FULL PAPER

Ab initio prediction of structural phase-transition temperature of SrTiO₃ from finite-temperature phonon calculation

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The cubic-to-tetragonal phase transition temperature T_c of SrTiO₃ is predicted from first-principles anharmonic lattice dynamics simulation. By using the self-consistent phonon approach, we compute finite-temperature phonon dispersion of cubic and tetragonal SrTiO₃. By comparing the Helmholtz free energies of the two phases calculated with anharmonic effects included, we obtain $T_c \sim 80$ K, which is comparable with the experimental value of 105 K. In addition, we show that the nuclear quantum effect is significant for predicting T_c . Our approach is efficient and provides a convenient way of predicting the phase stability of solids including ceramics, where the conventional approach based on the harmonic approximation often breaks down.

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1. Introduction

Structural phase transition is observed in many materials including alloys and ceramics. In many of these materials, lattice vibration (phonons) plays a central role in making a phase transformation at a finite temperature. Perovskite oxides (ABO₃) are among the most studied families that show a structural transition from the high-temperature cubic phase to a lower-symmetry phase with cooling. Previous experimental studies have shown that the types of (*A*, *B*) cations influence not only the order but also the critical temperature (T_c) of the phase transition. For example, the ferroelectric (FE) phase transition occurs in PbTiO₃ at ~ 760 K,¹⁾ while T_c is much lower in BaTiO₃ (403 K). Since the dielectric constant becomes large just above the FE transition temperature, optimizing T_c is important for developing FE devices that are efficient near room temperature. Hence, there is great need for a convenient and accurate method to predict T_c only from crystal structure.

First-principles calculation based on density functional theory (DFT) has been widely used to predict the phase stability of materials at absolute zero. Also, phase stability at finite temperature can be assessed by performing phonon calculation within the harmonic approximation

(HA). While the HA gives reasonable phonon dispersion in many materials, it completely breaks down in high-temperature phases of perovskite oxides and other materials because of the presence of unstable (imaginary) phonon modes. To overcome the limitation of the HA, we have recently developed a first-principles method that incorporates anharmonic effects based on self-consistent phonon (SCP) theory.³⁾ The method successfully reproduces⁴⁾ a finite temperature phonon dispersion of cubic SrTiO₃ (STO) that agrees well with experimental inelastic neutron-scattering data.⁵⁾ More recently, the method has been extended to compute the anharmonic free energy of materials and used to explain the negative thermal expansion of ScF₃.⁶⁾

In this study, we predict the cubic-to-tetragonal phase transition temperature of STO from first-principles lattice dynamics simulations. By applying the SCP scheme to the cubic (Pm $\bar{3}$ m) and tetragonal (I4/mcm) phases (**Fig. 1**), we obtain the finite-temperature phonon dispersion curves and Helmholtz free energy for each phase without empirical parameters. Our approach gives a reasonable T_c value for STO, thus showing its potential to explain and predict the behavior of T_c for ceramics and other materials.

2. Helmholtz free-energy from first-principles phonon calculation

2.1 Harmonic theory

The Helmholtz free energy plays a central role in determining the thermodynamic stability of materials at finite temperature, and is given for non-metallic systems as

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$$F(V, T) = E_{\text{el}}(V) + F_{\text{vib}}(V, T). \quad (1)$$

Here, $E_{\text{el}}(V)$ is the electronic energy that can be obtained from a static DFT calculation, and $F_{\text{vib}}(V, T)$ is the vibrational contribution to the free energy. The vibrational free energy can be calculated from the result of phonon calculations within the quasi-harmonic approximation (QH) approximation, by which $F_{\text{vib}}(V, T)$ is given as

$$F_{\text{vib}}^{(\text{QH})}(V, T) = \frac{1}{N_q} \sum_{q\nu} \left[\frac{\hbar\omega_{q\nu}(V)}{2} + \frac{1}{\beta} \ln(1 - e^{-\beta\hbar\omega_{q\nu}(V)}) \right]. \quad (2)$$

Here, $\omega_{q\nu}$ is the frequency of phonons with quasi-momentum $\mathbf{q}$ and the band index ν obtained from the HA, and $\beta = (kT)^{-1}$. While the QH approach has been successfully used to predict the phase boundary and thermal expansion coefficients of materials,⁷⁾ it completely breaks

down in many ceramics including STO because soft modes are unstable ($\omega_{q\nu}^2 < 0$) within the HA, as shown in **Fig. 2** (dotted lines). Therefore, anharmonic effects must be considered beyond the QH level for computing the Helmholtz free energy of cubic and tetragonal STO.

