An efficient implementation of the reverse Monte Carlo method for EXAFS analysis in crystalline materials

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Abstract. Lattice dynamics of crystalline materials can be efficiently studied using reverse Monte Carlo (RMC) simulations of EXAFS spectra. In this work we demonstrate potentiality of the method on an example of the thermal disorder study in rhenium trioxide ReO$_3$.

1. Introduction
Reverse Monte Carlo (RMC) method is an atomistic simulation technique that allows one to reconstruct the 3D atomic structure of the material by minimizing the difference between its structure-related experimental and calculated properties [1]. In our recent work [2] we have shown that the RMC is a useful tool for the analysis of the extended x-ray absorption fine structure (EXAFS) in crystalline materials. The efficient implementation of the RMC algorithm allows us to obtain reliable results by simulating configurations with relatively small number of atoms (several hundreds in contrast to several thousands, usually required for the analysis of disordered materials). Our approach [2] significantly reduces the computational costs and accounts for the multiple-scattering (MS) contributions thus allowing one to extract from EXAFS spectrum the information not only on the interatomic distances, but also on the bond angles, anisotropy of atomic vibrations and even bond strength. Considering the MS effects is essential for crystals with cubic symmetry as rhenium trioxide (ReO$_3$), where the MS contributions are strongly enhanced due to the "focusing effects" within the collinear atomic chains [3, 4].

Here we present the results of the RMC-EXAFS study of lattice dynamics in ReO$_3$ over a broad range of temperatures from 10 K to 573 K.

2. RMC simulations for the model data
Before applying the proposed method to experimental data, we have validated it using the model Re L$_3$-edge EXAFS signal for ReO$_3$, obtained from molecular dynamics (MD) simulations [5]. The RMC calculations have been carried out for $4\times4\times4$ supercell (256 atoms) and 40000 iterations. A difference between the model and RMC EXAFS spectra has been minimized by the best fit of their wavelet transforms, i.e., simultaneously in $k$-space (from 3 to 18 Å$^{-1}$) and in $R$-space (from 0 to $R_{\text{max}}=4.5$ Å) [2, 6]. The EXAFS spectra for the MD model and during the RMC simulations have been calculated using ab initio self-consistent real space multiple-scattering FEFF8 code [7]. As one can see in Fig. 1, due to the cubic perovskite-type structure

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Figure 1. Model (dots) and reconstructed by the RMC simulation (lines) Re L₃-edge EXAFS spectra χ(k)k² for ReO₃. The SS and MS contributions are shown separately.

of ReO₃, the contribution of MS effects to the total EXAFS signal is comparable to the one from SS paths. Moreover, our RMC scheme allows us to reconstruct and analyze simultaneously both SS and MS parts of the EXAFS signal.

The evaluated values of the mean-square radial displacements (MSRD) for the first two coordination shells (Re₀–O₁ and Re₀–Re₂) differ from that in the MD model by only about 0.0001 Å², and the average value of the Re₀–O₁–Re₂ angle is determined with noteworthy precision better than 0.01°. The MSRD value for the third coordination shell (Re₀–O₃) shows slightly worse agreement (within about 10%) due to the fact that this MSRD value is large and therefore the contribution of the third shell to the total EXAFS signal is relatively small.

3. RMC analysis of experimental data
Next we applied our method to the experimental temperature-dependent Re L₃-edge EXAFS spectra for ReO₃ [8]. The experimental EXAFS spectra for T=10 K and 573 K and the corresponding theoretical EXAFS spectra, calculated for the final atomic configurations obtained in the RMC simulations, are shown in Fig. 2. The agreement between the experimental and simulated EXAFS spectra is very good and implies that the obtained atomic configurations are representative sample of ReO₃ structure. One can consider separately the SS and MS contributions and analyze for the first-time the temperature dependence of the MS effects. Note that the MS effects give the maximum contribution to the total EXAFS signal in ReO₃ at about k=16 Å⁻¹, where it is about two times larger than the contribution of the SS effects, and this ratio is nearly independent on temperature.

The conventional EXAFS analysis can provide in ReO₃ only very limited accuracy beyond the first coordination shell due to the pronounced MS effects. Using RMC simulations, in turn, the structural information can be obtained straightforwardly. The radial distribution functions (RDFs) for Re₀–O₁, Re₀–Re₂, and Re₀–O₃ pairs are shown in Fig. 3(a), and the temperature dependences of the MSRDs, extracted from the RDFs, are given in Fig. 3(b) for the first three coordination shells. It should be emphasized that the proposed method gives us reliable information even at low temperatures - in the region where, for example, the classical molecular dynamics cannot be applied. For the first coordination shell Re₀–O₁, the RMC results are close to that obtained using the FEFFIT code [9].

