Ab initio calculations of the structure of ScF_3

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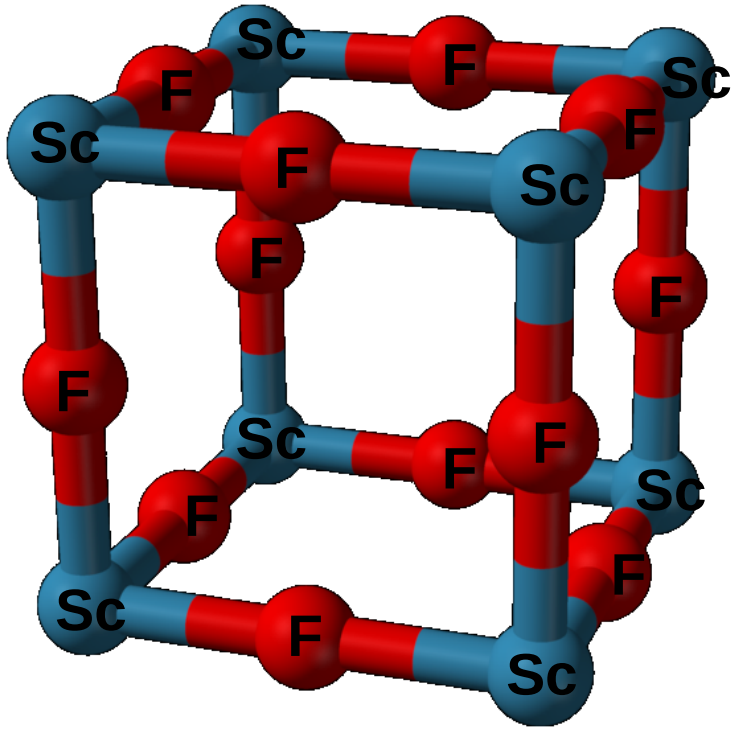
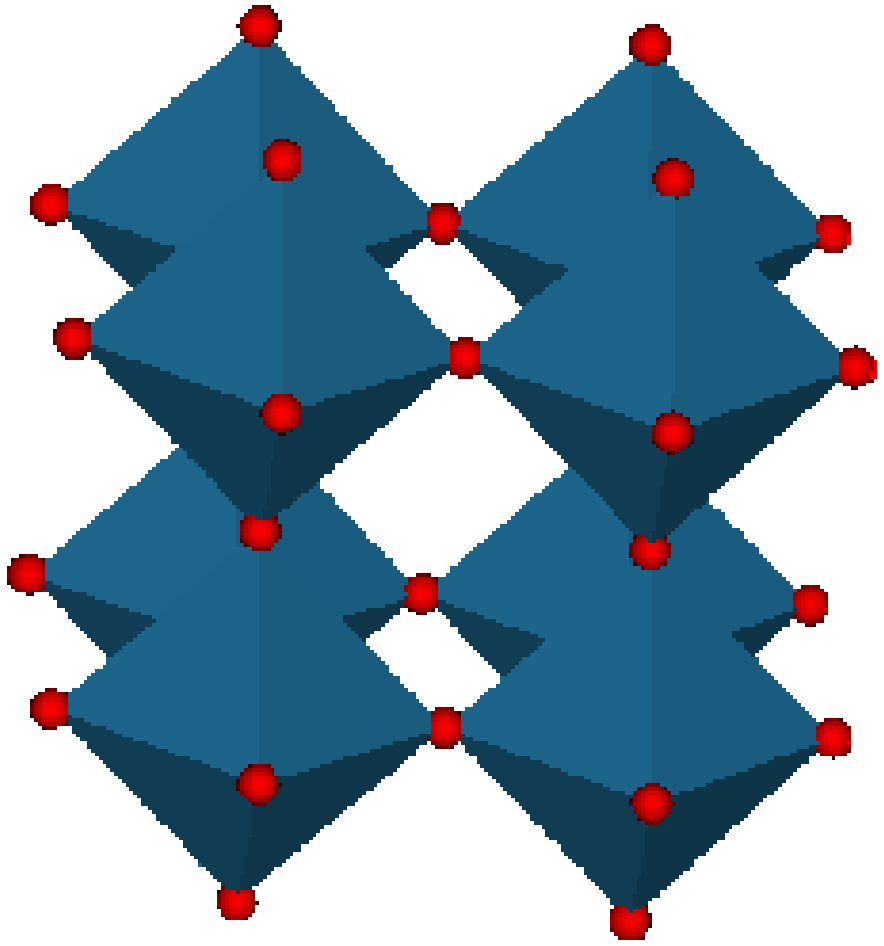
ScF_3 structure

