Electronic Structure and Lattice Dynamics of ScF_3 from First-Principles LCAO Calculations

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Motivation Phonon DOS

ScF_3 is a peculiar compound, which has simple ReO_3-type cubic structure (Fig. 1). While ReO_3 shows moderate negative thermal expansion (NTE) from 2 to 200 K [1], recent discovery [2] reveals that its ionic counterpart ScF_3 surprisingly has stronger NTE coefficient (- 7.5 ppm/K at 300 K) over wider span of temperatures – from 10 K up to 1100 K (Fig. 1), thus making investigation of ScF_3 challenging.

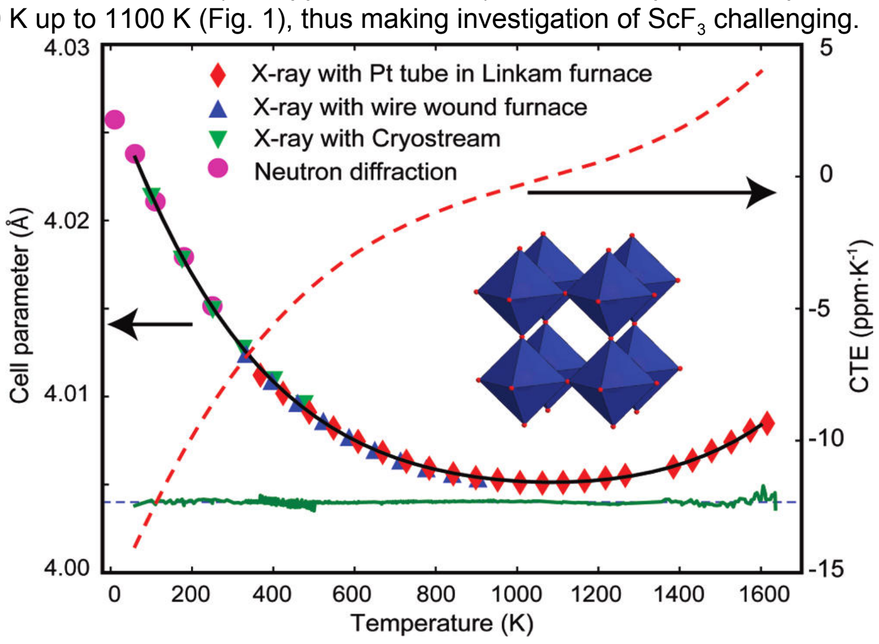

Fig. 1. Recent discovery [2] of NTE in ScF_3 (Pm3m space group).

The main experimental data known about ScF_3 is shown in Fig. 1 and Fig. 4.

In spite of a number attempts made to explain the NTE in ScF_3 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 structure and phonon dispersions along direction Γ-X-M-R-Γ in Brillouin zone, as well as estimation of phonon DOS.

Electronic structure

We have performed *ab initio* LCAO calculations of ScF_3 using hybrid HF-DFT approach as implemented in CRYSTAL09 total energy program [4]. 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 (a0 = 4.026 Å [2]) with PBESOL hybrid functional [5].

Calculated electronic structure of cubic ScF_3 is shown in Fig. 2 and prove that ScF_3 is the insulator with band gap greater than 7-8 eV, as proposed in [6]. Also, charge density difference maps are presented in Fig. 3. and give us a ground to discuss the ionicity of the compound.

