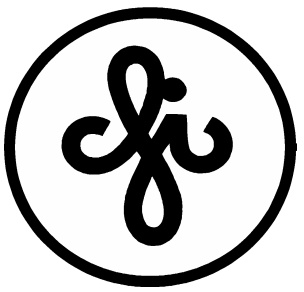




Electronic Structure and Lattice Dynamics of ScF₃ from *ab initio* LCAO Calculations



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Motivation

ScF₃ is a peculiar compound, which has simple ReO₃-type cubic structure (Fig. 1). While ReO₃ shows moderate NTE from 2 to 200 K [1], recent discovery [2] reveals that its ionic counterpart ScF₃ surprisingly has stronger NTE coefficient (-7.5 ppm/K at 300 K) over wider span of temperatures – from 10 K up to 1100 K, thus making investigation of ScF₃ challenging.

The main experimental data known about ScF₃ is its lattice constant dependence on temperature [2], bulk modulus at room temperature [2], total phonon DOS [3]; it is also proposed that its band gap should be greater than ~7-8 eV [4].

In spite of a number attempts made to explain the NTE in ScF₃ by estimating anharmonicity of a certain phonon modes within the framework of Rigid Unit Modes model, the origin of the NTE is still under debate [3]. In order to provide a deeper understanding of the problem, we have performed thorough investigation based on the first-principles calculations.

In this work we present electronic band structure, bulk modulus, phonon frequencies in high symmetry *k*-points across Brillouin zone (BZ), Grüneisen parameters as calculated by means of density functional theory (DFT) as well as results obtained using force field model. Nature of the NTE in ScF₃ is discussed.

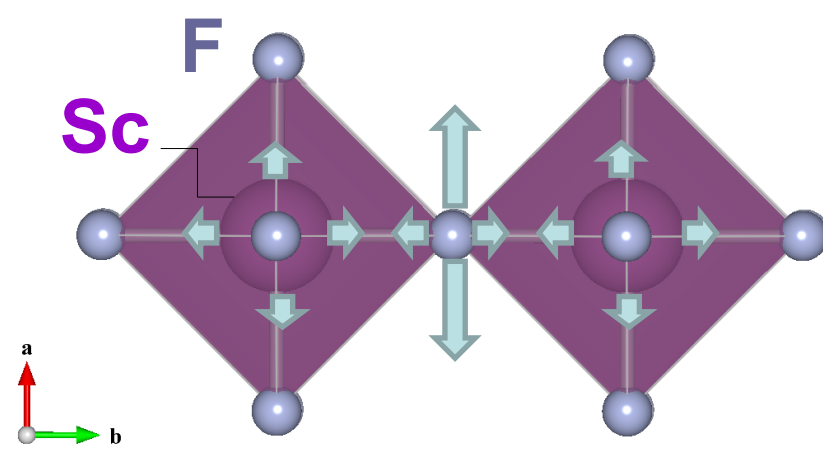


Fig. 1. ScF₃ has simple cubic structure (*Pm3m*): six fluorine atoms form octahedron with one scandium in its centre.

Phonons and Grüneisen parameters

We performed calculations of phonon modes in high symmetry *k*-points (Γ , M, X, R) across the Brillouin zone for different non-equilibrium values of lattice constant, thus obtaining mode specific Grüneisen parameters: for all low frequency modes below 40 meV they are moderately negative and contributes to NTE. Grüneisen function $\gamma(T)$ is an average weighted of Grüneisen parameters and predetermines the sign of the coefficient of thermal expansion (CTE). Within quasiharmonic approximation (and assuming, that bulk modulus B_T does not changes with temperature) we have estimated Grüneisen function and temperature dependence of linear CTE (Fig. 3). However, within this approximation CTE remains negative at all temperatures, while in the experiment [2] it becomes positive above 1100 K.

