

Ab initio molecular dynamics simulations of the Sc K-edge EXAFS of scandium trifluoride

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Abstract. Scandium fluoride ScF_3 has a simple cubic structure and attracts attention due to its large negative thermal expansion (NTE) over a wide range of temperatures (0-1100 K). In this study we present ab initio molecular dynamics (AIMD) simulations of ScF_3 and their validation using the Sc K-edge EXAFS spectra in the temperature range from 300 K to 1000 K measured at the XAFS beamline of ELETTRA. The obtained results allow an assesment of the employed AIMD model and provide insight into the local structure and the lattice dynamics of ScF_3 beyond the harmonic approximation. A strong anisotropy of the fluorine atom vibrations in the direction orthogonal to the $-\text{Sc}-\text{F}-\text{Sc}-$ chain is observed. An expansion of the ScF_6 octahedra is found upon increasing temperature despite of the overall NTE of the crystal.

1. Introduction

At atmospheric pressure ScF_3 has a cubic perovskite-type structure (space group $Pm\bar{3}m$) down to at least 10 K [1] and undergoes a strong negative thermal expansion (NTE) below 1100 K [1]. In spite of the experimental and theoretical efforts [1, 2, 3] that have been performed to understand the large NTE observed for ScF_3 , its behaviour in respect with similar isostructural crystals is still under debate. Most often it is explained in terms of the so-called rigid unit modes (RUMs) model [4, 5], which involves coupled vibrations of the rigid ScF_6 octahedra. When neighboring rigid octahedra librate in opposite directions, the distance between the centers of the octahedra decreases leading to the lattice contraction. Thus, to elucidate the nature of the NTE phenomena in details, one needs to follow temperature dependent changes of the lattice dynamics and structure of ScF_3 at the atomic scale.

Molecular dynamics (MD) simulations are a native approach to take into account vibrational and other dynamical properties that could be important for the observed NTE effect [2, 6, 7, 8]. In this study, ab initio molecular dynamics (AIMD) simulations were performed to address the problem beyond the harmonic approximation. The AIMD simulations were validated based on the Sc K-edge EXAFS spectra, previously measured at the XAFS beamline of ELETTRA from 10 K up to 1100 K.



2. Computational details

AIMD simulations based on Kohn-Sham density functional theory (DFT) [9] were performed at three temperatures (300 K, 600 K, and 1000 K) using the CP2K code [10]. A spin polarized implementation of the exchange-correlation functional PBEsol [11] was selected for this study, because it performs better for equilibrium properties of densely packed solids than the original PBE functional proposed by Perdew, Burke, Ernzerhof [12], in particular for lattice constants.

CP2K employs a localized basis set of Gaussian-type orbital functions for the description of the Kohn-Sham matrix within the framework of the Gaussian Plane Waves method [13, 14]. An auxiliary basis set of plane waves is employed to expand the electronic density using a density cutoff of 600 Hartree. Scalar-relativistic norm-conserving Goedecker-Teter-Hutter pseudopotentials [15, 16, 17] were employed for Sc and F atoms including 11 ([Ne] $3s^2 3p^6 4s^2 3d^1$) and 7 ([He] $2s^2 2p^5$) valence electrons, respectively. All calculations were performed at the Gamma point only using MOLOPT basis sets [18] optimized for these pseudopotentials. In this way fully unconstrained cell optimizations were performed for a ScF₃ model system consisting of $4 \times 4 \times 4$ unit cells, i.e. no symmetry was employed neither for the atomic position nor for the cell shape during the optimization procedure. A relaxed lattice constant of $a_0 = 4.027 \text{ \AA}$ for $T = 0 \text{ K}$ was obtained using the PBEsol functional whereas PBE resulted in a value of $a_0 = 4.065 \text{ \AA}$.

A set of atomic configurations was generated within the canonical ensemble (NVT) for a supercell $4a_0 \times 4a_0 \times 4a_0$ (a_0 is the lattice parameter of ScF₃ taken from [1] for the respective temperature: 4.013 Å for 300 K, 4.0075 Å for 600 K, and 4.0055 Å for 1000 K temperature, correspondingly) containing 256 atoms. After an equilibration run of 5 ps, an AIMD sampling run was performed for 10 ps. The required temperature was maintained during the simulation runs using the Nosé-Hoover thermostat. The generated atomic configurations were used in the next step to calculate the Sc K-edge configuration-averaged EXAFS spectra using the *ab initio* real-space multiple-scattering (MS) FEFF9.64 code [19] within the MD-EXAFS scheme [20, 21].