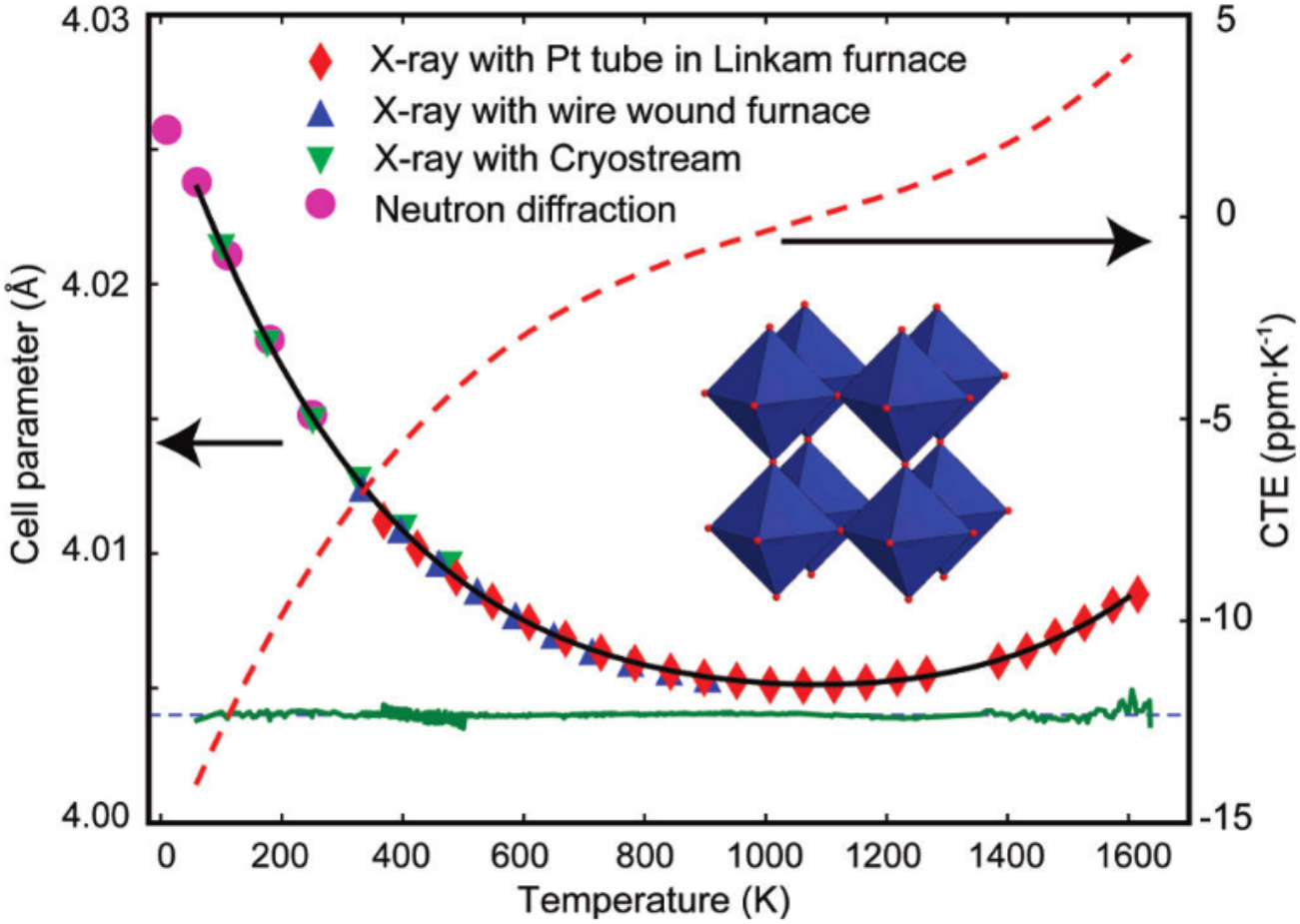
Primitive cubic unit cell
Space group Pm3m