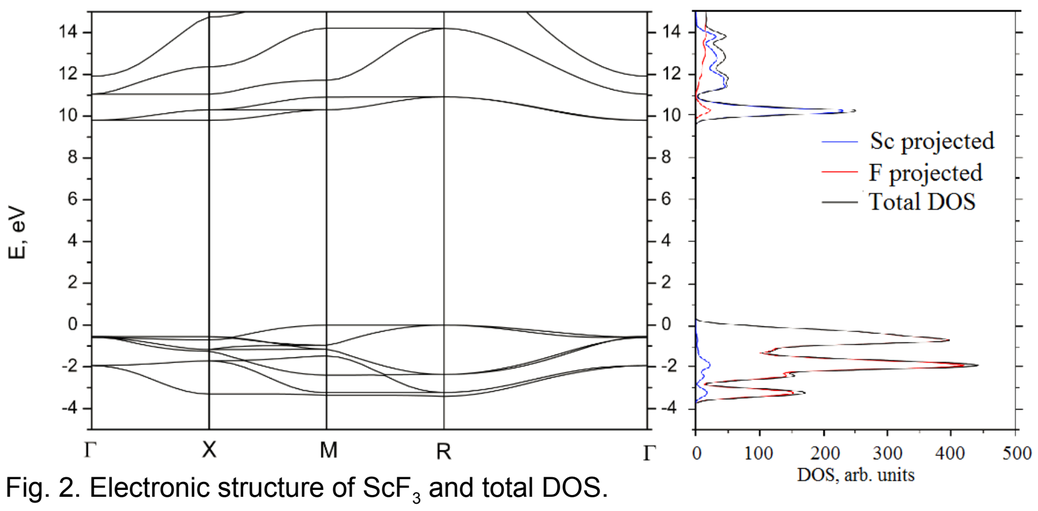

Fig. 2. Electronic structure of ScF_3 and total DOS.

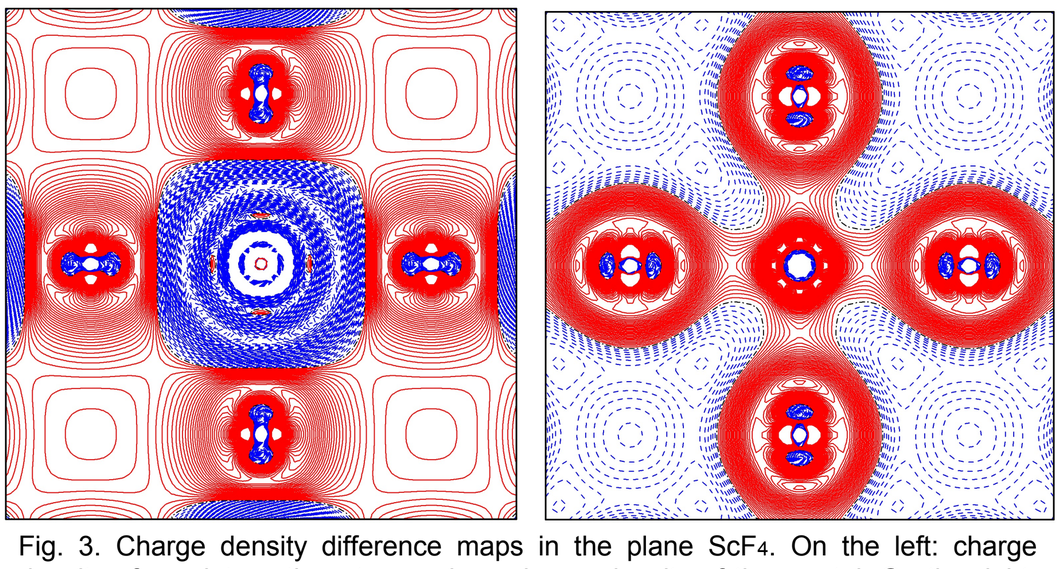

Fig. 3. Charge density difference maps in the plane ScF_4. On the left: charge density of non-interacting atoms minus charge density of the crystal. On the right: charge density of non-interacting ions minus charge density of the crystal. Red and blue refers to positive and negative differences respectively.

Phonon DOS and dispersion curves

Recently, in the article [3] were published the results of the inelastic neutron scattering measurements, performed with ARCS, a time-of-flight Fermi chopper spectrometer at the Spallation Neutron Source at Oak Ridge National Laboratory (see Fig. 4.).

In the same work [3] phonon properties were calculated from first principles within the harmonic approximation (see Fig. 5).

As authors [3] mention, "The agreement between the experimental and calculated phonon DOS curves is good after accounting for instrumental broadening and neutron weighting (neutrons are scattered about twice as efficiently from motions of Sc atoms than F atoms)."

Here we present our own *ab initio* LCAO calculations of phonon properties (see Fig. 6.), which is in a good agreement with experiment [3], thus validating the correctness of our calculations.

