Local structure and lattice dynamics of cubic Y$_2$O$_3$: an x-ray absorption spectroscopy study

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Abstract. Classical molecular dynamics was used to interpret the temperature dependent (300-1273 K) Y K-edge x-ray absorption spectra of cubic c-Y$_2$O$_3$ and to validate two force-field models. It was shown that both models reproduce well thermal disorder effect, however are less accurate in description of static octahedra distortion around yttrium atoms. The temperature dependencies of mean-square displacements and mean-square relative displacements were obtained from molecular dynamics simulations for the first two shells of yttrium. The importance of anharmonic effects was demonstrated by comparison of molecular dynamics and lattice dynamics results.

1. Introduction
Cubic yttrium oxide, c-Y$_2$O$_3$ (space group Ia$ar{3}$ (No. 206), Z = 16), is technologically important material with complex crystallographic structure [1]. In particular, an addition of nanosized yttria to steel matrix allows one to produce oxide dispersion strengthened (ODS) steels with improved mechanical properties and radiation resistance [2, 3, 4]. The optimization of ODS steel properties requires development of reliable theoretical models [5, 6]. Among different theoretical tools, molecular dynamics (MD) [6, 7] and Monte Carlo [8, 9] simulations open an access to in-depth understanding of materials properties at the atomic scale. However, their reliable use is challenging and demands the precise knowledge of interatomic potentials. Low concentration and nanosize of oxide particles in ODS steels makes x-ray absorption spectroscopy (XAS) a natural and highly efficient tool to probe their local structure [10, 11, 12, 13]. Besides, it was shown recently that XAS can be efficiently used as a validation tool for force-fields employed in the MD simulations [14, 15, 16].

In this study we have used the Y K-edge XAS to probe the local structure and lattice dynamics of yttria in a wide range of temperatures from 300 to 1273 K. The experimental results are analysed using classical molecular dynamics [17] and lattice dynamics [18] simulations.

2. Experimental
Temperature-dependent x-ray absorption spectroscopy of cubic c-Y$_2$O$_3$ (99.99%, Aldrich) was performed at the Y K-edge in transmission mode at the ELETTRA storage ring (Trieste, Italy) XAFS bending-magnet beamline [19]. The synchrotron radiation was monochromatized using a Si(111) double-crystal monochromator, and its intensity before and after the sample was measured by two ionization chambers. Polycrystalline c-Y$_2$O$_3$ powder was mixed with boron nitride and pressed into pellets. The sample thickness was optimized to obtain the absorption
Figure 1. Comparison of the experimental (solid line) and configuration-averaged (dotted line - Model 1, dashed line - Model 2) Y K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms (modulus and imaginary parts) for c-Y$_2$O$_3$ at several selected temperatures.

Y K-edge jump value $\Delta \mu \approx 1$. The sample temperature was controlled using the vacuum glass furnace [19] in the range from 300 to 1273 K. The experimental Y K-edge extended x-ray absorption fine structure (EXAFS) (figure 1) was extracted using the conventional procedure [20].

3. Molecular and lattice dynamics simulations

Classical molecular dynamics (MD) and lattice dynamics (LD) simulations were performed using the GULP code [21, 22]. Note that classical MD does not include quantum effects, therefore it can be used only at relatively high temperatures. On the contrary, the LD simulations are limited by harmonic approximation and thus will fail upon increasing temperature. Therefore, the two methods complement each other in a description of material vibrational properties.

The MD simulation box was built up of eight unit cells with periodic boundary conditions ($2a_0 \times 2a_0 \times 2a_0$ supercell where $a_0$ is the lattice parameter). The crystallographic structure of c-Y$_2$O$_3$ [1] was used as starting configuration (figure 2). The unit cell contains two non-equivalent yttrium atoms, Y1 and Y2, which occupy 8(b) (1/4, 1/4, 1/4) and 24(d) (u, 0, 1/4) Wyckoff positions, respectively, and are octahedrally coordinated by oxygens. The octahedra around Y1 atoms are regular, thus all Y1–O distances are equal to 2.29 Å, whereas the octahedra around Y2 atoms are distorted with Y2–O bond lengths being in the range from 2.24 Å to 2.33 Å.

