Local structure of perovskites ReO_3 and ScF_3 with negative thermal expansion: interpretation beyond the quasiharmonic approximation

Juris Purans[1], Sergei Piskunov[1], Dmitry Bocharov[1,], Aleksandr Kalinko[1], Alexei Kuzmin[1], Shehab E. Ali[2,3], Francesco Rocca[2]

[1]Institute of Solid State Physics, University of Latvia, Kengaraga Str. 8, LV-1063, Riga, Latvia
[2]IFN-CNR, Institute for Photonics and Nanotechnologies, Unit FBK-Photonics of Trento, Povo, Trento, Italy
[3]Physics Department, Faculty of Science Suez Canal University, Ismailia, Egypt
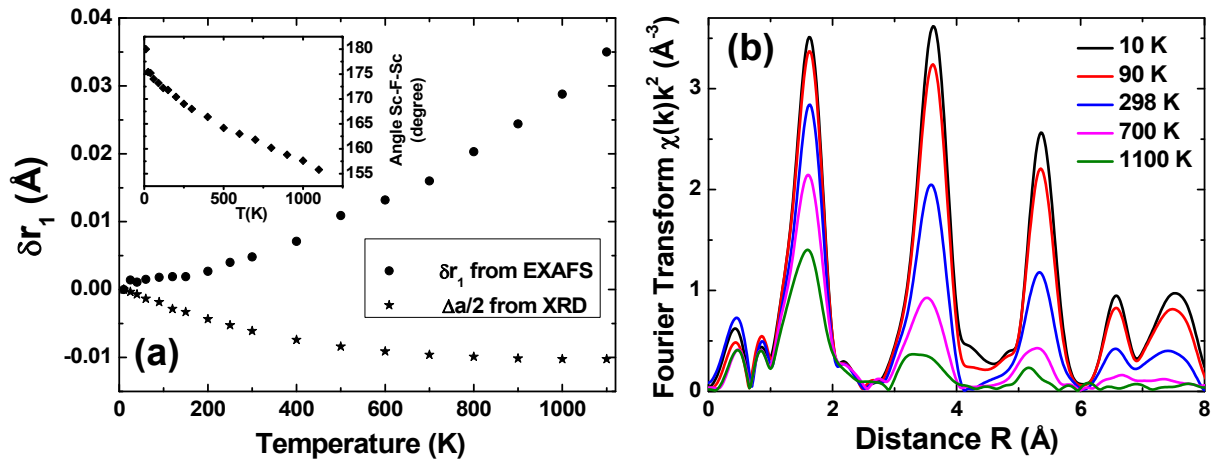
E-mail: purans@cfi.lu.lv

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 ScF_3 were performed using the linear combination of atomic orbitals (LCAO) method. The band gap obtained in calculations for ScF_3 is equal to 10.54 eV and agree well with the expected value. The calculated infrared spectra of F displaced (FD) cubic ScF_3 allow us to predict that its mean Sc–F–Sc angle within NTE deviates from 180 degree.

1. Introduction

The interest towards ReO_3-type perovskites has been recently renewed by the discovery of large negative thermal expansion (NTE) in cubic ScF_3 structure in a wide temperature range [1], to be compared with a much less intense effect measured for the cubic 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
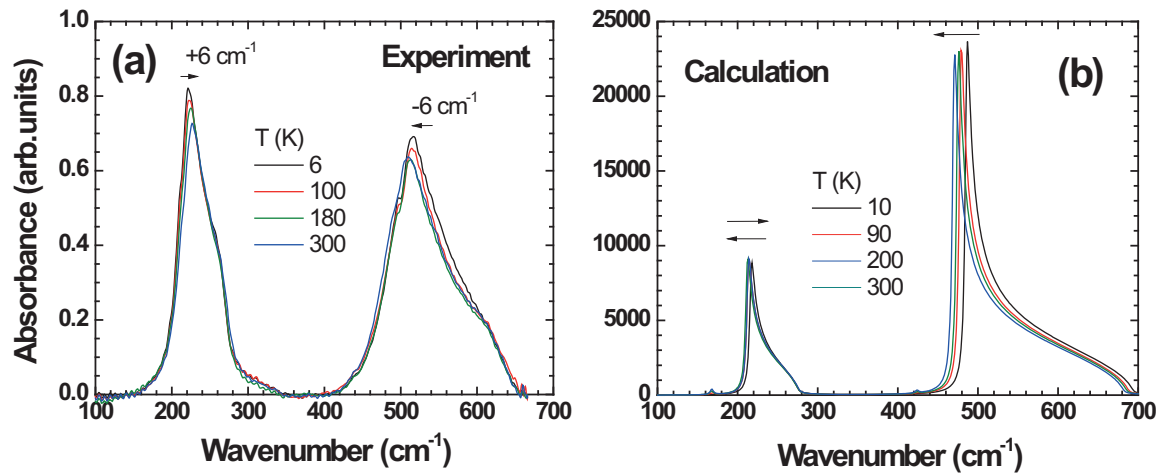
Figure 1. (Color online) (a) The variation of the Sc–F bond length measured by EXAFS and crystallographic distance measured by XRD (in house work). The angle Sc–F–Sc is calculated from EXAFS (Sc–F) and XRD (Sc–Sc) data. (b) Temperature dependence of the experimental Sc K-edge $\chi(k)k^2$ Fourier transforms (FT) for polycrystalline ScF_3.