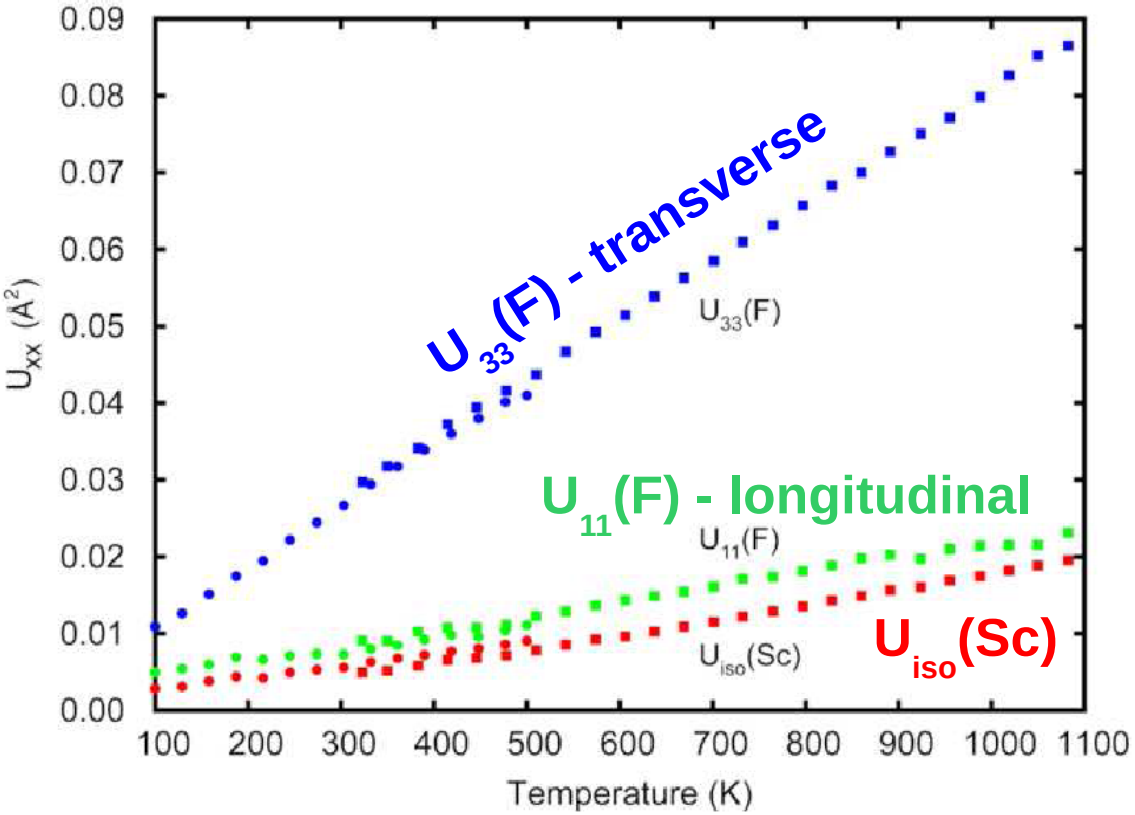
ScF_3 is a **simple model system** to study the origin of **negative thermal expansion (NTE)**.

