Ab initio structural optimization at finite T based on anharmonic phonon theory

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Collaborators

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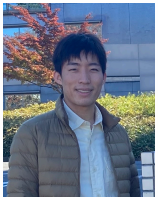


Phys. Rev. B 106 224104 (2022)
Phys. Rev. B 110 094102 (2024)

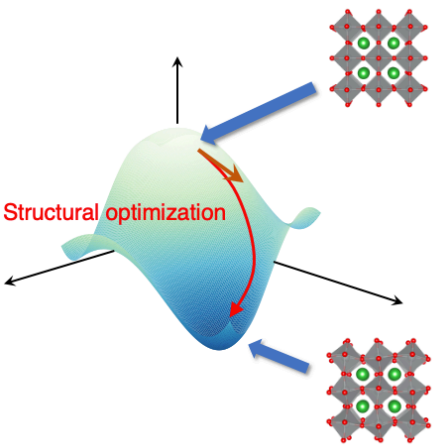
Introduction

As the crystal structure changes, a wide variety of materials exhibit fascinating properties

- Ferroelectric phase transitions in perovskite oxides
- charge density wave in transition metal dichalcogenides
- enhancement of thermoelectric effect
- enhancement of superconductivity
- ...

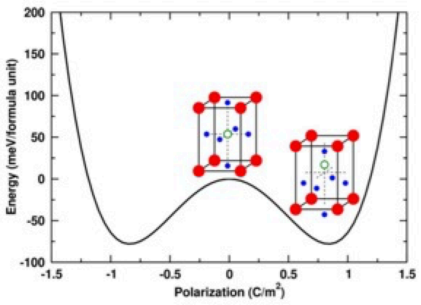
Introduction

- Temperature dependence of crystal structure is one of the most fundamental problems in solid state physics
- Structural optimization based on DFT accurately calculates the crystal structure at $T = 0$
- Prediction of crystal structures at finite T is a significant challenge



Introduction

- Finite T phases of strongly anharmonic crystals have unstable phonon modes: the harmonic approximation does not work
- Nuclear quantum effect also has a significant impact on the structures of materials with light atoms or those in the vicinity of the structural phase transition



S. P. Beckman *et al.*, PRB 79, 144124 (2009)

Introduction

- We formulate a theory of structural optimization at finite T based on the self-consistent phonon (SCP) theory.
- We apply the present method to the three-step structural phase transition of $BaTiO_3$ and polar metals $LiBO_3$ (B=Ta, W, Re, Os).

R. Masuki, T. Nomoto, RA, T. Tadano, Phys. Rev. B 106 224104 (2022)
R. Masuki, T. Nomoto, RA, T. Tadano, Phys. Rev. B 110 094102 (2024)

Taylor expansion of the potential energy surface

The Born-Oppenheimer potential energy surface can be Taylor-expanded in terms of the atomic displacement operator $\hat{u}_{\boldsymbol{R}\alpha\mu}$ (α: atom index in the primitive cell, $\mu = x, y, z$)

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

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

$\Phi_{\mu_1 \cdots \mu_n}(\boldsymbol{R}_1\alpha_1, \cdots, \boldsymbol{R}_n\alpha_n)$: interatomic force constants (IFCs)

Taylor expansion of the potential energy surface

In momentum space:

$$\hat{q}_{\boldsymbol{k}\lambda} = \frac{1}{\sqrt{N}} \sum_{\boldsymbol{R}\alpha\mu} e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \epsilon^*_{\boldsymbol{k}\lambda,\alpha\mu} \sqrt{M_\alpha}\, \hat{u}_{\boldsymbol{R}\alpha\mu},$$

$$\widetilde{\Phi}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n) = \sum_{\{\alpha\mu\}} \frac{\epsilon_{\boldsymbol{k}_1\lambda_1,\alpha_1\mu_1}}{\sqrt{M_{\alpha_1}}} \cdots \frac{\epsilon_{\boldsymbol{k}_n\lambda_n,\alpha_n\mu_n}}{\sqrt{M_{\alpha_n}}}$$

$$\times \sum_{\boldsymbol{R}_1\cdots\boldsymbol{R}_{n-1}} \Phi_{\mu_1\cdots\mu_n}(\boldsymbol{R}_1\alpha_1, \cdots, \boldsymbol{R}_{n-1}\alpha_{n-1}, 0\alpha_n) e^{i(\boldsymbol{k}_1\cdot\boldsymbol{R}_1 + \cdots + \boldsymbol{k}_{n-1}\cdot\boldsymbol{R}_{n-1})}.$$

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

Anharmonic terms ($n \geq 3$) neglected in the harmonic approx.

