

# Local structure of perovskites $\text{ReO}_3$ and $\text{ScF}_3$ with negative thermal expansion: interpretation beyond the quasiharmonic approximation

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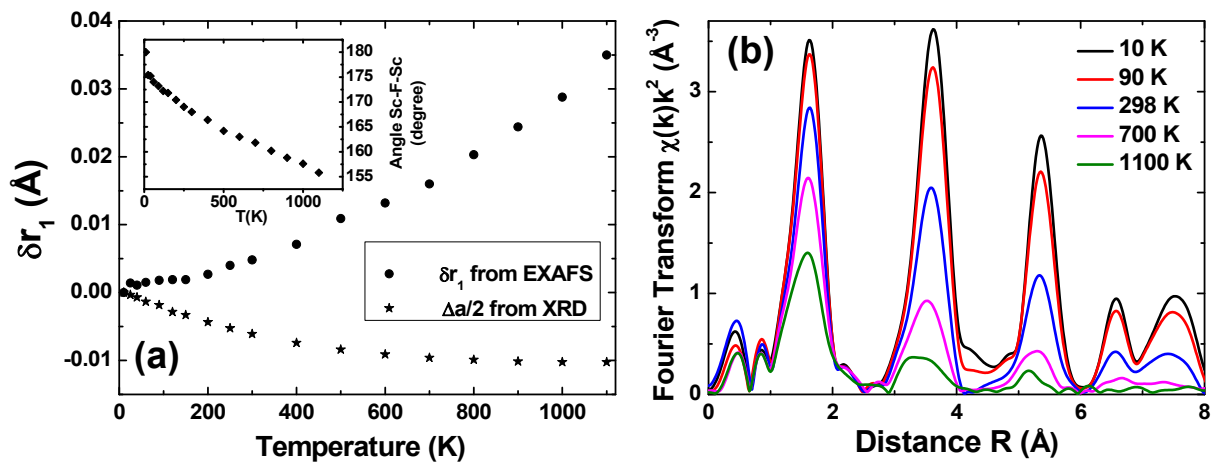
**Abstract.** We propose an approach beyond the quasiharmonic approximation for interpretation of EXAFS and XRD data and for *ab initio* calculations of electronic and vibration properties of materials with negative thermal expansion. *Ab initio* electronic structure and lattice dynamics calculations for cubic and distorted  $\text{ScF}_3$  were performed using the linear combination of atomic orbitals (LCAO) method. The band gap obtained in calculations for  $\text{ScF}_3$  is equal to 10.54 eV and agree well with the expected value. The calculated infrared spectra of F displaced (FD) cubic  $\text{ScF}_3$  allow us to predict that its mean Sc–F–Sc angle within NTE deviates from 180 degree.

## 1. Introduction

The interest towards  $\text{ReO}_3$ -type perovskites has been recently renewed by the discovery of large negative thermal expansion (NTE) in cubic  $\text{ScF}_3$  structure in a wide temperature range [1], to be compared with a much less intense effect measured for the cubic  $\text{ReO}_3$  [2, 3, 4]. At present, the great difference between the isostructural compounds is not yet explained, but it is found that the materials represent a case of strong anharmonic effects [4, 5]. Anharmonicity is of general importance in condensed matter in relation to thermal expansion, structural phase transitions, soft modes in ferroelectrics, melting and related phenomena. Usually anharmonicity in crystals is weak enough and thus so called implicit anharmonicity can be described in the framework of quasiharmonic approximation (QHA) as a variation of the phonon frequency due to the change in volume with temperature or pressure. However, this might be not the case for strongly explicit anharmonic systems, like perovskites with NTE. The explicit anharmonic effect links the phonon frequencies to the amplitude of the atomic vibrations.