NTE in ReO_3 and ScF_3, 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_6 (ScF_6) 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 $Pm\overline{3}m$) and fluorine displaced (FD) cubic (space group $Im\overline{3}$) ScF_3 were performed using the linear combination of atomic orbitals (LCAO) method.

2. Computational details
Both perfect and FD cubic ScF_3 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_3 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_3 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_3 ($a_0 = 4.0257$ Å) suggest that ScF_3 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 ScF_3. Two bands due to the F–Sc–F bending mode (at 220 cm^{-1}) and Sc–F stretching (at 520 cm^{-1}) are visible. A shift of the band maxima by about 6 cm^{-1} in the opposite directions occurs upon increasing temperature. (b) Calculated infrared absorption spectra of F-displaced cubic ScF_3 for several values of contracting lattice parameter a_0 and fluorine atoms displacements. The tilt angle Sc–F–Sc changes from 180° at 10 K to 158° at 300 K.

3. Results and discussions

The perovskite-type ScF_3 structure consists of corner-linked 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 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 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 ScF_3, obtained by Fourier transform infrared (FTIR) spectroscopy.

Fig. 2a shows the experimental temperature dependence of the far-IR absorption in ScF_3. Two absorption bands at 220 and 520 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 cm^{-1}. Note that infrared spectra calculated for perfect cubic ScF_3 show opposite directions of band shifted with respect to contracted lattice constant. At the same time, the FD cubic ScF_3 model (Fig. 2b) yield good agreement with measured data: the band near 500 cm^{-1} shifts to the left as a_0 contracts, while the band near 220 cm^{-1} starts shifting to the right when the Sc–F–Sc angle is smaller than $\sim$172°.

4. Conclusions

In this study three experimental techniques (EXAFS, XRD and FTIR) were used to probe the structure of polycrystalline ScF_3 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_3. The electronic structure and infrared spectra of locally distorted ScF_3 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_6 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.

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] Purans J, Fornasini P, Ali S E, Dalba G, Kuzmin A and Rocca F 2015 *Phys. Rev. B* **92** 014302
[3] Timoshenko J, Kuzmin A and Purans J 2014 *Journal of Physics: Condens. Matter* **26** 055401
[4] Chatterji T, Henry P, Mittal R and Chaplot S 2008 *Phys. Rev. B* **78** 134105
[5] Li C, Tang X, Muñoz J, Keith J, Tracy S, Abernathy D and Fultz B 2011 *Phys. Rev. Lett.* **107** 195504
[6] Purans J, Afify N D, Dalba G, Grisenti R, De Panfilis S, Kuzmin A, Ozhogin V I, Rocca F, Sanson A, Tiutiunnikov S I and Fornasini P 2008 *Phys. Rev. Lett.* **100** 055901
[7] Dovesi R, Saunders V R, Roetti C, Orlando R, Zicovich-Wilson C M, Pascale F, Civalleri B, Doll K, Harrison N M, Bush I J, DArco P, Llunell M, Causá M and Noël Y 2014 *CRYSTAL14 User's Manual* University of Torino Torino
[8] Peintinger M F, Oliveira D V and Bredow T 2013 *J. Comp. Chem.* **34** 451–459
[9] Guido C A, Brémond E, Adamo C and Cortona P 2013 *J. Chem. Phys.* **138** 021104
[10] Umeda M, Tezuka Y, Shin S and Yagishita A 1996 *Phys. Rev. B* **53** 1783–1789