Self-consistent Phonon Theory

Variational principle of the free energy:

$$\begin{aligned} \mathcal{F} &= -k_B T \log \mathrm{Tr}\, e^{-\beta \hat{\mathcal{H}}_0} + \langle \hat{H} - \hat{\mathcal{H}}_0 \rangle_{\hat{\mathcal{H}}_0} \geq F \\ \hat{\mathcal{H}}_0 &= \sum_{\boldsymbol{k}\lambda'} \hbar \Omega_{\boldsymbol{k}\lambda'} \hat{a}^\dagger_{\boldsymbol{k}\lambda'} \hat{a}_{\boldsymbol{k}\lambda'}. \end{aligned}$$

Minimizing $\mathcal{F}$ in terms of $\Omega_{\boldsymbol{k}\lambda'}$ we get the SCP equation:

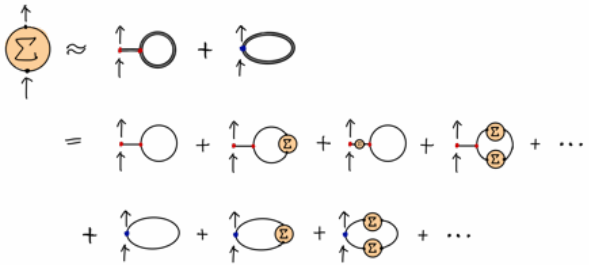
$$\begin{aligned} \Omega^2_{\boldsymbol{k}\lambda_1} &= \omega^2_{\boldsymbol{k}\lambda_1} + \sum_{n=2}^{\infty} \frac{1}{(n-1)! N^{n-1}} \sum_{\{\boldsymbol{k}\lambda'\}} \left(\frac{\hbar}{2}\right)^{n-1} \\ &\quad \frac{\widetilde{\Phi}(\boldsymbol{k}\lambda_1, -\boldsymbol{k}\lambda_1, \boldsymbol{k}_1\lambda'_1, -\boldsymbol{k}_1\lambda'_1, \cdots, -\boldsymbol{k}_{n-1}\lambda'_{n-1})}{\Omega_{\boldsymbol{k}_1\lambda'_1} \cdots \Omega_{\boldsymbol{k}_{n-1}\lambda'_{n-1}}} \\ &\quad \times \left(n_B(\hbar\Omega_{\boldsymbol{k}_1\lambda'_1}) + \frac{1}{2}\right) \cdots \left(n_B(\hbar\Omega_{\boldsymbol{k}_{n-1}\lambda'_{n-1}}) + \frac{1}{2}\right) \end{aligned}$$

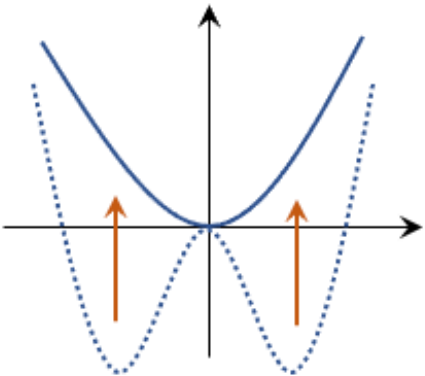
D. J. Hooton. Philosophical Magazine 3.25 (1958), T. Tadano, S. Tsuneyuki JPSJ 87 041015 (2018)