Synchrotron radiation EXAFS studies of local structure with femtometer accuracy [6] offer the possibility to study implicit and explicit anharmonic effects for perovskites with NTE, since the temperature dependent EXAFS spectra include both anharmonic effects. The relative contributions of these two effects can be estimated by the extent to which quasiharmonic calculations of amplitude of the atomic vibrations reproduce the experimental EXAFS data. In spite of the experimental and theoretical efforts that have been performed to understand the





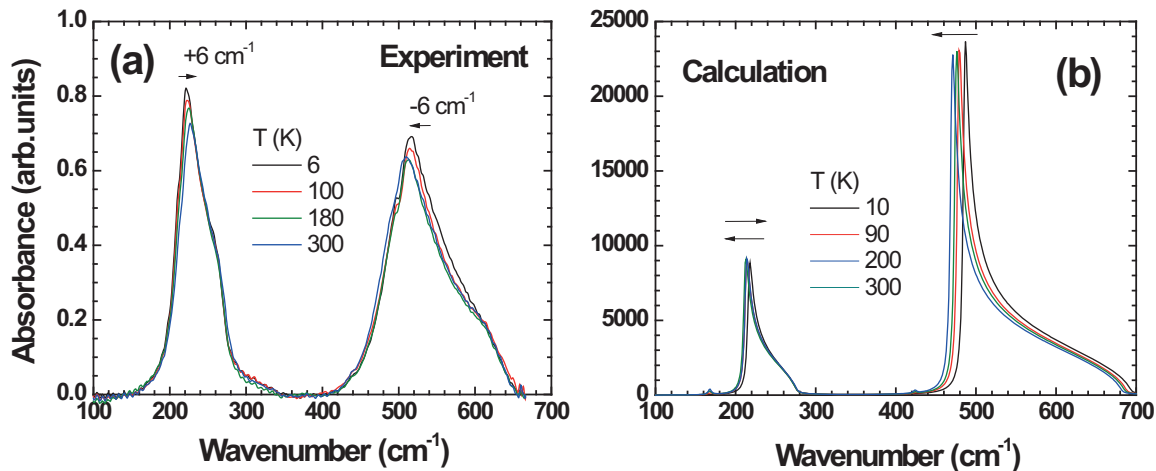
**Figure 1.** (Color online) (a) The variation of the Sc–F bond length measured by EXAFS and crystallographic distance measured by XRD (in house work). The angle Sc–F–Sc is calculated from EXAFS (Sc–F) and XRD (Sc–Sc) data. (b) Temperature dependence of the experimental Sc K-edge  $\chi(k)k^2$  Fourier transforms (FT) for polycrystalline ScF<sub>3</sub>.

NTE in ReO<sub>3</sub> and ScF<sub>3</sub>, its origin is still under debate. Most often it is explained in terms of so-called rigid unit modes (RUMs) model, which involves coupled vibrations of rigid ReO<sub>6</sub> (ScF<sub>6</sub>) octahedra. When neighboring octahedra librate in opposite directions the distance between the centers of octahedra decreases leading to the lattice contraction. Obviously, the distance Sc–F must decrease in the QHA according to the coefficient of NTE. On the other hand, our EXAFS data (Fig. 1) demonstrate the positive thermal expansion of the distance in the first coordination shell. Thus, to elucidate the nature of the NTE phenomena in details, one needs to follow temperature dependent changes of lattice dynamics and structure at the atomic scale beyond the QHA.

In this study, we propose an approach beyond the QHA for the interpretation and *ab initio* calculation of electronic and vibration properties of materials with NTE on the basis of local structure reconstructed from EXAFS analysis. *Ab initio* electronic structure and lattice dynamics calculations for cubic (space group  $Pm\bar{3}m$ ) and fluorine displaced (FD) cubic (space group  $Im\bar{3}$ ) ScF<sub>3</sub> were performed using the linear combination of atomic orbitals (LCAO) method.

## 2. Computational details

Both perfect and FD cubic ScF<sub>3</sub> crystals were simulated by means of LCAO within the framework of the hybrid HF/DFT approach. In order to perform hybrid LCAO calculations, we used the periodic crystal code [7], which employs Gaussian-type functions (GTFs) centered on atomic nuclei as the basis sets (BSs). In the current study, the triple-zeta all-valence BSs with polarization functions were used for both fluorine and scandium atoms as suggested in Ref. [8]. The revised version of the PBE0 hybrid exchange-correlation DFT functional with 33.3333% of Hartree-Fock exchange [9] was used in our calculations. Chosen exchange-correlation functional yields ScF<sub>3</sub> lattice constant  $a_0 = 4.0257$  Å, which is in excellent agreement with the experimental value of 4.026 Å [1]. Until now the band gap of ScF<sub>3</sub> was not precisely measured experimentally, but it is estimated to be larger than 7–8 eV [10]. Our calculations for the equilibrium structure of perfect cubic ScF<sub>3</sub> ( $a_0 = 4.0257$  Å) suggest that ScF<sub>3</sub> is an insulator with relatively large band gap  $E_g = 10.54$  eV that correlates very well with expected experimental value.