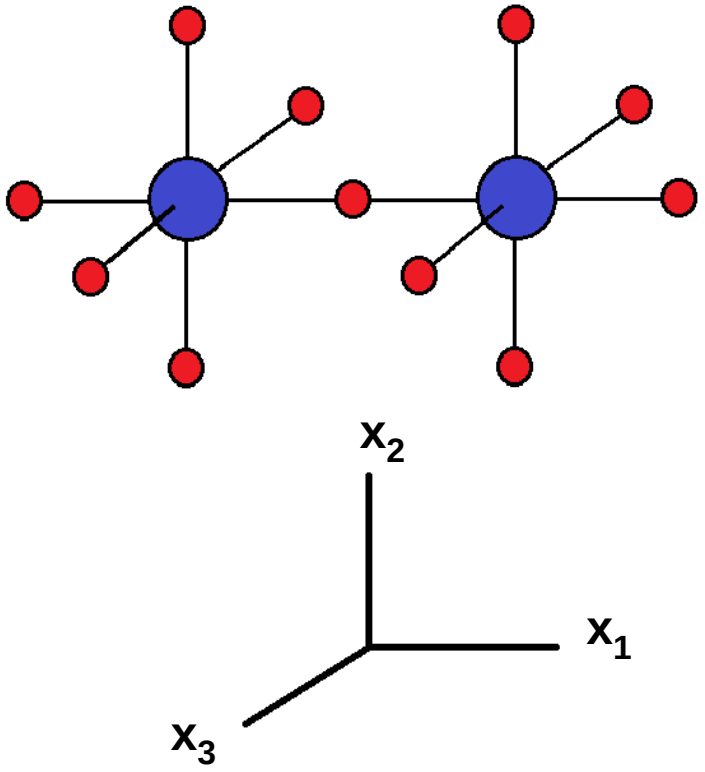
Negative thermal expansion (NTE) coefficient



B. K. Greve, et al., J. Am. Chem. Soc. 132, 15496 (2010).

Thermal displacement parameters





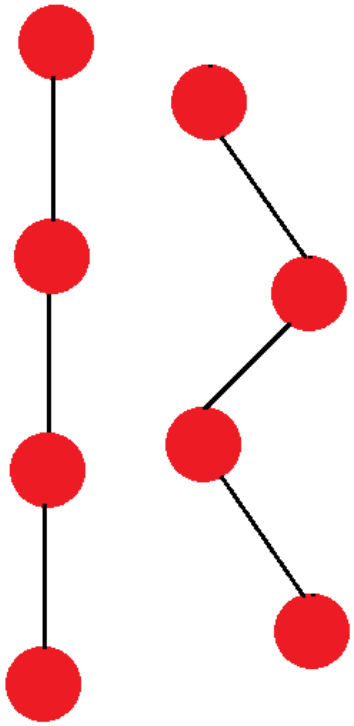
Experimental mean-squared displacement versus temperature for Sc (isotropic U_{iso}) and F (anisotropic U_{11}, U_{33}) atoms. The thermal parameters for ScF_3 indicate large amplitude displacements for fluorine transverse to the Sc-Sc axes.

