ab initio Study of Strain-Induced Ferroelectricity in SrTiO$_3$

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Valley lines on total-energy surfaces for the zone-center distortions of free-standing and in-plane strained SrTiO$_3$ are investigated with a newly developed first-principles structure optimization technique [Jpn. J. Appl. Phys. 43 (2004) 6785]. The results of numerical calculations confirmed that ferroelectricity is induced and the Curie temperature is increased by applying biaxial compressive or tensile strains. Along the distortion, strong nonlinear coupling between the soft- and hard-modes is demonstrated. [DOI: 10.1143/JJAP.44.7134]

KEYWORDS: density functional theory, local density approximation, biaxial strain, potential surface, Slater mode, Last mode

1. Introduction

Perovskite structure strontium titanate, SrTiO$_3$, is an extremely important material. Because of its wide range of physical properties, such as semiconductivity, superconductivity, incipient ferroelectricity and catalytic activity, SrTiO$_3$ is expected to be used for a variety of technological applications. Bulk SrTiO$_3$ crystalizes in the cubic centrosymmetric (O$_h^c$) structure, and is paraelectric at room temperature. The atomic fractional coordinates are Sr(0,0,0), Ti($\frac{1}{2},\frac{1}{2},\frac{1}{2}$), O$_I$(0,0,$\frac{1}{2}$), O$_{II}$(0,0,$\frac{1}{2}$), and O$_{III}$(0,0,0), as depicted in Fig. 1. SrTiO$_3$'s tolerance factor,$^3$ calculated with Shannons’s ionic radii,$^2$ is $t = 1.002$. This value of almost unity suggests that the cubic structure is moderately stable. Below 105 K, SrTiO$_3$ undergoes a structural phase transition from cubic to an antiferrodistortive (AFD) tetragonal (D$_{4h}^1$) structure, which is associated with zone-boundary phonon condensation at the R point.$^{3-7}$ This transition is driven by TiO$_6$ octahedral rotational mode instabilities; the rotation angle is less than 2°. At lower temperatures, the dielectric constant exhibits Curie-Weiss-like behavior, but does not exhibit divergence. The dielectric constant saturates to a value of $\sim 2 \times 10^4$ under 10 K.$^8,10$ but no transition, e.g., to a ferroelectric state, actually occurs with decreasing temperature. Because of its failure to exhibit a ferroelectric phase transition, SrTiO$_3$ is generally regarded as an incipient ferroelectric, in which quantum fluctuations suppress ferroelectricity. The observed temperature dependence of SrTiO$_3$'s dielectric constant is well described by Barrett’s formula,$^{11}$

$$\varepsilon = M \left( \frac{T_1}{\cosh \left( \frac{T_1}{2T} \right) - T_0} \right),$$  

where $T_0$ is the transition temperature, $T_1$ is a characteristic dividing point below which quantum effects are important, and $M$ is a constant. In ref. 12, these values for SrTiO$_3$ were given as $T_0 = 38$ K, $T_1 = 84$ K, and $M = 9 \times 10^4$ K, respectively. Thus, it had been long expected that SrTiO$_3$ would exhibit ferroelectricity under some stresses or strains.

In recent years, the preparation of oxide thin films by thermal nonequilibrium techniques such as molecular beam epitaxy (MBE) and pulsed laser deposition (PLD), have enabled the growth of heteroepitaxial thin films, and have attracted a great deal of attention. In 2004, Haeni et al. demonstrated that thin films of SrTiO$_3$ are ferroelectric near room temperature.$^{13}$ Using MBE, they grew SrTiO$_3$ thin films on a DyScO$_3$ substrate, to induce a biaxial tensile strain of the order of 1%, and measured the temperature dependence of the in-plane dielectric constant. Their results indicate that the nonpolar ground state of SrTiO$_3$ can be markedly transformed, to a polar state, by applying small strains.

Ab initio calculations are attractive for atomistically analyzing the effects of structural distortions on properties such as Curie temperature. Schimizu studied the frequencies of 1' transverse-optical phonons in the cubic SrTiO$_3$ using the frozen-phonon scheme, and found that the dielectric constant strongly depends on strain.$^{14}$ Antons et al. have confirmed that the dielectric constant of SrTiO$_3$ epitaxial thin films varies significantly with strain using density functional theory (DFT) within the local-density approximation (LDA).$^{15}$ However, the mechanism by which in-plane biaxial strain induces ferroelectricity in SrTiO$_3$ has not been clarified. We investigate the relationship between SrTiO$_3$ ferroelectricity and in-plane biaxial strains, compressive and tensile, by analyzing valley lines of total-energy surfaces with the ab initio structure optimization technique that we had developed.$^{16}$ Compared with the conventional soft-mode-only structure optimization technique, our approach has the advantages that it can (1) accurately estimate total energy as a function of the amplitude of atomic
displacements, and (2) correctly investigate nonlinear coupling between soft-mode atomic displacements, hard-mode displacements, and lattice deformations.

