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

Dmitry Bocharov¹,², Matthias Krack¹, Aleksandr Kalinko², Juris Purans², Francesco Rocca³, Shehab E. Ali⁴, Alexei Kuzmin²

¹Paul Scherrer Institute, Laboratory for Reactor Physics and Systems Behaviour, Villigen, CH-5232, Switzerland
²Institute of Solid State Physics, University of Latvia, Kengaraga street 8, LV-1063, Riga, Latvia
³IFN-CNR, Institute for Photonics and Nanotechnologies, Unit FBK-Photonics of Trento, Povo, Trento, Italy
⁴Physics Department, Faculty of Science Suez Canal University, Ismailia, Egypt

E-mail: bocharov@latnet.lv

Abstract. Scandium fluoride ScF₃ 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 ScF₃ 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 assessment of the employed AIMD model and provide insight into the local structure and the lattice dynamics of ScF₃ beyond the harmonic approximation. A strong anisotropy of the fluorine atom vibrations in the direction orthogonal to the -Sc–F–Sc– chain is observed. An expansion of the ScF₆ octahedra is found upon increasing temperature despite of the overall NTE of the crystal.

1. Introduction
At atmospheric pressure ScF₃ has a cubic perovskite-type structure (space group Pm₃m) 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 ScF₃, 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 ScF₆ 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 ScF₃ 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 an 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 calculation 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 x 4 x 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 \( a_0 = 4.027 \) Å for \( T = 0 \) K was obtained using the PBEsol functional whereas PBE resulted in a value of \( a_0 = 4.065 \) Å.

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 \textit{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 ScF of 8 Å around the absorbing Sc atom (7 coordination shells composed of 110 atoms). The real-space multiple-scattering (MS) FEFF9.64 code [19] within the MD-EXAFS scheme [20, 21].

The Sc K-edge EXAFS spectra, obtained from the AIMD simulations, are compared with the experimental data at \( T = 300 \) 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 \( T = 300 \) 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 \( \sim 2.5 \) Å 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–F$_1$ (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 $G$(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.

Acknowledgments
The calculations were performed on the Paul Scherrer Institute cluster Merlin4, HPC resources of the Swiss National Supercomputing Centre (CSCS) in Lugano as well as at the Latvian SuperCluster (LASC). We gratefully acknowledge the assistance of Giuliana Aquilanti and of the staff members of XAFS beamline at Elettra during the EXAFS experiment (proposal no. 20120215). Sergei Piskunov gave us important suggestions, in the initial stage of the MD simulations. The work was partially supported by the Latvian Science Council grant no. 187/2012.

References
[1] Greve B K, Martin K L, Lee P L, Chupas P J, Chapman K W and Wilkinson A P 2010 J. Am. Chem. Soc. 132 15496
[2] Li C, Tang X, Muñoz J, Keith J, Tracy S, Abernathy D and Fultz B 2011 Phys. Rev. Lett. 107 195504
[3] Liu Y, Wang Z, Wu M, Sun Q, Chao M and Jia Y 2015 Comp. Mater. Sci. 107 157–162
[4] Barrera G D, Bruno J A O, Barron T H K and Allan N L 2005 J. Phys.: Condens. Matter 17 R217
[5] Takenaka K 2012 Sci. Tech. Adv. Mater. 13 013001
[6] Zhou W, Wu H, Yildirim T, Simpson J R and Walker A R H 2008 Phys. Rev. B 78 054114
[7] Fang H, Dove M T, Rimmer L H N and Misquitta A J 2013 Phys. Rev. B 88 104306
[8] Sanson A 2014 Chem. Mater. 26 3716
[9] Kolm W and Sham L J 1965 Phys. Rev. 140 A1133
[10] CP2K developers group 2000–2015 (http://www.cp2k.org)
[11] Perdew J P, Ruzsinszky A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[12] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[13] Lippert G, Hutter J and Parrinello M 1997 Mol. Phys. 92 477
[14] VandeVondele J, Krack M, Mohamed F, Parrinello M, Chassaing T and Hutter J 2005 Comput. Phys. Commun. 167 103
[15] Goedecker S, Teter M and Hutter J 1996 Phys. Rev. B 54 1703
[16] Hartwigsen C, Goedecker S and Hutter J 1998 Phys. Rev. B 58 3641
[17] Krack M 2005 Theor. Chem. Acc. 114 145
[18] VandeVondele J and Hutter J 2007 J. Chem. Phys. 127 114105
[19] Rehr J J, Kas J J, Vila F D, Prange M P and Jorissen K 2010 Phys. Chem. Chem. Phys. 12 5503
[20] Kuzmin A and Evarestov R A 2009 J. Phys.: Condens. Matter 21 055401
[21] Kuzmin A and Evarestov R A 2009 J. Phys.: Conf. Series 190 012024
[22] Kuzmin A, Purans J, Benfatto M and Natoli C R 1993 Phys. Rev. B 47 2480
[23] Hui Q, Tucker M G, Dove M T, Wells S A and Keen D A 2005 J. Phys.: Condens. Matter 17 S111
[24] Kalinko A, Evarestov R A, Kuzmin A and Purans J 2009 J. Phys.: Conf. Series 190 012080
[25] Wdowik U D, Parisinski K, Chatterji T, Rols S and Schober H 2010 Phys. Rev. B 82 104301
[26] Purans J, Fornasini P, Ali S E, Dalba G, Kuzmin A and Rocca F 2015 Phys. Rev. B 92 014302