2.2 Self-consistent phonon theory

The SCP theory is a powerful approach to treat anharmonic effects beyond the QH level. In the first-order SCP theory, anharmonic effects are considered at the mean-field level. Therefore, we can include a Debye–Waller type renormalization from the even-order terms of the anharmonic potential, such as the fourth- and sixth-order terms. Since the sixth- and higher-order terms are usually negligible compared with the dominant fourth-order term, we may consider the fourth-order term only, with which the SCP equation becomes⁸⁾

$$\Omega_{q\nu}^2 = \omega_{q\nu}^2 + \frac{1}{2} \sum_{q_1\nu'} \Phi(\mathbf{q}\nu; -\mathbf{q}\nu; \mathbf{q}_1\nu'; -\mathbf{q}_1\nu') \alpha_{q_1\nu'}. \quad (3)$$

Here, $\Omega_{q\nu}$ is the anharmonic phonon frequency, $\Phi(\mathbf{q}\nu; -\mathbf{q}\nu; \mathbf{q}_1\nu'; -\mathbf{q}_1\nu')$ is the reciprocal representation of the fourth-order force constants, and $\alpha_{q\nu} = \hbar[1 + 2n(\Omega_{q\nu})]/(2\Omega_{q\nu})$ is the temperature-dependent term proportional to the mean square displacement of the normal coordinate of the phonon mode $\mathbf{q}\nu$, with $n(\omega) = [\exp(\beta\hbar\omega) - 1]^{-1}$ being the Bose–Einstein distribution function. Once we obtain the SCP solution $\Omega_{q\nu}$, we can calculate the vibrational free energy as⁶⁾

$$\begin{aligned} F_{\text{vib}}^{(\text{SCP})}(V, T) &= \frac{1}{N_q} \sum_{q\nu} \left[\frac{\hbar\Omega_{q\nu}(V, T)}{2} + \frac{1}{\beta} \ln(1 - e^{-\beta\hbar\Omega_{q\nu}(V, T)}) \right] \\ &\quad - \frac{1}{4N_q} \sum_{q\nu} [\Omega_{q\nu}^2(V, T) - \omega_{q\nu}^2(V)] \alpha_{q\nu} \\ &= \tilde{F}_{\text{vib}}^{(\text{QH})}(V, T) + \Delta F_{\text{vib}}^{\text{corr}}(V, T). \end{aligned} \quad (4)$$

Fig. 1. Crystal structures of cubic and tetragonal SrTiO₃ (top, created with VESTA²⁾) and schematic of the double-well potential along the normal coordinate of the R₂₅ soft mode relevant to the cubic-to-tetragonal phase transition observed at 105 K (bottom). The red circle represents the location of each structure in the double-well potential.

Fig. 2. Calculated phonon dispersion of (a) tetragonal and (b) cubic phase of SrTiO₃ along high-symmetry lines of the Brillouin zone. The dotted lines show the results based on the HA, and the solid lines represent the finite-temperature phonons obtained with the SCP scheme from 50 to 300 K in steps of 50 K. Imaginary frequency is shown as negative.

The first term is the same as the QH contribution [Eq. (2)], where the SCP frequency is used instead of the harmonic frequency, and the second term is the correction term necessary to satisfy the thermodynamic relationship $-dF/dT =$

$$S_{\text{vib}} = k \sum_{q\nu} [(n_{q\nu} + 1) \ln(n_{q\nu} + 1) - n_{q\nu} \ln n_{q\nu}].$$

In Eqs. (3) and (4), we omitted the change of phonon polarization vectors by anharmonic effects for brevity. However, we showed in our previous work⁴⁾ that polarization mixing is significant for the FE soft mode of cubic STO. Therefore, we consider polarization mixing in this work.

3. Computational details

To compute the Helmholtz free energies within SCP theory, harmonic and quartic interatomic force constants (IFCs) are necessary, which are, respectively, the second- and fourth-order derivatives of the potential energy surface with respect to atomic displacements. To calculate the IFCs, we used the supercell approach and estimated IFCs via linear-regression optimization using DFT forces calculated for various atomic configurations as training data. We calculated harmonic and anharmonic IFCs in steps. First, the harmonic terms were fitted to displacement-force datasets generated by displacing an atom in a supercell from its equilibrium position by 0.01 Å. Then, we used compressive sensing lattice dynamics⁹⁾ to extract the anharmonic terms from the displacement-force training datasets obtained for randomly displaced structures. Efficiently generating the training structures is not trivial. In this study, we followed the published procedure^{4),8),9)} and generated the training structures by combining ab initio molecular dynamics (AIMD) and random displacements. For the tetragonal phase, we performed AIMD simulation at 10 K for 2000 steps and sampled 100 structures from the MD trajectory. For each sampled structure, we further displaced all atoms in the supercell by 0.1 Å in random directions. We found that the temperature of the AIMD for the tetragonal phase should be sufficiently low compared with the energy difference between the cubic and tetragonal phases. Otherwise, the starting tetragonal structure readily changes into another tetragonal structure on the other side of the double-well potential (Fig. 1), which seriously reduces the accuracy of the estimated force constants. For the cubic phase, we used the 40 displacement-force datasets obtained in our previous study.⁴⁾

