Structural Optimization at finite temperature based on anharmonic phonon theory

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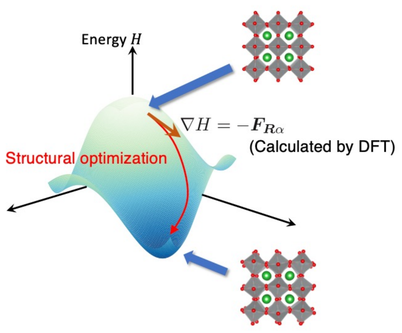
Highlights

- ✓ We have developed the theory and the efficient computational scheme of structural optimization at finite temperature based on self-consistent phonon (SCP) theory.
- ✓ We applied the method to $BaTiO_3$ and succeeded in reproducing its three-step structural phase transition and the $P-T$ diagram.
- ✓ The presented methodology is applicable to a wide range of materials. It is expected to be an essential tool in exploring exotic properties near the structural phase transition or in computational material discoveries at finite temperature.

Background and Introduction

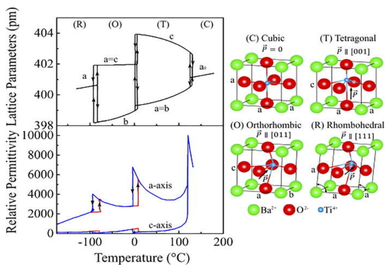
The structural optimization based on DFT (density functional theory)

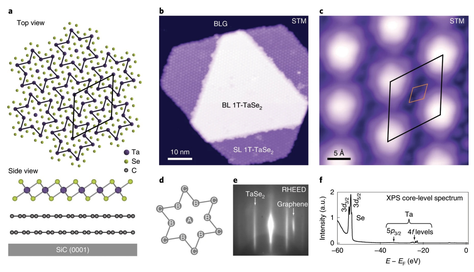


- ✓ The effect of lattice vibrations (finite-temperature effect) and zero point motions (nuclear quantum effect) are disregarded.
  → zero-temperature method
- ✓ The finite-temperature method (molecular dynamics, ...) are computationally expensive.
  → cannot be applied to complex crystals

Crystal structures at finite temperature

- ✓ structural phase transitions of $BaTiO_3$ [1]
- ✓ Charge density wave (CDW) in 1T-$TaSe_2$ [2]





- ✓ A wide range of materials show structural phase transition by varying temperature and pressure.
- ✓ Exotic phenomena are observed near the structural phase transition.

The purpose of this study

- ✓ Development of efficient first-principles method of crystal structures at finite temperatures that takes into account the phonon anharmonicity and the nuclear quantum effect.

Theory

Interatomic force constants (IFCs)

- ✓ We start from the Taylor expansion of the potential energy surface.

$$\hat{U} = \sum_{n=0}^{\infty} \hat{U}_n$$

Interatomic force constants (IFCs)

$$\hat{U}_n = \frac{1}{n!} \sum_{\{R\alpha\mu\}} \Phi_{\mu_1\cdots\mu_n}(\boldsymbol{R}_1\alpha_1, \cdots, \boldsymbol{R}_n\alpha_n)\hat{u}_{\boldsymbol{R}_1\alpha_1\mu_1}\cdots\hat{u}_{\boldsymbol{R}_n\alpha_n\mu_n}$$

$$= \frac{1}{n!}\frac{1}{N^{n/2-1}} \sum_{k\lambda} \delta_{\boldsymbol{k}_1+\cdots+\boldsymbol{k}_n} \widetilde{\Phi}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n)\hat{q}_{\boldsymbol{k}_1\lambda_1}\cdots\hat{q}_{\boldsymbol{k}_n\lambda_n}.$$

$n \geq 3$: anharmonic terms

$$\widetilde{\Phi}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n)$$

$$= \sum_{\{\alpha\mu\}} \frac{\epsilon_{\boldsymbol{k}_1\lambda_1,\alpha_1\mu_1}}{\sqrt{M_{\alpha_1}}} \cdots \frac{\epsilon_{\boldsymbol{k}_n\lambda_n,\alpha_n\mu_n}}{\sqrt{M_{\alpha_n}}} \sum_{\boldsymbol{R}_1\cdots\boldsymbol{R}_{n-1}} \Phi_{\mu_1\cdots\mu_n}(\boldsymbol{R}_1\alpha_1, \cdots, \boldsymbol{R}_{n-1}\alpha_{n-1}, \boldsymbol{0}\alpha_n) e^{i(\boldsymbol{k}_1\cdot\boldsymbol{R}_1+\cdots\boldsymbol{k}_{n-1}\cdot\boldsymbol{R}_{n-1})}.$$