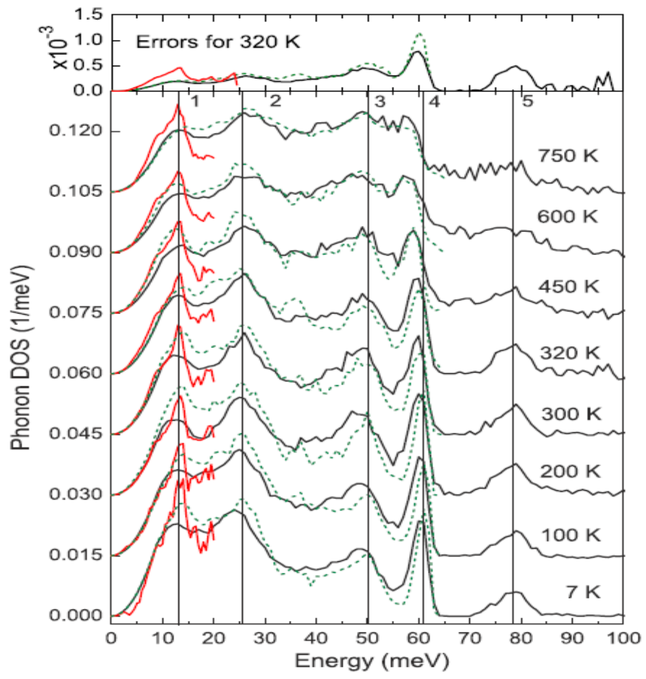

Fig. 4. (From [3]). Neutron-weighted ScF_3 phonon DOS from incident energies of 118.7 (black lines), 79.5 (green dashed lines), and 30.0 meV (red or grey lines), scaled to conserve spectral areas and offset for clarity.

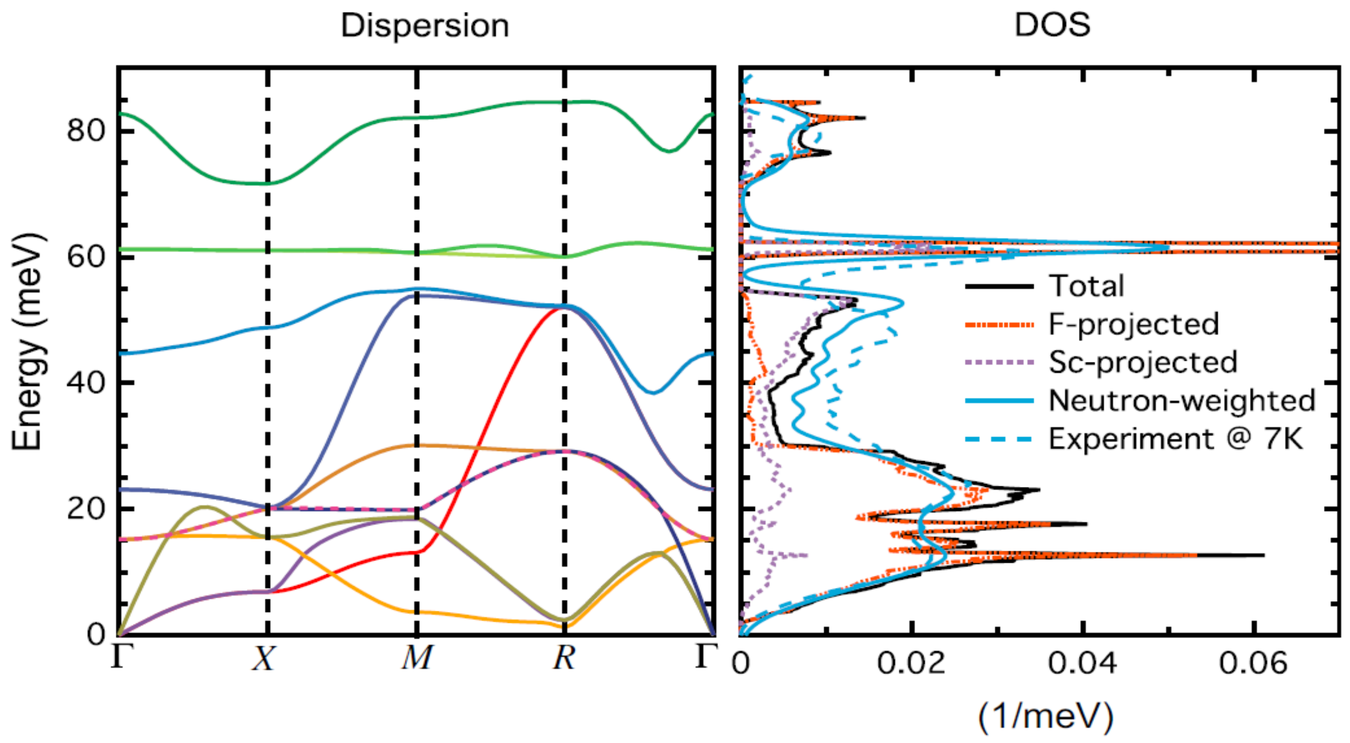

Fig. 5. (From [3]). On the left: calculated phonon dispersions along high symmetry directions of ScF_3 at 0 K. On the right: total and partial phonon DOS curves at 0 K from first-principles calculation, neutron-weighted phonon DOS with instrument broadening at 120 meV added, and experimental neutron-weighted phonon DOS at 7 K.