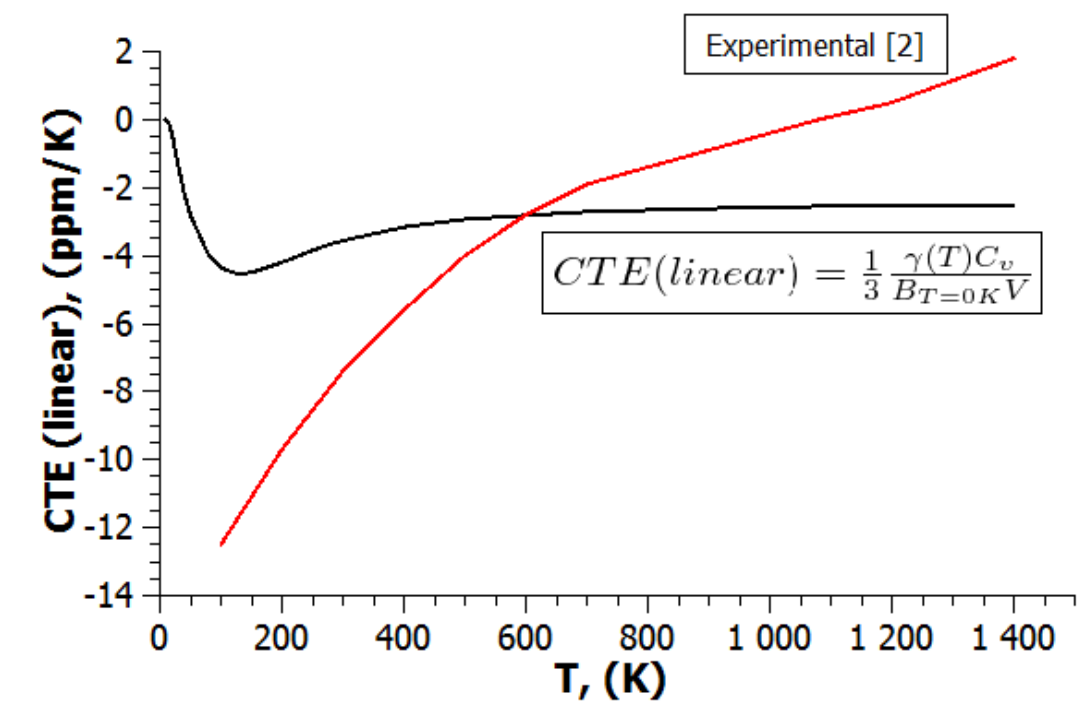


Fig. 3. CTE (linear) estimated within quasiharmonic approximation.

Electronic structure, band gap and bulk modulus

We have performed *ab initio* LCAO calculations of ScF₃ using hybrid HF-DFT approach as implemented in CRYSTAL09 total energy program [5]. Hybrid HF-DFT computational scheme was used. Variation of the weight of non-local Fock exchange part allowed us to reproduce the experimentally observed lattice constant ($a_0 = 4.026$ Å [2]) with several hybrid functionals tested (see Table 1). For phonon frequency calculations we have chosen hybrid functional PBESOL [6] (both exchange and correlation parts). Computational details: primitive 4 atom unit cell (32 atom supercell for phonons), $8 \times 8 \times 8$ *k*-point mesh.

Table 1. Band gap and bulk modulus for several hybrid correlation exchange functionals.

Exchange functional	Correlation functional	Fock exchange*, [%]	Band gap, [eV]	Bulk modulus, [GPa] (0 K)
PBESOL	PBESOL	18	9,8	101
PBE	PBE	55	15,1	103
PBESOL	PBE	20	10,1	101
PBE	PBESOL	53	14,8	104
BECKE	LYP	75	18,1	106
BECKE	PWWGA	60	15,9	103
Experimental data			> 8 [4]	57 (3) at 300 K [2]

* weight of non-local Fock exchange part

Variation of the weight of non-local Fock exchange part in hybrid E_{xc} leads to different values of the band gap for each functional (Table 1). However, all obtained values were greater than 8 eV. Thus, results are consistent with the available experimental data [4]. Electronic structure of cubic ScF₃ as calculated using PBESOL [6] functional is shown in Fig. 2.

To the best of our knowledge, the band gap and bulk modulus are not known experimentally at low temperatures. The calculation of electronic structure (Fig. 2) proves that ScF₃ is an insulator with a band gap greater than 8 eV [4].

Bulk modulus values (Table 1) do not vary significantly for all functionals used. Our calculated values are twice as big as the experimental value at room temperature [2].