Self-consistent Phonon Theory

$G^{-1} = G_0^{-1} - \Sigma[G]$

Anharmonicity+Thermal fluctuation
=positive effective frequency



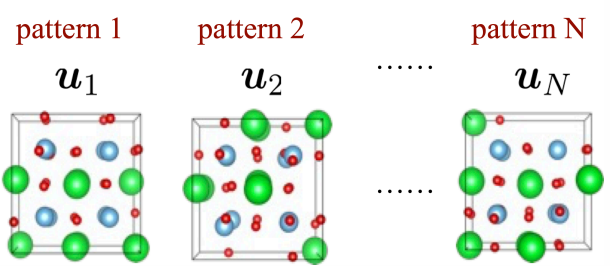


ALAMODE

- Open-source software of anharmonic phonon calculation
  https://github.com/ttadano/alamode
- Perform phonon calculations based on IFCs extracted from DFT calculations
- Truncate the Taylor expansion at 4th order in SCP calculation
- Efficient SCP calculation by using reciprocal-space formulation

T. Tadano (NIMS)

1. Generate displacement patterns



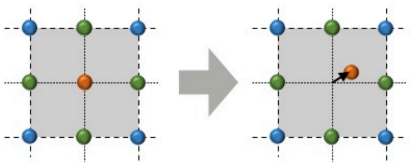
2. Calculate atomic forces in each configuration
   - Use external DFT packages (VASP, Quantum Espresso, ⋯)
3. Extract IFCs from the displacement-force data
   - Compressive sensing method [1,2]
     →efficiently calculate IFCs from a small number of displacement-force data

[1] F. Zhou, *et al.* PRL 113, 185501 (2014) [2] T. Tadano, S. Tsuneyuki PRB 92, 054301 (2015)

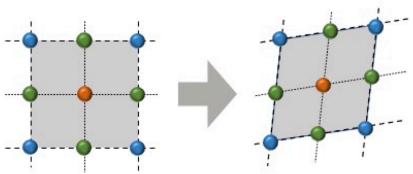
Change of Crystal Structure

Structural optimization based on SCP theory
Minimizes the SCP free energy with respect to the atomic positions and the strain.

atomic shift



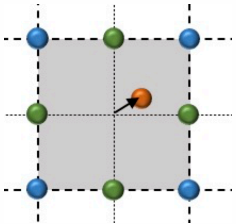
strain



1. SCP calculation in updated structure → calculate IFCs in the updated structure
2. Optimization of the SCP free energy → Gradient of the SCP free energy

IFC renormalization

- IFCs in the updated structure is necessary
- Calculation of IFCs from force-displacement data is numerically expensive



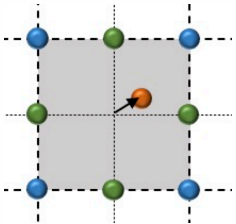
$$
\begin{aligned}
q^{(0)}_{\alpha\mu} &= \sqrt{M_\alpha} u^{(0)}_{\alpha\mu} \\
q^{(0)}_{\lambda} &= \sum_{\alpha\mu} \epsilon_{0\lambda,\alpha\mu} q^{(0)}_{\alpha\mu}
\end{aligned}
$$

Update IFCs from the IFCs in the original structure

$$
\begin{aligned}
&\hat{U} = \sum_{n=0}^{\infty} \hat{U}_n^{(q^{(0)}=0)} \\
&\hat{U}_n^{(q^{(0)}=0)} \\
&= \frac{1}{n!} \frac{1}{N^{n/2-1}} \sum_{\{\boldsymbol{k}\lambda\}} \delta_{\boldsymbol{k}_1+\cdots+\boldsymbol{k}_n} \widetilde{\Phi}^{(q^{(0)}=0)}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n) \\
&\times (\hat{q}_{\boldsymbol{k}_1\lambda_1} + \delta_{\boldsymbol{k}_1}\sqrt{N} q^{(0)}_{\lambda_1}) \cdots (\hat{q}_{\boldsymbol{k}_n\lambda_n} + \delta_{\boldsymbol{k}_n}\sqrt{N} q^{(0)}_{\lambda_n})
\end{aligned}
$$