DFT calculations in this study were performed using the projector augmented wave (PAW) method,^{10),11)} as implemented in the VASP.¹²⁾ We used the Perdew–Burke–Erzerhof exchange-correlation functional for solids (PBEsol)¹³⁾ since it reportedly¹⁴⁾ gives better predictions of lattice parameters for ionic solids than the local-density approximation (LDA) or Perdew–Burke–Erzerhof (PBE) functional. A kinetic energy cutoff of 550 eV was adopted, and a $12 \times 12 \times 12$ ($8 \times 8 \times 8$) Monkhorst–Pack $\mathbf{k}$ mesh was used for the Brillouin zone sampling of the primitive cell of the cubic (tetragonal) phase. We used a $2 \times 2 \times 2$

supercell containing 40 (80) atoms for calculating harmonic IFCs of the cubic (tetragonal) phase. For anharmonic IFCs, a supercell containing 40 atoms was used for both phases. The SCP equation [Eq. (3)] was solved with a $2 \times 2 \times 2$ gamma-centered $\mathbf{q}$ mesh and a $4 \times 4 \times 4$ $\mathbf{q}_1$ mesh. The Brillouin zone sampling of $F_{\text{vib}}^{(\text{SCP})}(V, T)$ was conducted with a $20 \times 20 \times 20$ ($10 \times 10 \times 10$) $\mathbf{q}$ mesh for the cubic (tetragonal) phase. We confirmed that these $\mathbf{q}$ mesh densities were sufficient, and the deviation from the values obtained with the dense $50 \times 50 \times 50$ $\mathbf{q}$ mesh was less than 0.02 meV/f.u. at 300 K. When calculating the free energies, we treated the non-analytic correction to the dynamical matrix using the Ewald method¹⁵⁾ with Born effective charges calculated from density functional perturbation theory.⁷⁾ All phonon calculations in this work were performed by the software ALAMODE.¹⁶⁾

4. Results and discussion

4.1 Ground state structural property

We first optimized the structural parameters of the primitive cell by minimizing the energy $E_{\text{el}}(V)$. As reported in our previous study, the optimized lattice constant of the cubic phase is 3.896 Å, which agrees well with the experimental value of 3.905 Å (Ref. 17, 293 K). For the tetragonal phase, we obtained $a = 3.886$ Å and $c/a = 1.006$. These results are in reasonable agreement with the experimental data of $a = 3.898$ Å and $c/a = 1.00056$ (Ref. 18, 65 K), while the c/a value is slightly overestimated. We also calculated the energy gain for the tetragonal phase defined as $\Delta E = E_{\text{el}}^{\text{cubic}} - E_{\text{el}}^{\text{tetra}}$ (Fig. 1) and obtained $\Delta E = 5.68$ meV/f.u., in accord with the previous PBEsol result of 5.5 meV/f.u.¹⁹⁾

In this work, we used the cell parameters optimized at 0 K in all the studied temperature range and neglected the thermal expansion mainly owing to the computational limitations. This approximation can affect the accuracy of predicting the phase stability. Nonetheless, we expect that the error associated with the thermal expansion is small in STO since the experimental lattice constants of the cubic and tetragonal phases are very close to each other.

4.2 Phonon dispersion

Figure 2 shows the calculated phonon dispersion curves of cubic and tetragonal STO. The low-energy phonons are unstable within the HA at gamma in both phases, which corresponds to the FE soft mode and R point of the cubic phase, which is the antiferrodistortive (AFD) soft mode relevant to the cubic-to-tetragonal phase transition. After considering the quartic anharmonicity via the SCP scheme, all of these soft modes are stabilized. At room temperature, the frequency of the FE mode becomes 136 (145) cm⁻¹ and that of the AFD mode becomes 42 (65) cm⁻¹ for the cubic (tetragonal) phase. The values for the cubic phase agree well with our previous results of 138 cm⁻¹ (FE) and 46 cm⁻¹ (AFD).⁴⁾ In our previous study on cubic STO, we used the mixed-space approach²⁰⁾ to treat the non-analytic correction and observed unusual oscillation in the highest-energy longitudinal optical mode near the gamma point.

The phonon dispersion obtained in this work is free from such oscillation since we have used the Ewald method instead of the mixed-space approach.