Self-consistent phonon theory

- ✓ The "mean field theory" of phonon anharmonicity.
- ✓ Based on variational principle of the free energy.

$$\mathcal{F} = -k_B T \log \mathrm{Tr} e^{-\beta\hat{\mathcal{H}}_0} + \langle \hat{H} - \hat{\mathcal{H}}_0 \rangle_{\hat{\mathcal{H}}_0}$$

- ✓ SCP equation is obtained by minimizing $\mathcal{F}$ with respect to $\Omega_{\boldsymbol{k}\lambda'}, \epsilon_{\boldsymbol{k}\lambda,\alpha\mu}$ of the trial harmonic Hamiltonian $\hat{\mathcal{H}}_0 = \sum_{\boldsymbol{k}\lambda'} \hbar\Omega_{\boldsymbol{k}\lambda'}\left(\hat{a}^\dagger_{\boldsymbol{k}\lambda'}\hat{a}_{\boldsymbol{k}\lambda'} + \frac{1}{2}\right)$ [3,4].

$$\Omega^2_{\boldsymbol{k}\lambda_1\lambda_2} = \sum_{n=1}^{\infty} \frac{1}{(n-1)!N^{n-1}} \sum_{\{\boldsymbol{k}\lambda'\}} \left(\frac{\hbar}{2}\right)^{n-1} \frac{\widetilde{\Phi}(-\boldsymbol{k}\lambda_1, \boldsymbol{k}\lambda_2, \boldsymbol{k}_1\lambda'_1, -\boldsymbol{k}_1\lambda'_1, \cdots, -\boldsymbol{k}_{n-1}\lambda'_{n-1})}{\Omega_{\boldsymbol{k}_1\lambda'_1}\cdots\Omega_{\boldsymbol{k}_{n-1}\lambda'_{n-1}}}$$

$$\times\left(n_B(\hbar\Omega_{\boldsymbol{k}_1\lambda'_1}) + \frac{1}{2}\right)\cdots\left(n_B(\hbar\Omega_{\boldsymbol{k}_{n-1}\lambda'_{n-1}}) + \frac{1}{2}\right)$$

Structural optimization based on SCP theory

- ✓ Calculate the crystal structure (internal coordinates and the shape of the unit cell) that minimizes the SCP free energy.
- ✓ The gradient of the SCP free energy with respect to a structural degree of freedom A is

$$\frac{1}{N}\frac{\partial\mathcal{F}(\widetilde{\Phi}^{(q^{(0)},u_{\mu\nu})}, \Omega_{\boldsymbol{k}\lambda_1\lambda_2}(q^{(0)}, u_{\mu\nu}))}{\partial A} = \sum_{n=0}^{\infty} \frac{1}{n!N^n} \sum_{\{\boldsymbol{k}\lambda\}} \left(\frac{\hbar}{2}\right)^n \frac{\partial\widetilde{\Phi}(\boldsymbol{k}_1\lambda'_1, -\boldsymbol{k}_1\lambda'_1, \cdots, \boldsymbol{k}_n\lambda'_n, -\boldsymbol{k}_n\lambda'_n)}{\partial A}$$

$$\times \frac{(n_B(\hbar\Omega_{\boldsymbol{k}_1\lambda'_1}) + 1/2)}{\Omega_{\boldsymbol{k}_1\lambda'_1}} \cdots \frac{(n_B(\hbar\Omega_{\boldsymbol{k}_n\lambda'_n}) + 1/2)}{\Omega_{\boldsymbol{k}_n\lambda'_n}},$$