U_{11}(F) – longitudinal to Sc-Sc

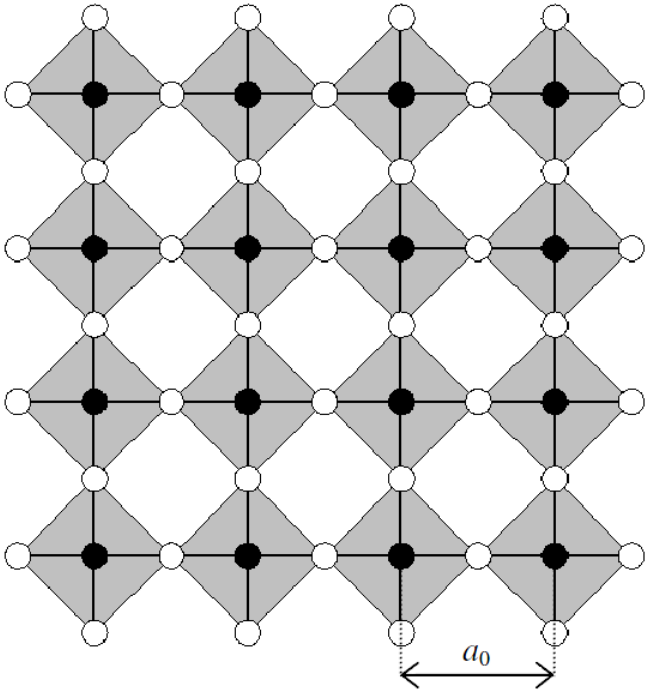
U_{33}(F) – transverse to Sc-Sc

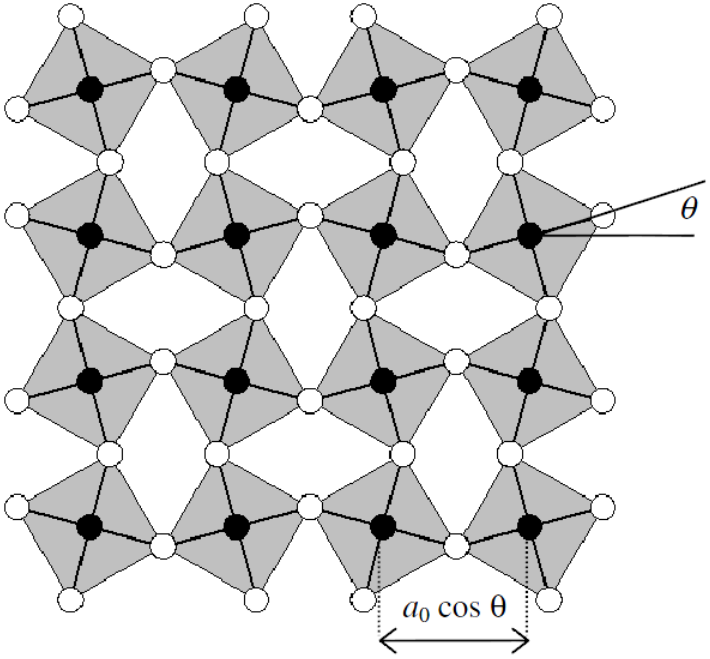
B. K. Greve, et al., J. Am. Chem. Soc. 132, 15496 (2010).