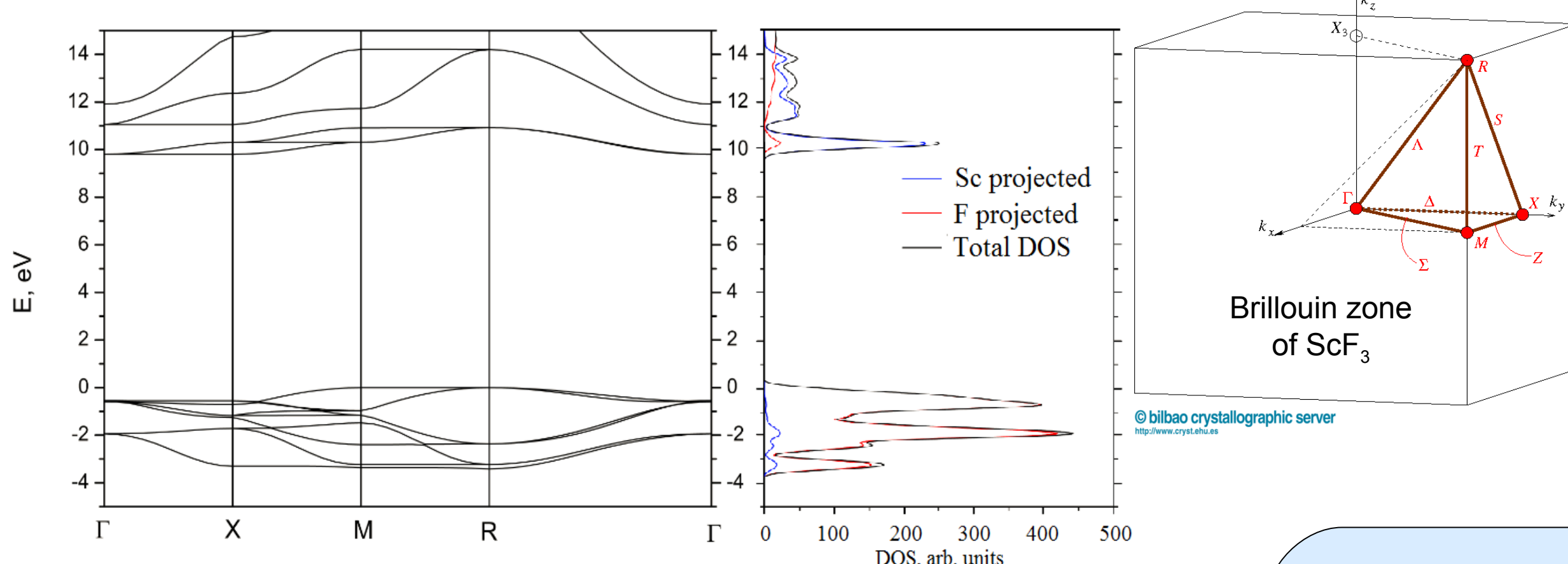


Fig. 2. Electronic structure of ScF₃ and total DOS.

Empirical force field model

The empirical force field potential model was developed in the form of the Buckingham and covalent exponential interatomic potentials to describe Sc-F and F-F interactions [7]. The model parameters were optimized using the GULP4.0 code [8] to reproduce a set of experimental data (lattice parameter, three elastic constants and bulk modulus) and theoretically calculated phonon frequencies (Fig. 4). The ions charges were fixed to that obtained in our LCAO calculations.

The classical Molecular Dynamics simulation was performed by the GULP4.0 code [8] in the NVT-ensemble for a supercell $5 \times 5 \times 5$, containing 500 atoms, at temperature 300 K. The obtained atomic configurations were used to estimate the mean square displacements (MSD) of Sc and F atoms. The MSD of Sc atoms is isotropic and equals to about 0.08 Å, whereas the MSD of F is strongly anisotropic being about 0.08 Å along the Sc-F-Sc chain and about 0.14 Å in the perpendicular direction. The mean square relative displacement (MSRD) of the Sc-F bond is about 0.06 Å. These results allow one to estimate the displacement correlation function (DCF) for the Sc-F bond as

$$DCF(Sc-F) = MSD^2(Sc) + MSD^2(F) - MSRD^2(Sc-F) = 0.0064 \cdot 2 - 0.0036 \sim 0.009 \text{ Å}^2.$$

Thus, a very pronounced correlated motion of neighbouring Sc and F atoms is observed, suggesting enough strong chemical Sc-F bonding.