**Figure 2.** (Color online) (a) Temperature dependence of the experimental infrared spectra of  $\text{ScF}_3$ . Two bands due to the F–Sc–F bending mode (at  $220\text{ cm}^{-1}$ ) and Sc–F stretching (at  $520\text{ cm}^{-1}$ ) are visible. A shift of the band maxima by about  $6\text{ cm}^{-1}$  in the opposite directions occurs upon increasing temperature. (b) Calculated infrared absorption spectra of F-displaced cubic  $\text{ScF}_3$  for several values of contracting lattice parameter  $a_0$  and fluorine atoms displacements. The tilt angle Sc–F–Sc changes from  $180^\circ$  at 10 K to  $158^\circ$  at 300 K.

### 3. Results and discussions

The perovskite-type  $\text{ScF}_3$  structure consists of corner-linked  $\text{ScF}_6$  regular octahedra with Sc atoms at the centers and linear Sc–F–Sc chains. The space between eight octahedra forming the cube is fully vacant allowing for a significant rotation of the  $\text{ScF}_6$  octahedra and, thus, may result in the anisotropy of fluorine atom thermal vibration. Our recent EXAFS measurements confirm the expansion of the first shell Sc–F (Fig. 1) and that the amplitude of fluorine thermal vibrations is larger in the direction perpendicular to the Sc–F–Sc chain, while, according to XRD, the vibrations of scandium are almost isotropic. In fact, this may lead to the mean displacement of fluorine atom forming Sc–F–Sc bond with the mean angle Sc–F–Sc reported in the insert in Fig. 1. To simulate the  $\text{ScF}_3$  behavior at elevated temperatures with expanded Sc–F bond length, as measured by EXAFS, and contracted lattice constant (mean length of the linear Sc–F–Sc chain, as measured by x-ray diffraction (XRD)), we elaborated a model allowing for fluorine atom displacement in the direction perpendicular to the Sc–F–Sc chain, but keeping its original cubic structure (FD model). For this purpose larger supercell consisting of 32 atoms was adopted. The FD model was also used to describe temperature dependence of the far-infrared (far-IR) absorption spectra of  $\text{ScF}_3$ , obtained by Fourier transform infrared (FTIR) spectroscopy.

Fig. 2a shows the experimental temperature dependence of the far-IR absorption in  $\text{ScF}_3$ . Two absorption bands at  $220$  and  $520\text{ cm}^{-1}$  correspond to the F–Sc–F bending and Sc–F stretching modes, respectively. As temperature increases from 6 K to 300 K, the two bands shift toward each others of  $\sim 6\text{ cm}^{-1}$ . Note that infrared spectra calculated for perfect cubic  $\text{ScF}_3$  show opposite directions of band shifted with respect to contracted lattice constant. At the same time, the FD cubic  $\text{ScF}_3$  model (Fig. 2b) yield good agreement with measured data: the band near  $500\text{ cm}^{-1}$  shifts to the left as  $a_0$  contracts, while the band near  $220\text{ cm}^{-1}$  starts shifting to the right when the Sc–F–Sc angle is smaller than  $\sim 172^\circ$ .

#### 4. Conclusions

In this study three experimental techniques (EXAFS, XRD and FTIR) were used to probe the structure of polycrystalline ScF<sub>3</sub> in the wide temperature range. We found that the temperature dependence of the Sc–F distance, reconstructed from the analysis of the first coordination shell of scandium, shows opposite behaviour to that of the lattice parameter due to negative thermal expansion. Based on this structural information, we propose an approach beyond the quasiharmonic approximation for interpretation of the electronic and vibration properties of cubic ScF<sub>3</sub>. The electronic structure and infrared spectra of locally distorted ScF<sub>3</sub> were studied within the framework of the first-principles hybrid density functional theory calculations. The calculated band gap of 10.5 eV agrees with that experimentally observed. It has been found that the position of scandium atoms in the middle of regular ScF<sub>6</sub> octahedra is relatively stable, while the mean Sc–F–Sc angle deviates from 180° due to the anisotropy of thermal vibrations of fluorine atoms. Good agreement between calculated and experimentally obtained far-IR spectra was found, that additionally supports the accuracy of our predictions.

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