Attempt to understanding NTE mechanism: Rigid Unit Modes



1D

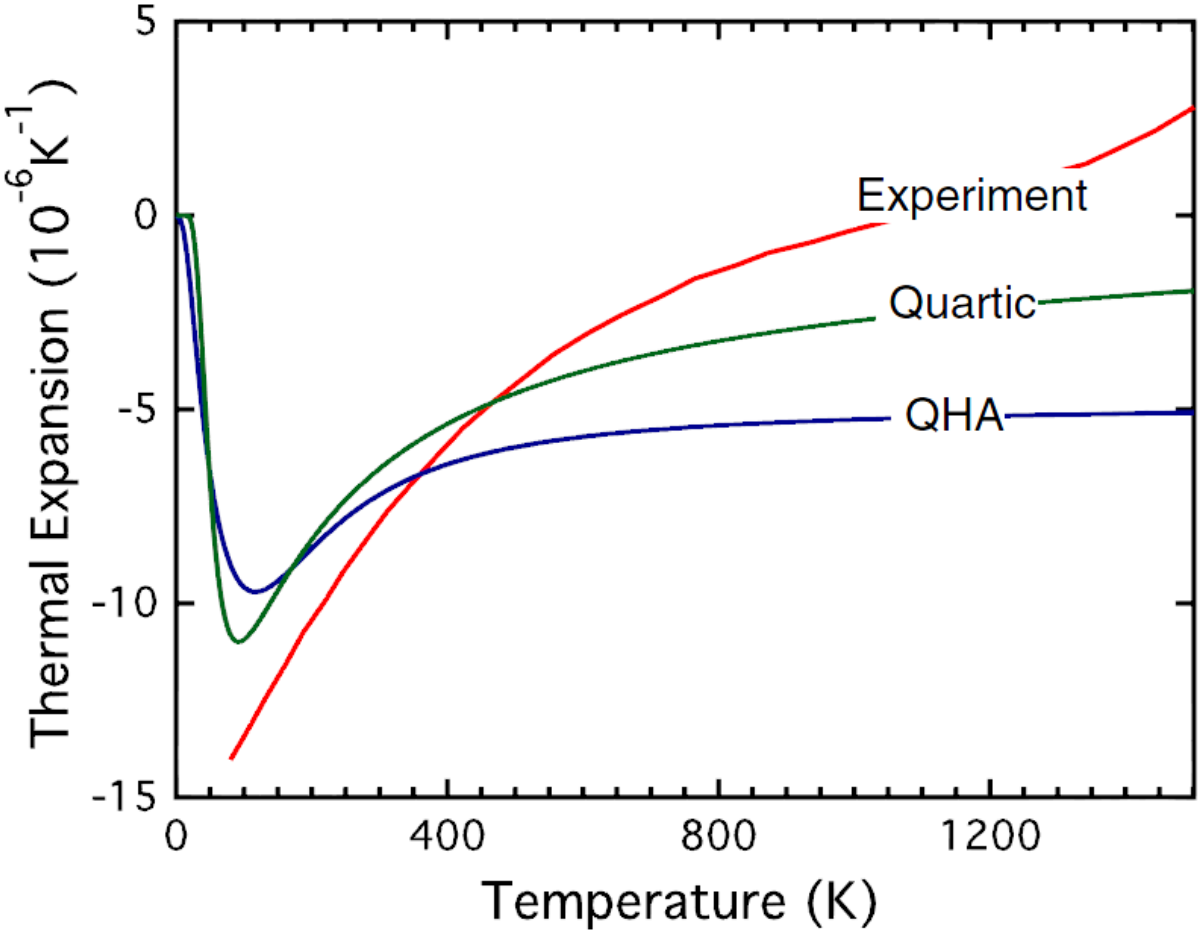




2D

G. D. Barrera, et al., J. Phys.: Condens. Matter, 17, R217, (2005).

Recent investigations on NTE in ScF_3



C.W. Li, et al, Phy. Rev. Lett. 107, 195504 (2011).

Ab Initio LCAO calculations with *CRYSTAL09*

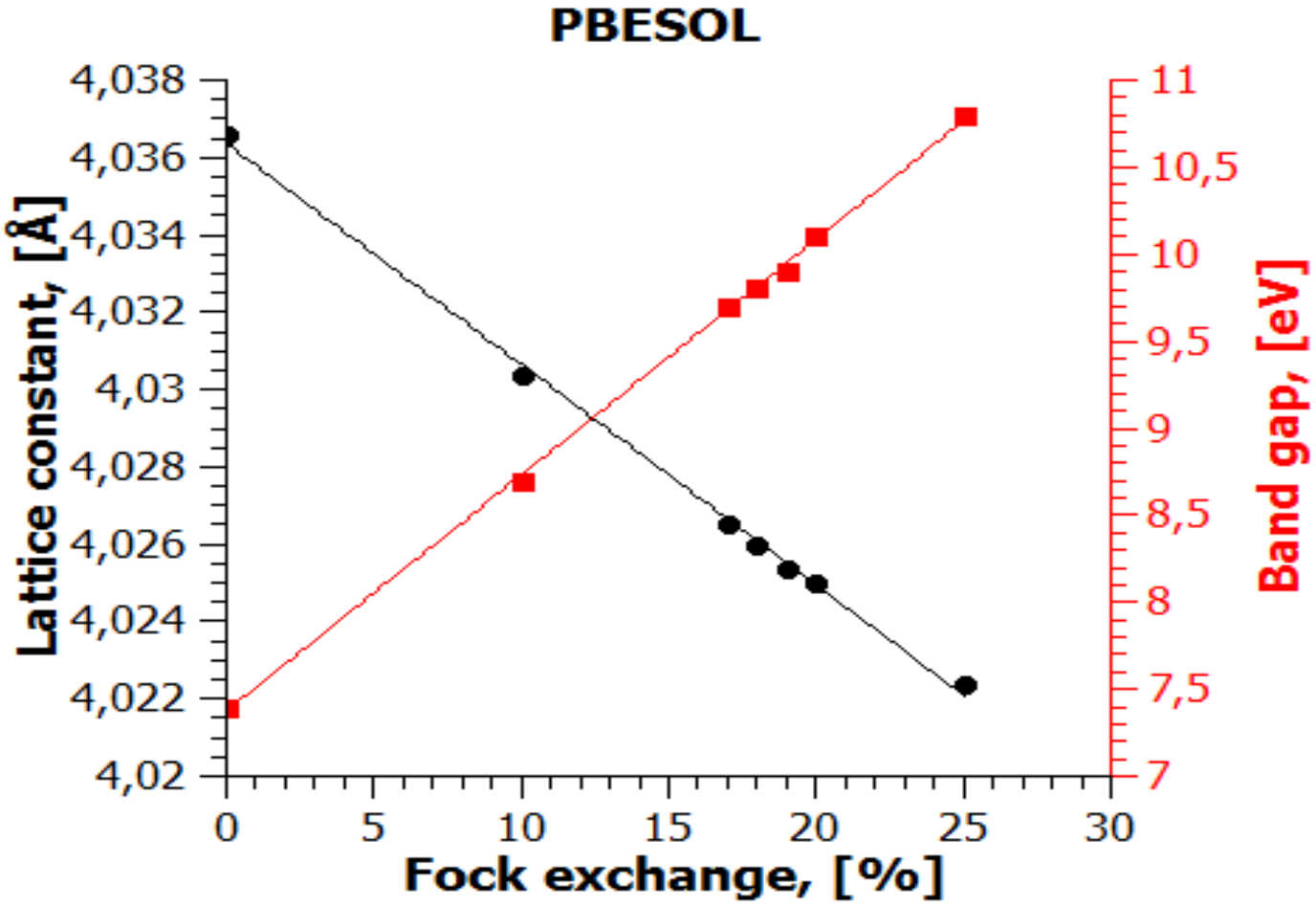
The *CRYSTAL09* code have been used:
- the Gaussian-type functions centered on the atomic nuclei;
- basis sets for expansion of the linear combination of atomic orbitals (LCAO)
- different non-local exchange-correlation functionals PBE, PBESOL, B_3LYP, B_3PW;
- Monkhorst-Pack scheme with 8×8×8 *k*-point mesh for the BZ sampling;
- truncation criteria for bielectronic integrals 10^{-7}.