IFC renormalization

- IFCs in the updated structure is necessary
- Calculation of IFCs from force-displacement data is numerically expensive



$$q^{(0)}_{\alpha\mu} = \sqrt{M_\alpha}\, u^{(0)}_{\alpha\mu}$$
$$q^{(0)}_{\lambda} = \sum_{\alpha\mu} \epsilon_{0\lambda,\alpha\mu} q^{(0)}_{\alpha\mu}$$

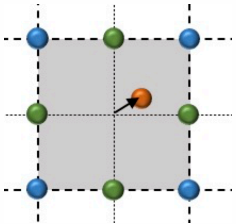
Update IFCs from the IFCs in the original structure

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

$$\hat{U}_n^{(q^{(0)})} = \frac{1}{n!} \frac{1}{N^{n/2-1}} \sum_{\{\boldsymbol{k}\lambda\}} \delta_{\boldsymbol{k}_1+\cdots+\boldsymbol{k}_n} \widetilde{\Phi}^{(q^{(0)})}(\boldsymbol{k}_1\lambda_1, \cdots, \boldsymbol{k}_n\lambda_n) \times \hat{q}_{\boldsymbol{k}_1\lambda_1} \cdots \hat{q}_{\boldsymbol{k}_n\lambda_n}$$

IFC renormalization

- IFCs in the updated structure is necessary
- Calculation of IFCs from force-displacement data is numerically expensive



Update IFCs from the IFCs in the original structure

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

$$q^{(0)}_{\alpha\mu} = \sqrt{M_\alpha}\,u^{(0)}_{\alpha\mu}$$
$$q^{(0)}_{\lambda} = \sum_{\alpha\mu}\epsilon_{0\lambda,\alpha\mu}q^{(0)}_{\alpha\mu}$$

IFC in the updated structure $\leftarrow$ IFC in the original structure

Similar formula can be derived for the structure change by strain

Gradient of the SCP free energy

- Gradient of the SCP free energy with respect to the atomic positions

$$
\begin{aligned}
&\frac{1}{N}\frac{\partial \mathcal{F}\big(\widetilde{\Phi}^{(q^{(0)},u_{\mu\nu})},\Omega_{\boldsymbol{k}\lambda_1\lambda_2}(q^{(0)},u_{\mu\nu})\big)}{\partial q_\lambda^{(0)}} \\
= &\sum_{n=0}^{\infty}\frac{1}{n!N^n}\sum_{\{\boldsymbol{k}\lambda\}}\left(\frac{\hbar}{2}\right)^n\frac{\widetilde{\Phi}(\boldsymbol{k}_1\lambda_1',-\boldsymbol{k}_1\lambda_1',\cdots,\boldsymbol{k}_n\lambda_n',-\boldsymbol{k}_n\lambda_n',0\lambda)}{\Omega_{\boldsymbol{k}_1\lambda_1'}\cdots\Omega_{\boldsymbol{k}_n\lambda_n'}} \\
&\times\left(n_B(\hbar\Omega_{\boldsymbol{k}_1\lambda_1'})+\frac{1}{2}\right)\cdots\left(n_B(\hbar\Omega_{\boldsymbol{k}_n\lambda_n'})+\frac{1}{2}\right)
\end{aligned}
$$

Updating the structure

- The shift from the optimal atomic positions $\delta q_\lambda^{(0)}$ can be estimated by

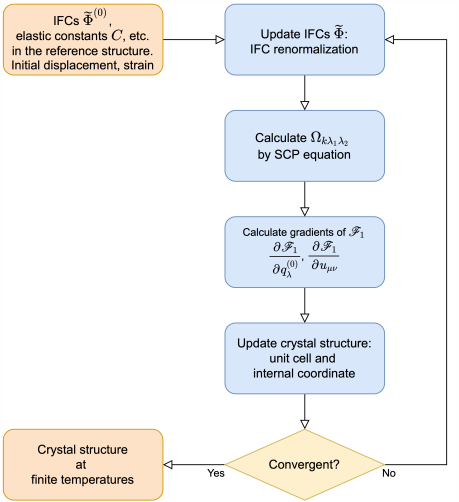
$$\frac{1}{N}\frac{\partial \mathcal{F}}{\partial q_\lambda^{(0)}} = \sum_{\lambda_1} \Omega_{0\lambda\lambda_1} \delta q_{\lambda_1}^{(0)},$$