Temperature dependences of the MSRDs in Fig. 3(b) can be approximated using the correlated Einstein model [10]. The Einstein frequency for the first coordination shell ωₑ=94.9 THz is in good agreement with previously published result (ωₑ=94.1 THz [11]). The Einstein frequencies for the second (36.2 THz) and third (60.8 THz) coordination shells are
obtained for the first time. It is important to note that while the Einstein frequency for the second shell (Re₀–Re₂ pairs) is significantly smaller than for the first one, due to the larger masses of involved rhenium atoms, the effective bond-strength coefficient \( \kappa = \frac{\omega^2}{\mu} \) (\( \mu \) is the effective mass) for the Re₀–Re₂ pairs (203 N/m) is almost as large as for the Re₀–O₁ pairs (222 N/m) and is about twice larger than the effective bond-strength coefficient (91.2 N/m) for the third coordination shell.

This means that a strong correlation is present between the motion of the neighbouring Re₀ and O₁ atoms (the fact, usually emphasized in the explanation of negative thermal expansion (NTE) of ReO₃ lattice [12, 13]), but also between the motion of the next-neighbouring Re₀ and Re₂ atoms.

The NTE phenomenon in ReO₃ is usually explained in terms of the rigid-unit model (RUM) [12]. The strong correlation in the Re₀–O₁ atomic motion leads to the nearly temperature-independent Re₀–O₁ bond length, thus ensuring the rigidity of the ReO₆ octahedra. At the same time, an increase of temperature raises the vibration amplitude of oxygen atoms in the direction, orthogonal to the Re₀–Re₂ bonds. The two effects together result in a reduction of the Re₀–Re₂ interatomic distances. According to this model, the average value of the Re₀–O₁–Re₂ angle should decrease with the increasing temperature, and this effect can be accurately determined from the results of the RMC simulations. The described trend is clearly seen in Figs. 3(c) and (d). The average value of the Re₀–O₁–Re₂ angle decreases almost linearly from 174.7° at 10 K to 173.3° at 573 K. In turn, the statistical dispersion of the Re₀–O₁–Re₂ angle values increases from 3.1° at 10 K to 3.7° at 573 K (we used the so-called median absolute deviation as a robust estimator of dispersion). Thus, the temperature dependence of the Re₀–O₁–Re₂ angle agrees well with the structural model of the NTE in ReO₃.

Figure 2. Experimental (dots) and RMC (lines) Re L₃-edge EXAFS spectra \( \chi(k)k^2 \) for ReO₃ at temperatures \( T = 10 \) K (a) and 573 K (b). Temperature dependences of the SS (c) and MS (d) contributions are also shown.
4. Conclusions

We have demonstrated that reverse Monte Carlo (RMC) method can be successfully used to interpret EXAFS spectra of crystalline materials even in case, when the multiple-scattering effects are very pronounced. The analysis of the Re $L_3$-edge EXAFS data from the second and third coordination shells of rhenium in ReO$_3$ has been carried out for the first time taking into account both thermal disorder and multiple-scattering effects. The obtained results are in agreement with the rigid unit model of lattice dynamics in ReO$_3$. We affirm the strong correlation (i) between displacements of oxygen and nearest rhenium atoms and (ii) between oxygen motion in the direction orthogonal to the Re$_0$–Re$_2$ bond and the variation of the average Re$_0$–Re$_2$ distance. Our results reveal also the strong correlation between the motion of two nearest rhenium atoms.

Acknowledgments

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References

[1] McGreevy R and Pusztai L 1988 *Mol. Simul.* 1 359
[2] Timoshenko J, Kuzmin A and Purans J 2012 Comp. Phys. Commun. 183 1237
[3] Alberding N, Crozier E, Ingalls R and Houser B 1986 J. Physique IV (France) 47 C8–681
[4] Kuzmin A, Purans J, Benfatto M and Natoli C 1993 Phys. Rev. B 47 2480
[5] Kalinko A, Evarestov R, Kuzmin A and Purans J 2009 J. Phys.: Conf. Ser. 190 012080
[6] Timoshenko J and Kuzmin A 2009 Comp. Phys. Commun. 180 920
[7] Ankudinov A, Ravel B, Rehr J and Conradson S 1998 Phys. Rev. B 58 7565
[8] Purans J, Dalba G, Fornasini P, Kuzmin A, de Panfilis S and Rocca F 2007 AIP Phys. Conf. Ser. 882 422
[9] Newville M, Ravel B, Haskel D, Rehr J, Stern E and Yacoby Y 1995 Physica B 208 154
[10] Rehr J and Albers R 2000 Rev. Mod. Phys. 72 621
[11] Dalba G, Fornasini P, Kuzmin A, Purans J and Rocca F 1995 J. Phys.: Condens. Matter 7 1199
[12] Tao J and Sleight A 2003 J. Solid State Chem. 173 442
[13] Chatterji T, Henry P, Mittal R and Chaplot S 2008 Phys. Rev. B 78 134105