By changing the weight of non-local Fock exchange part it is possible to achieve an appropriate value of lattice constant. Below: B3LYP functional case – coefficient 0.2 could be changed.

$$E_{\mathrm{x}}^{\mathrm{B3LYP}} = (1\text{-}0.2)\,E_{\mathrm{x}}^{\mathrm{LDA}} + 0.2\,E_{\mathrm{x}} + 0.72\Delta E_{\mathrm{x}}^{\mathrm{B88}}$$

$$E_{\mathrm{c}}^{\mathrm{B3LYP}} = 0.19E_{\mathrm{c}}^{\mathrm{VWN3}} + 0.81E_{\mathrm{c}}^{\mathrm{LYP}}$$

Ab Initio LCAO calculations with *CRYSTAL09*



Lattice constant, band gap, isothermal bulk modulus

Main ScF_3 parameters calculated with different hybrid HF-DFT functionals.

In each case lattice constant is equal to experimental[1] value 4,026 Å.

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	PWGGA	60	15,9	103
*weight of non-local Fock exchange part				
Experimental data			**> 8** [2]	**57(3)** [1] (300 K)

[1]B. K. Greve, et al., J. Am. Chem. Soc. 132, 15496 (2010).

[2]M. Umeda, et al., PRB, 53, 1783 (1996)

Conclusions, open questions and further plans

- Appropriate weight of non-local Fock exchange was found for each examinated hybrid HF-DFT functional to reproduce experimental value of lattice constant (4,026 Å) with 0,001 Å uncertainty.

- All examinated functionals satisfy availible experimental data. As main functional PBESOL was choosed.

- Bulk modulus calculated at 0K is equal to 103(3) GPa. This value is for 40 GPa greater than experimental one, measured at room temperature. Thus, temperature dependence of bulk modulus is of a great interest.

- Origins of NTE in ScF_3 remains an open problem.

- Further investigation requires calculations of phonon frequencies, which are important for the reliable construction of the force field model. The latter, together with the forthcoming EXAFS experiment, will be helpful to understand the origin of NTE in ScF_3.

Thank You!

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