  with the SCP dynamical matrix $\Omega_{0\lambda_1\lambda_2}$.
- The internal coordinate is updated as

$$q_\lambda^{(0)} \leftarrow q_\lambda^{(0)} - \beta_{\mathrm{mix,ion}} \delta q_\lambda^{(0)}.$$

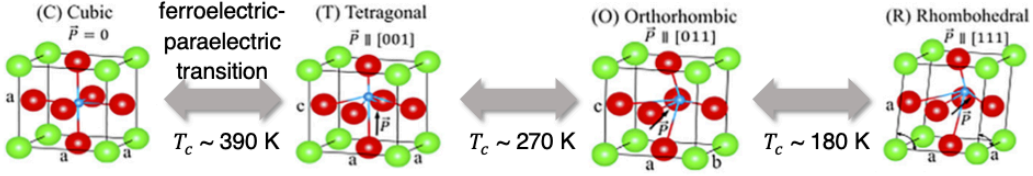
  $\beta_{\mathrm{mix,ion}}$ is introduced to make the calculation scheme more robust and is usually chosen to be $0 < \beta_{\mathrm{mix,ion}} < 1$.
- We can formulate a similar procedure for strain.

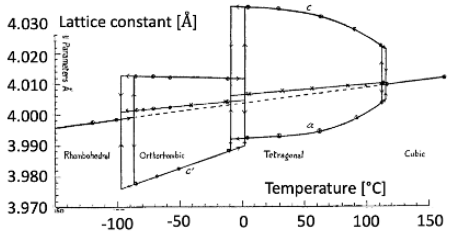
Calculation Scheme

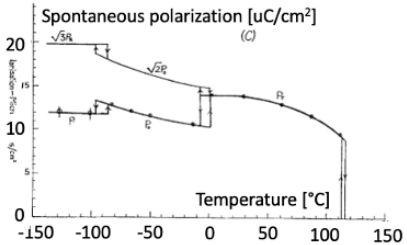


- No additional DFT calculation in the structural optimization loop
  $\rightarrow$ efficient!
- Both the atomic positions and the shape of the unit cell are optimized.
- We have implemented the calculation scheme to the ALAMODE package

3-step structural phase transition in $BaTiO_3$





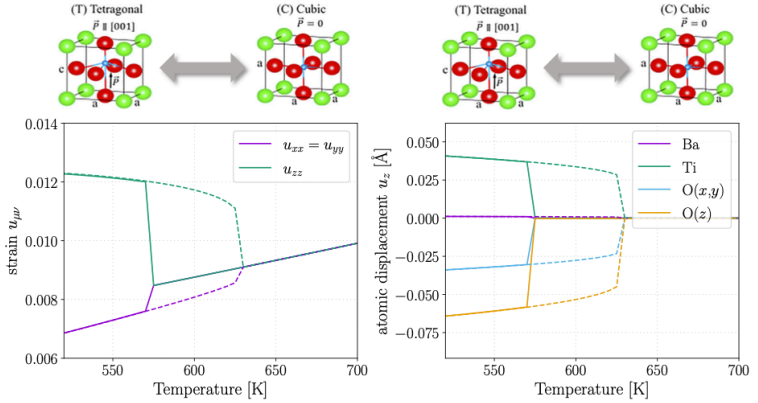


H. F. Kay, P. Vausden (1949)

Calculation Details

- $2\times2\times2$ supercell containing 40 atoms.
- Used VASP implementation of the PBEsol exchange-correlation functional and PAW pseudopotentials.
- Basis cutoff is 600 eV. $4\times4\times4$ Monkhorst-Pack kmesh.
- Extracted IFCs from displace-force data of 300 configurations, which we take from AIMD snapshots with little correlation and added random displacements.
  The AIMD calculation were run with basis cutoff 400 eV, $2\times2\times2$ Monkhorst-Pack kmesh, because it is just for sampling the potential energy surface and calculation with high accuracy is unnecessary.