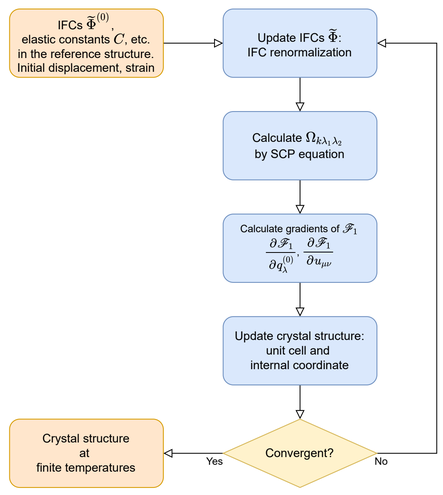
Calculation scheme

IFC renormalization

- ✓ Calculate the set of IFCs in the updated structure from the set of IFCs in the reference structure [5].

$$\widetilde{\Phi}^{(q^{(0)})}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n) = \sum_m \frac{1}{m!} \sum_{\{\rho\}} \widetilde{\Phi}^{(q^{(0)}=0)}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n, \boldsymbol{0}\rho_1, \cdots \boldsymbol{0}\rho_m) q^{(0)}_{\rho_1}\cdots q^{(0)}_{\rho_m}.$$

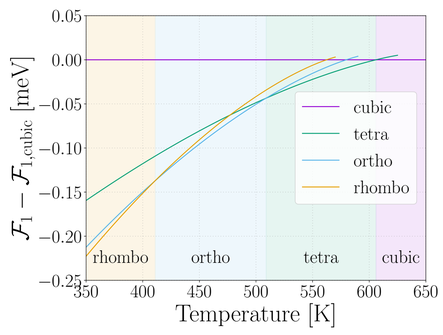
Calculation scheme



- ✓ No need for expensive DFT calculations in the structural optimization loop.
  → efficient!
- ✓ Both the atomic positions and the shape of the unit cell are optimized.
- ✓ We have implemented the calculation scheme to the ALAMODE package [4]
  → will be made public in future release

Results and Discussion

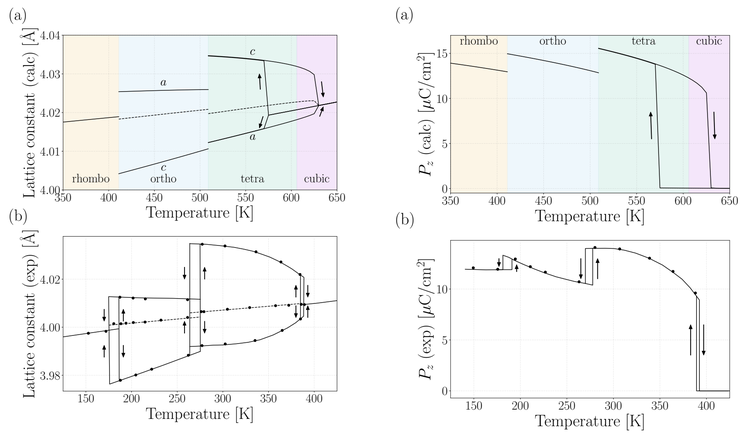
Free energy of the four phases



T_c [K]	calculation	experiment [6]
cubic-tetra	606	∼390
tetra-ortho	509	∼ 270
ortho-rhombo	411	∼ 180

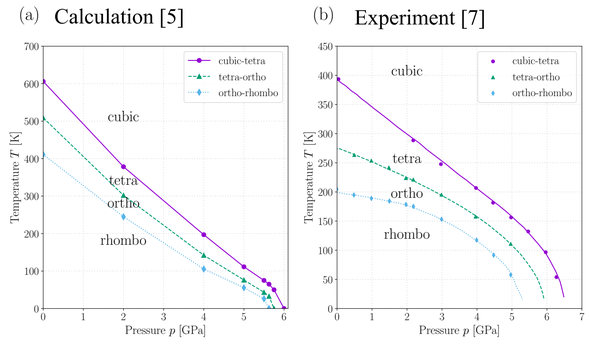
- ✓ Three-step structural phase transition is successfully reproduced [5].

Temperature-dependent crystal structure



Experiment data is taken Ref [6].

Temperature-dependent crystal structure



- ✓ The three phase boundary curves reach 0 K as pressure is applied.
- ✓ Cubic phase is stable at 0 K above ∼6 GPa.

Reference

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