

the cube is fully vacant that allows for a significant rotation of the ReO$_6$ units [16] and results in the anisotropy of oxygen atoms thermal vibration. The obtained MD trajectories in the (100) plane, visualized in figure 1 for 573 K, confirm that the amplitude of oxygen thermal vibrations is

larger in the direction perpendicular to the Re–O–Re chains, but the vibrations of Re atoms are isotropic. Recent pressure-dependent EXAFS study [12] suggests that even at normal conditions the Re–O–Re bond angle deviates from the linear one, observed by diffraction, and is equal to about 172°. Our temperature dependent MD simulations allowed us to estimate the mean value of the Re–O–Re angle from the angles distributions (figure 2) to be 174.5° at 300 K, 173.0° at 423 K and 172.2° at 573 K. A decrease of the mean angle value indicates larger amplitude of oxygens vibrations at higher temperatures.

The reliability of our MD simulations is well supported by a good agreement between experimental and theoretical Re L_3-edge EXAFS signals observed in the simulation range up to about 6 Å that includes the first five coordination shells around absorbing Re atom. In figures 3(a,b) we compare the two EXAFS $\chi(k)k^2$ signals and corresponding Fourier transformations (FTs) at 300 K. The SS and MS contributions are shown in figures 3(c,d) and allow to conclude unambiguously on the origin of the peaks in FTs. As it was suggested before [9], the peak at 2.2-3.0 Å is due to pure MS effects from the first shell, and the MS contributions within the next two main peaks at 3.6 Å and 5.0 Å are about 30-40%.

4. Conclusions

Temperature dependence of the Re L_3-edge EXAFS signals in cubic ReO_3 has been successfully interpreted using a combination of classical NVT molecular dynamics and *ab initio* multiple-scattering approach [5]. This method allows a straightforward accounting of thermal disorder effects in any scattering path and reduces gradually the number of model parameters, which are solely determined by the force field potential model. The construction of the force field model was performed based on the known experimental data, i.e. the lattice parameter and elastic properties, and the results of the first-principles calculations, i.e. ions charges and phonon frequencies. Note that the latter information is crucial for the modeling procedure but is often not available or is difficult to obtain experimentally.

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