In the next section, we briefly explain our structure optimization technique and the numerical methods used in this study. Results of calculations are shown in §3. In §4, we summarize the paper.

2. Method

2.1 Structure optimization technique

To investigate the total-energy surfaces of perovskite oxides, we improve King-Smith and Vanderbilt’s scheme and redefine the amplitude of atomic displacements $u_a$ as

$$u_a = \sqrt{(v_{a1}^2 + (v_{a2}^2) + (v_{a3}^2) + (v_{a4}^2) + (v_{a5}^2) + (v_{a6}^2)},$$

where $v_{a\tau}$ is the displacement of each atom $\tau$ (A, B, O) in the Cartesian directions of $\alpha$ ($x$, $y$, $z$) from the symmetric perovskite structure ($O_{1}^{h}$ or $D_{4h}^{1}$). The total energy is evaluated as a function of $u = \sqrt{u_1^2 + u_2^2 + u_3^2}$ under the condition that $v_{a\tau}$ and the strain components $\eta_i$ ($i = 1, \ldots, 6$; Voigt notation) minimize the total energy for each $u$ using an ab initio norm-conserving pseudopotential method and geometric optimization. To simulate $D_{4h}^{1}$ epitaxial SrTiO$_3$ thin films, as illustrated in Fig. 2(a), under an induced biaxial in-plane strain on the substrate, only the $c$-axis (i.e., $\eta_2$) is permitted to relax but other parameters $a = b, \alpha = \beta = \gamma = 90^\circ$ (i.e., $\eta_1$, $\eta_2$, $\eta_4$, $\eta_5$, and $\eta_6$) are fixed for all directions of polarization, [001] [Fig. 2(b)], [110] [Fig. 2(c)], and [100] [Fig. 2(d)], to satisfy symmetry constraints. Total energy minimization under the constant-$u_a$ constraint (i.e., on the sphere surface with a radius $u_a$) is performed iteratively. A fully detailed formalism of this structure optimization technique is given in ref. 16. We continue iterative optimization of the atomic and lattice structure until differences in total energies remain less than $10^{-7}$ Hartree for two successive iterations.

2.2 Calculation methods

For all ab initio calculations, we use the ABINIT package, adapting it for our structure optimization technique in its source code of Src9drive/brdmin.f. Bloch wave functions of electrons are expanded into plane waves with an energy cutoff of 40 Hartree, using Teter’s extended norm-conserving pseudopotentials. To maintain a constant energy cutoff and to avoid nonphysical discontinuities in total energy as a function of volume, a correction to the kinetic energies of plane waves just below the energy cutoff is introduced as implemented in the ABINIT. This “energy cutoff smearing” technique is efficient not only for constant-pressure molecular dynamics but also for comparing total energies in different volumes. With this technique, one does not have to achieve convergence between constant-number-of-plane-waves calculations and constant-energy-cutoff calculations with respect to the basis set and, therefore, does not have to adopt a superfluously large energy cutoff. The pseudopotentials include O 2s and 2p, Ti 3s, 3p, 3d and 4s, Sr 4s, 4p and 5s, as valence electrons. Bloch wave functions are sampled on an 8 x 8 x 8 grid of k-points in the first Brillouin zone. The exchange-correlation energy is treated within the local density approximation (LDA). As the parametrized correlation energy, we use Teter’s rational polynomial parameterization, which reproduces the results obtained by Ceperley and Alder. The electronic states are calculated by the iterative scheme to reach a tolerance of convergence that requires differences in forces to be less than $5 \times 10^{-7}$ Hartree/Bohr for two successive iterations.

With these calculation methods, the calculated equilibrium lattice constant for cubic SrTiO$_3$ is 7.27 Bohr, which is ~1.3% less than the experimental value of 7.36 Bohr obtained by linearly extrapolating the lattice constant at high temperatures to its value at zero temperature (see Fig. 1 in ref. 23). This underestimation is commonly considered to be a result of errors from LDA. Properties of ferroelectrics, particularly total-energy surfaces, are very sensitive to the lattice constant. Semiempirical constraints on lattice constants in calculations of perovskite oxides have commonly been used to acquire agreements between the experimentally observed values and calculated results. Although artificial constraints can be introduced in our structure optimization technique, we do not employ such semiempirical constraints. Nevertheless, we believe that calculations using LDA clarify some trends of displacive transitions in strained SrTiO$_3$.

The Berry-phase method is used to evaluate spontaneous polarizations.