The MS contributions into EXAFS were accounted up to the sixth order within the radius of 8 Å around the absorbing Sc atom (7 coordination shells composed of 110 atoms). The calculation of the cluster potential was performed only once for the average crystallographic ScF₃ structure [1], thus neglecting its small variation due to thermal disorder. The complex exchange-correlation Hedin-Lundqvist potential and default values of muffin-tin radii ($R_{\text{mt}}(\text{Sc})=1.31 \text{ \AA}$ and $R_{\text{mt}}(\text{F})=1.01 \text{ \AA}$), as provided within the FEFF9.64 code [19], were employed. The amplitude of the theoretical EXAFS spectrum was multiplied by the $S_0^2 = 0.9$ factor.

3. Results and discussions

The Sc K-edge EXAFS spectra, obtained from the AIMD simulations, are compared with the experimental data at $T = 300 \text{ K}$, 600 K and 1000 K in Fig. 1. The agreement between the theoretical and experimental data is quite good, but not ideal. Note that no fitting parameters were employed, and all MS contributions were accounted. Some overestimation of the amplitude of the first two peaks, located at 1.6 Å and 3.6 Å, is visible at $T = 300 \text{ K}$ which can be caused by the neglect of quantum effects in AIMD simulations, leading to underestimation of thermal disorder. The best agreement is observed for the 600 K spectra up to 4.5 Å, i.e. for the first three coordination shells around the absorbing Sc atoms. The poorer agreement for the next peak at 5.5 Å can be tentatively attributed to the beginning of the border effect, since the supercell half size is about 8 Å. One can also note that in spite of an octahedral coordination of Sc, the MS contribution from its first coordination shell, expected at $\sim 2.5 \text{ \AA}$ between the first and second main peaks, is significantly reduced due to the dependence of the MS terms on the final l state ($l = 1$ for the Sc K-edge) [22].

The atomic coordinates obtained in the AIMD simulations were used to calculate a number of structural properties as the radial distribution functions (RDFs) $G(\text{Sc-F})$ and $G(\text{Sc-Sc})$ and the inter-octahedral Sc-F-Sc bond angle distribution function (BADF) (Fig. 2). Note that for the

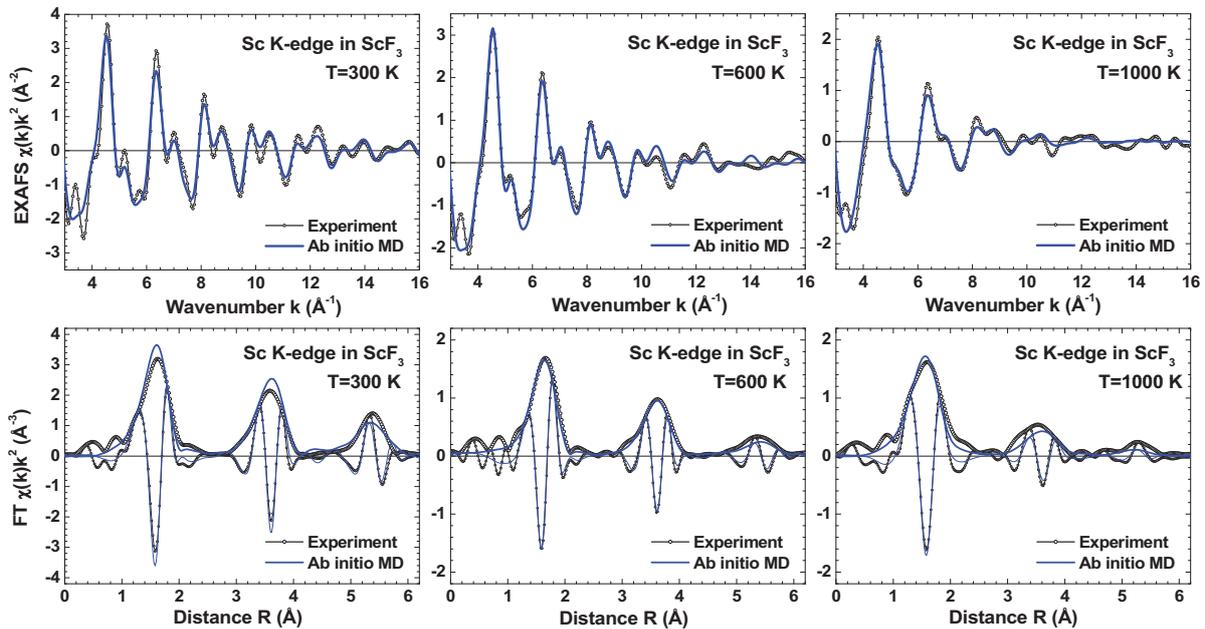


Figure 1. Experimental (open circles) and calculated (solid lines) Sc K-edge EXAFS and their Fourier transforms (modulus and imaginary parts are shown by thick and thin lines, correspondingly) at $T = 300$ K, 600 K and 1000 K.