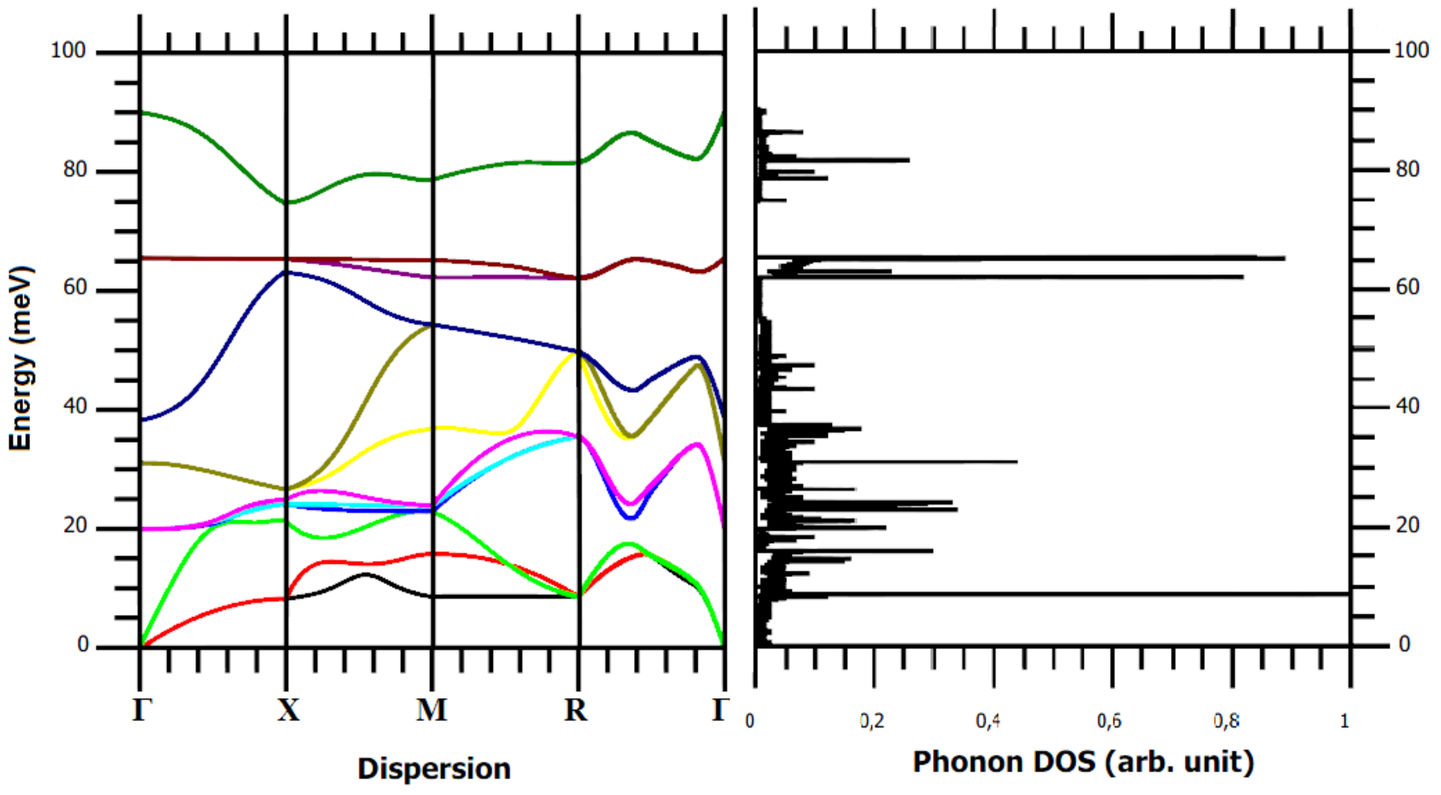

Fig. 6. Our *ab initio* LCAO calculations: phonon dispersion curves and phonon DOS.

Conclusions

- ***Ab initio* LCAO calculations were performed for ScF_3 obtaining novel electronic structure to the best of our knowledge not known yet.**
- **Calculated phonon dispersion curves and phonon DOS agree reasonably well with the available data [3].**

References

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