We have used the canonical (NVT) ensemble, so that the average temperature was kept constant during MD simulation run using Nosé-Hoover thermostat [23]. The Newton’s equations of motion were integrated using the Verlet leapfrog algorithm [24] with a time step of 0.5 fs. The equilibration and production times were 20 ps each. A set of 4000 atomic configurations were accumulated during each production run, and the configuration-averaged Y K-edge EXAFS spectra were calculated [17], taking into account the presence of two non-equivalent yttrium
Figure 2. Crystal structure of cubic c-Y$_2$O$_3$ [1]. The unit cell is indicated. Two non-equivalent yttrium atoms (Y1 and Y2) are marked.

4. Results and discussion
The experimental and calculated Y K-edge EXAFS spectra $\chi(k)k^2$ and their Fourier transforms at selected temperatures are compared in figure 1. The two force-field models (Model 1 and Model 2) give close EXAFS spectra in $k$-space, which are in good agreement with the experimental ones. However, the difference between theory and experiment is observed in $R$-space in the region of the first peak at $\sim1.6$ Å, which is due to the first coordination shell of atoms (Y1 and Y2) [1]. This approach will be referred to as the MD-EXAFS method.

EXAFS calculations were done using ab initio real-space multiple-scattering (MS) FEFF8 code [25], including the MS contributions up to the 7th order. The self-consistent muffin-tin (MT)-type cluster potential was evaluated only once for the average crystallographic structure of c-Y$_2$O$_3$ [1], thus neglecting its small variation due to thermal disorder. The complex exchange-correlation Hedin–Lundqvist potential was used to describe the inelastic losses, and the MT radii ($R_{mt}(Y)=1.57$ Å and $R_{mt}(O)=1.06$ Å), evaluated by the FEFF8 code [25], were employed.

Two force-field models (Model 1 and Model 2) based on the rigid-ion Buckingham potential were used in both MD and LD simulations to describe interactions in c-Y$_2$O$_3$ (table 1)

\[
U_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 + q_iq_je^2/r_{ij} \tag{1}
\]

where $e$ is the elementary charge and $r_{ij}$ is the interatomic distance for the $i$–$j$ atom pair. Model 1 is the re-optimized in the present work version of the model, originally developed in [26]: it includes three short-range Y–O, Y–Y and O–O interactions and long-range Coulomb interactions, defined by the effective ion charges $q(Y)=+1.8$ and $q(O)=-1.2$. In Model 2, taken from [27] excluding the shell, only two short-range interactions Y–O and O–O of the Buckingham-type were considered, and the effective ion charges were $q(Y)=+2.4$ and $q(O)=-1.6$.

Lattice dynamics simulations were performed using the second force-field model (Model 2). In the harmonic approximation, solving the eigenvalue problem of the dynamical matrix allows one to obtain its eigenvalues and eigenvectors, which in turn can be used to evaluate the mean-square displacements (MSDs) of Y and O atoms and the mean-square relative displacements (MSRDs) $\sigma^2_{ij}$ of the $i$–$j$ atom pairs [28, 18]. Thus obtained MSRD values for Y1–O and Y1–Y2 bonds are compared with that determined from the MD simulations in figure 3.
Table 1. Force-field parameters used in the MD and LD simulations.

| Pair of atoms | Model 1 | | Model 2 | |
|---------------|---------|---------|---------|---------|
|               | $A$ (eV) | $\rho$ (Å) | $C$ (eVÅ$^6$) | $A$ (eV) | $\rho$ (Å) | $C$ (eVÅ$^6$) |
| Y–O           | 162401.94 | 0.172628 | 0.0 | 1822 | 0.309042 | 0.0 |
| O–O           | 351366.27 | 0.187988 | 0.0 | 1822 | 0.305726 | 100.0 |
| Y–Y           | 112925.98 | 0.232299 | 0.0 | 1822 | 0.305726 | 100.0 |