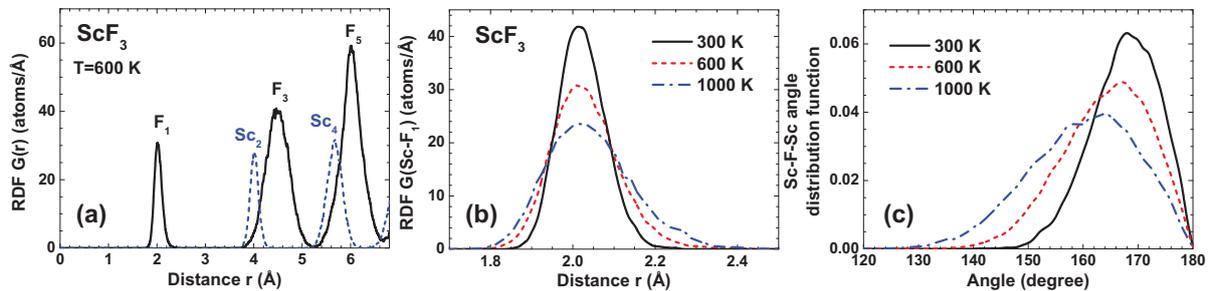


Figure 2. Radial distribution functions (RDFs) $G(r)$ for Sc-F and Sc-Sc atom pairs at $T = 600$ K (a). RDFs for the first coordination shell Sc-F₁ (b) and the inter-octahedral Sc-F-Sc bond angle distribution functions (c) at $T = 300$ K, 600 K and 1000 K.

atoms located in the crystallographic positions the Sc-F-Sc bond angle is equal to 180 degree. This value is reduced significantly when evaluated over instantaneous atomic positions with a broad distribution. Of course, the average value in the 3D space is still 180 degree, but with very low probability, as was well explained previously for SrTiO_3 in [23]. Note that similar but much narrower BADF for the inter-octahedral angle Re-O-Re was found at temperatures below 573 K in cubic ReO_3 [24], which has very weak NTE [25]. In ReO_3 [24] the smallest value of the inter-octahedral angle at $T < 600$ K is larger than $\sim 165^\circ$ against $\sim 140^\circ$ in ScF_3 , suggesting stronger tilting of ScF_6 octahedra than that of ReO_6 units in ReO_3 [26].

According to AIMD, the vibration of the F atoms is strongly anisotropic: the amplitude of their displacements along the -Sc-F-Sc- atomic chains is about 2-2.5 times smaller than in the orthogonal direction, and both amplitudes increase about 3-4 times upon increasing temperature

from 300 K to 1000 K. The vibration amplitude of the Sc atoms also increases, but only about 2 times in this temperature range, and its distribution remains isotropic. Another interesting result is that while the lattice parameter a_0 decreases by 0.01 Å from 300 K to 1000 K [1], the calculated average Sc–F distance increases by 0.02 Å, and the shape of the first coordination shell peak in RDF $G(\text{Sc–F})$ becomes asymmetric (Fig. 2(c)). This means that the ScF_6 octahedra expand slightly upon increasing temperature due to an anharmonicity of the Sc–F bonding.

4. Conclusions

We have demonstrated the efficiency of the MD-EXAFS approach [20] in combination with ab initio molecular dynamics method for theory validation and temperature dependent structural properties description in ScF_3 . In the framework of this approach configuration-averaged Sc K-edge EXAFS spectra were produced for three different temperatures $T = 300$ K, 600 K and 1000 K and compared with the experimental data, suggesting good qualitative agreement. It was found that upon temperature increase the ScF_6 octahedra do not behave as rigid units: the strong rotation of ScF_6 octahedra is accompanied by their expansion caused by the anharmonic Sc–F bonding, despite of a negative thermal expansion of the crystal lattice.

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