Since the SCP theory postulates that the renormalized phonons are stable, a solution to the SCP equation [Eq. (3)] must be positive definite ($\Omega_{qv}^2 > 0$) irrespective of the temperature. Thus, we have obtained stable phonons for the cubic phase even at temperatures below the phase transition temperature (105 K) as shown in Fig. 2(b). To correctly describe condensation of a soft mode below a transition temperature, it is necessary to include the bubble and higher-order Feynman diagrams associated with the cubic anharmonicity,^{8),21)} whose effects are neglected in the reported SCP frequencies. Still, it is possible to discuss the relative stability of competing phases within the SCP theory via a comparison of the Helmholtz free energies defined by Eq. (4).

4.3 Vibrational free energy

The calculated difference of the vibrational free-energy, $\Delta F_{\text{vib}}(T) = F_{\text{vib}}^{\text{cubic}}(T) - F_{\text{vib}}^{\text{tetra}}(T)$, is shown in Fig. 3. The figure shows that $\Delta F_{\text{vib}}(T)$ is negative, meaning that the vibrational entropy contribution gradually increases the relative stability of the cubic phase over the tetragonal phase. When the energy gain by the vibrational entropy, $-\Delta F_{\text{vib}}(T)$, exceeds ΔE , the cubic phase becomes more stable. Therefore, the phase transition temperature can be estimated from the intersection of the calculated $-\Delta F_{\text{vib}}(T)$ curve and $\Delta E = 5.68 \text{ meV/f.u.}$

By the SCP method, we obtain $T_c \sim 80 \text{ K}$, as shown in Fig. 3. Given that the energy scale of ΔE is very small, our prediction is in reasonable agreement with the experimental value of 105 K. In Sect. 2, we noted that the correction term $\Delta F_{\text{vib}}^{\text{corr}}(T)$ in Eq. (4) is necessary. Indeed, if we omit this term and compute $\Delta F_{\text{vib}}(T)$ only from the QH term $\tilde{F}_{\text{vib}}^{(\text{QH})}(T)$, the free-energy gain $-\Delta F_{\text{vib}}(T)$ does not exceed ΔE , and the tetragonal phase continues to be more stable even in the high-temperature range (Fig. 3, cross points).

Fig. 3. Calculated free-energy difference, $-\Delta F_{\text{vib}}(T) = -F_{\text{vib}}^{\text{cubic}}(T) + F_{\text{vib}}^{\text{tetra}}(T)$, as a function of temperature. The horizontal dashed line represents the difference of the static energy $\Delta E = 5.68 \text{ meV/f.u.}$

To see the nuclear quantum effect on T_c , we have derived the classical limit of Eq. (3), denoted as $F_{\text{vib}}^{(\text{SCP,CL})}(T)$, and used it to compute the free-energy gain of the cubic phase. As shown in Fig. 3 (squares), the value of $-\Delta F_{\text{vib}}(T)$ decreases and that of T_c increases to $\sim 170 \text{ K}$ when the nuclear quantum effect is turned off, showing that the quantum effect increases the stability of the cubic phase. The same tendency was found in a previous Monte Carlo study based on the ab initio effective Hamiltonian,²²⁾ though the quantum effect is more prominent in this study.

Our theoretical prediction based on SCP theory is not complete in that it neglects effects of cubic anharmonicity, such as thermal expansion, the anharmonic shift of the atomic coordinates, and the intrinsic frequency shift associated with the three-phonon interaction. We expect that including these effects would improve the accuracy of predicting T_c and help in precisely describing the second-order phase transition, which is left for future study. Still, we think that the simpler approach presented is powerful and useful, since it enables us to obtain the Helmholtz free energy in the thermodynamic limit while correctly accounting for nuclear quantum effects, which is impossible in thermodynamic integration based on AIMD. We expect our approach to give a reasonable estimate of T_c for various bulk solids if all of the involved calculations are done carefully.

5. Conclusion

We have performed a fully non-empirical computation of the cubic-to-tetragonal structural phase transition temperature of SrTiO_3 . By using the self-consistent phonon scheme, we have obtained finite-temperature phonons of the cubic and tetragonal phases, which are stable in the whole Brillouin zone. By comparing the calculated Helmholtz free energies, we have obtained $T_c \sim 80 \text{ K}$, which agrees fairly with the experimental value of 105 K. We have also shown that the nuclear quantum effect substantially increases the relative stability of the cubic phase and improves the predicted T_c value from $\sim 170 \text{ K}$ in classical statistics to $\sim 80 \text{ K}$ in quantum statistics. This approach overcomes the limitation of the conventional harmonic approximation and thereby is applicable to a variety of materials for predicting T_c with reasonable computational cost and accuracy.

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