Yttrium atoms surrounded by six oxygens. While the observed difference is rather small, the second force-field model (Model 2), which neglects the Y–Y interactions, gives slightly better account for the thermal disorder upon increasing temperature from 300 to 1273 K. Note that both models reproduce well the atomic structure and disorder effects in the outer coordination shells above 2.5 Å.

Thermal vibrations of atoms play an important role in thermal and transport properties of materials, phase transitions, thermal expansion and interaction of radiation with matter, which are of significant relevance for ODS steels. Therefore, the knowledge of vibration amplitudes and correlation effects represent significant interest. This information can be experimentally obtained by direct structural tools as diffraction and EXAFS. While diffraction technique allows one to determine the mean-square displacements (MSD) of atoms relative to their mean positions [29], EXAFS contains, in principle, information on both MSRD and MSD. However, conventional analysis of EXAFS for the nearest coordination shell(s) around an absorbing atom allows one to determine only MSRD values [30]. Thus, an extraction of the MSD values from EXAFS is challenging and requires to perform the analysis of distant coordination shells [31, 32]. At the same time, both MSD and MSRD values can be directly obtained from the MD simulations, validated in advance using EXAFS data.

Classical molecular dynamics cannot be used at low temperatures because it ignores quantum effects. On the contrary, lattice dynamics simulations give accurate picture of thermal vibrations at zero temperature, but fail at high temperatures due to neglect of anharmonic effects. Therefore, these two approaches complement each other and should be utilized together. In figure 3 the MSRD values for Y1–O and Y1–Y2 atom pairs and the MSD values for Y1, Y2 and O atoms are shown: they were calculated by MD and LD using the same force-field model (Model 2). We have selected only regular Y1 site to exclude the need to account for additional static distortions of yttrium–oxygen octahedra around Y2 site. The LD results deviate strongly from MD already above ~200 K for yttrium–oxygen pairs and above ~50 K for yttrium–yttrium pairs, indicating the importance of anharmonic effects. Temperature dependence of MSDs at high temperatures, i.e. in the classical limit, is linear, and heavier yttrium atoms vibrate with smaller amplitudes than light oxygen atoms, as expected. MSD and MSRD for the $i$–$j$ atom pair are connected by the equation $\text{MSRD}_{ij} = \text{MSD}_i + \text{MSD}_j - 2\sqrt{\text{MSD}_i}\sqrt{\text{MSD}_j}\phi$, where $\phi$ is a dimensionless correlation parameter [33], which is equal to +1 for perfectly in-phase atom motion, to zero for completely independent motion and to −1 for perfectly opposite-phase motion. From data reported in figure 3 one can find that $\phi = 0.45$ at 50 K and increases slightly to $\phi = 0.60$ at 1273 K for both Y1–O and Y1–Y2 pairs, indicating prevalent in-phase atom motion in c-Y$_2$O$_3$.

5. Conclusions
We have shown that experimental Y K-edge EXAFS spectra of c-Y$_2$O$_3$ can be used to validate the force-field models (table 1) within the MD-EXAFS approach. The agreement between theory and experiment is restricted by the simplicity of the models, which are not able to describe
accurately the distortion of yttrium–oxygen octahedra. However, the second model (Model 2) gives slightly better agreement for the first shell than the first one. Note that both models reproduce well thermal disorder in c-Y$_2$O$_3$ in a wide range of temperatures from 300 to 1273 K.

A comparison between molecular dynamics and lattice dynamics simulations (figure 3) allows one to conclude on the importance of anharmonic effects and on the temperature range, where quantum effects can be neglected.

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