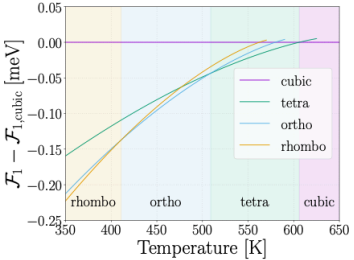
Cubic-tetragonal structural transition



solid line: cooling, dashed line: heating
Hysterisis $\rightarrow$ first-order phase transition

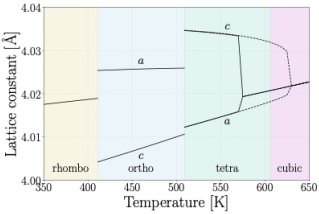
3-step structural transition

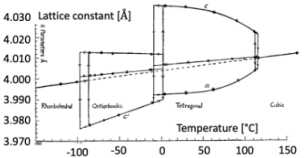
Free energy



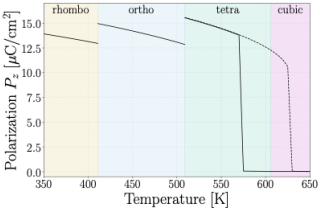
T_c [K]	calculation	experiment [1]
cubic-tetra	606	∼390
tetra-ortho	509	∼270
tetra-rhombo	411	∼180

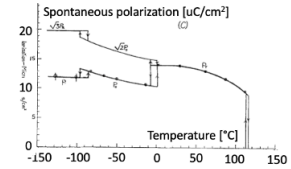
Lattice constant



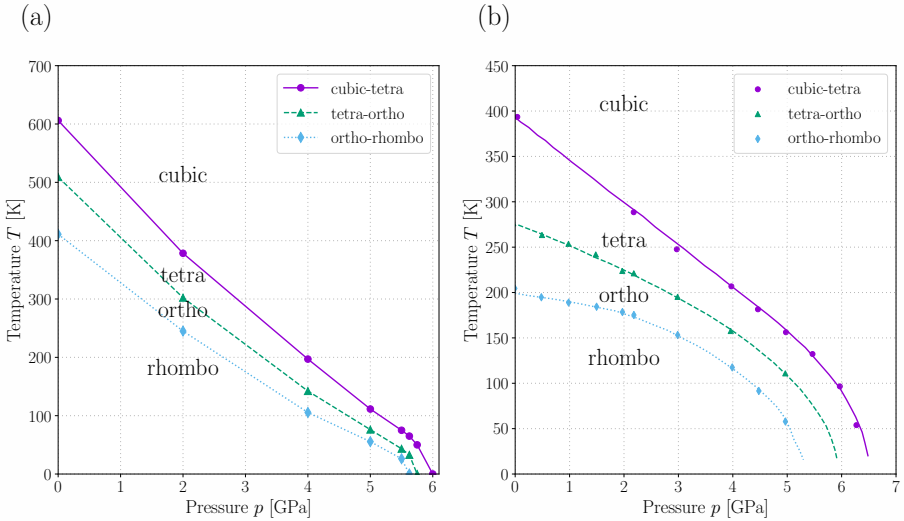


Spontaneous polarization





Pressure-Temperature phase diagram



(a) Calculation (b) Experiment

Discussion

The possible sources of the error of the transition temperatures are

- the error of the functional used in the DFT calculation (PBEsol): Lower T_c for smaller lattice constant
- the truncation of the Taylor expansion of the potential energy surface at the fourth order
- the approximation of the SCP theory

Summary

- We have developed an efficient calculation scheme of structural optimization at finite temperature based on SCP theory.
- We applied the method to $BaTiO_3$. The three-step structural phase transition of $BaTiO_3$ have been successfully reproduced.
- Our method can efficiently calculate the crystal structures of general materials at finite temperatures.