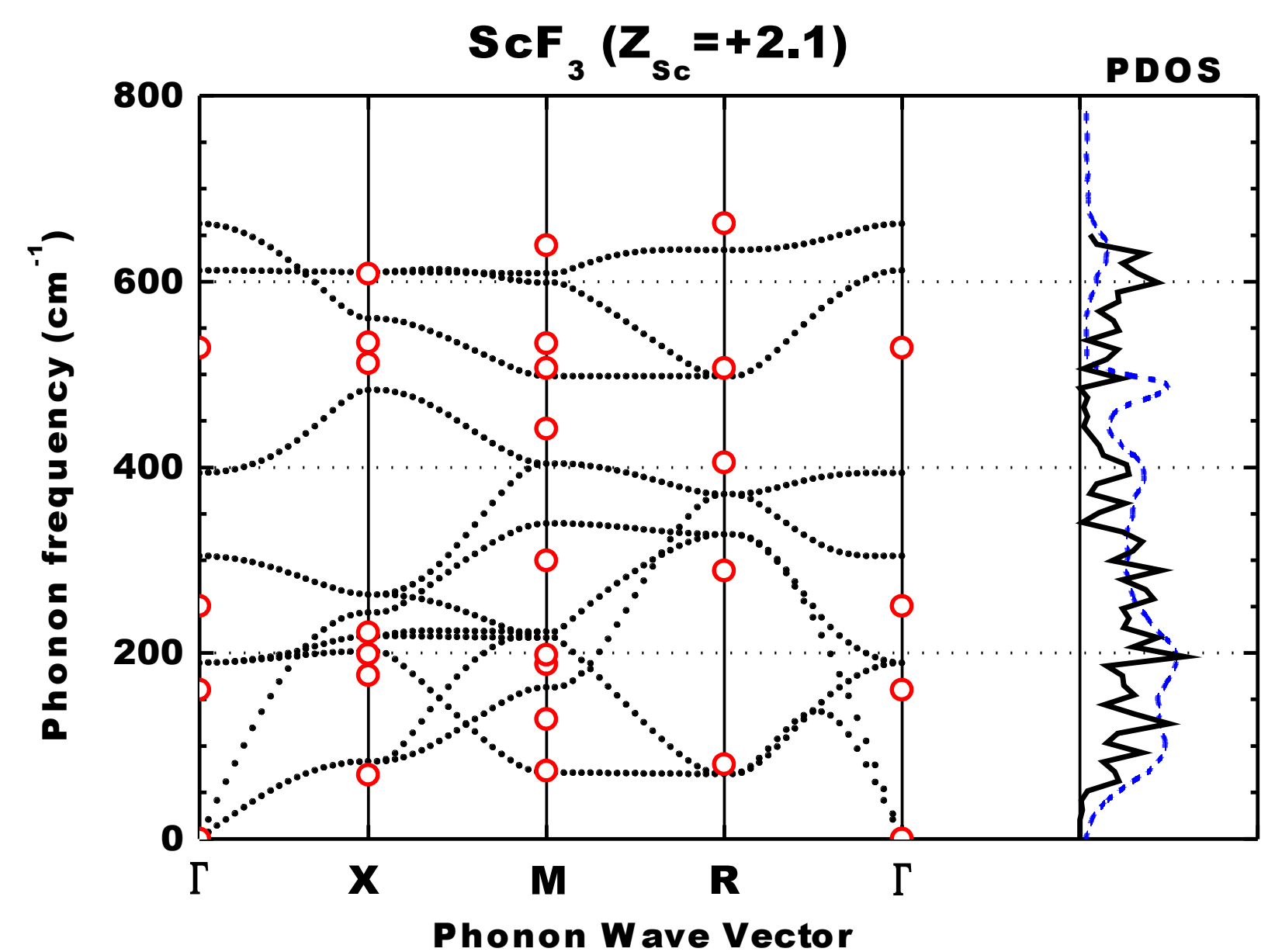


Fig. 4. Red circles indicate the LCAO calculated phonon frequencies. Blue dashed line is the experimental neutron-weighted phonon DOS at 7 K from [3].

Conclusions

- *Ab initio* LCAO calculations were performed for ScF₃ using several hybrid DFT-HF functionals.
- The atomic and electronic structure as well as phonon frequencies in high symmetry BZ (Γ , X, M, R) points were calculated and agree reasonably well with the available data [3,4].
- The force field model was constructed based on the LCAO results and used in the molecular dynamics simulations to estimate anisotropic amplitudes of thermal vibrations for Sc and F atoms.

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