For simplicity and to emphasize the origin of ferroelectricity in strained SrTiO$_3$, we neglect the AFD instabilities and use a single unit cell to calculate total-energy surfaces. We believe that this is a reasonable approximation because the effect of AFD on dielectric response is negligibly small.
3. Results and Discussion

3.1 Free-standing SrTiO$_3$

Before examining in-plane strained SrTiO$_3$, we evaluated the total-energy surface of free-standing SrTiO$_3$ that is distorted from cubic to tetragonal and has [001] polarization. Shown in Fig. 3(a) is the total energy as a function of the amplitude of atomic displacements $u_z$. Itoh et al. found that ferroelectricity was induced in SrTiO$_3$ by the isotope exchange of $^{16}$O for $^{18}$O.$^{10}$ This isotope exchange experiment and the incipient ferroelectricity with $T_0 = 38$ K > 0 in Barrett’s formula suggest that the total energy vs $u_z$ curve might have a double-well structure, but our calculated result does not. This is not just an artifact of the sensitivity of LDA total-energy surfaces to lattice constants, as described in refs. 24 and 28; instead, as we show in the next subsection, §3.2, the system is very close to having a double well.

Calculated lattice constants $a$ and $c$ are well fitted by quadratic functions in Fig. 3(b). It is surprising that the amplitude of Sr-displacement, $v^S$, is smaller than that of Ti, $v^T$, for the soft-mode eigenvector calculated by the frozen phonon method at $u_z = 0$, but $v^S$ becomes larger than $v^T$ for $u_z > 0.07$ as shown in Figs. 3(c) and 3(d).

3.2 Effects of in-plane strains on SrTiO$_3$

Total energies of SrTiO$_3$ as functions of the amplitude of atomic displacements $u$ are calculated for the tetragonal [001] distortion under in-plane biaxial compressive strains [Fig. 4(a)] and the monoclinic [110] [Fig. 4(b)] and [100] [Fig. 4(c)] distortions under in-plane biaxial tensile strains. It is confirmed that, for the biaxial-tensile-strained SrTiO$_3$, the [110] direction of ferroelectric polar distortion is energetically more preferable than that of [100] as compared with the case in Fig. 5. Energy gain, the difference between total energy at $u = 0$ and its minimum value, increases with both compressive and tensile biaxial strains, although it is zero in the zero-strain $a = a_0$ case. The value of $u$, at which the system exhibits minimum total energy and equilibrium structure, also increases with the biaxial strains. In Fig. 6, we show calculated spontaneous polarizations for the equilibrium structures under biaxial strains $a = 0.95a_0$–1.05$a_0$. Under the compressive strain, spontaneous polarization appears above 1% and increases linearly as a function of strain. Under the tensile strain, spontaneous polarization appears a little below 1% and increases more gradually with strain. These calculated results indicate that the transition temperature and the spontaneous polarization for ferroelectric ordering are predicted to be monotonically increasing functions of biaxial in-plane strains. In our calculated results, the energy gain becomes barely of the

![Fig. 3. Calculated results for free-standing SrTiO$_3$ with respect to atomic displacements in tetragonal [001] direction. (a) Calculated total energy (in meV) as a function of $u_z$ (in Bohr) (+’s connected with solid lines). Zero of the energy scale is placed at the total energy of the cubic structure when $u_z = 0$. (b) Lattice constants $a$ and $c$ in Bohr as functions of $u_z$ fitted by quadratic functions drawn with a dotted line and a dashed line, respectively. (c) Atomic displacements $v^{Sr}$, $v^T$, $v^O$ as functions of $u_z$. (d) Normalized atomic displacements $v^T/u_z$ as functions of $u_z$. The $\Gamma_{15}$ soft-mode eigenvector calculated by the frozen phonon method is additionally shown at $u_z = 0$.](image)

![Fig. 4. Calculated total energies (in meV) of SrTiO$_3$ as functions of $u = \sqrt{u_x^2 + u_y^2 + u_z^2}$ (in Bohr) for the tetragonal [001] distortion under in-plane biaxial compressive strains (a) and for the monoclinic [110] (b) and [100] (c) distortions under in-plane biaxial tensile strains. Zero of the energy scale is placed at the total energy of the paraelectric structure (i.e., $u = 0$) for each strain.](image)
order of room temperature \( (300 \text{ K} \approx 26 \text{ meV}) \) at 4% of compressive or tensile strains. The 4% of compressive or tensile strains is unrealistic even by the thermal nonequilibrium thin-film growth techniques, and is larger than the 1% of tensile strain under which ferroelectricity was experimentally found,\(^{13}\) although it is difficult to compare experiments and LDA-based calculations. On the other hand, Haeni et al. could not observe the ferroelectricity in the 0.9%-compressive-strained SrTiO\(_3\) thin film on a (La,Sr)(Al,Ta)O\(_3\) substrate.\(^{13}\) It is also difficult to conclude that a compressive strain of 0.9% is less than the critical strain required to induce ferroelectricity or that 0.9% is sufficient to induce the ferroelectricity, but that a surface effect (or any other effects) suppresses it.

To clarify the structural effects of in-plane biaxial strain, we analyze the detailed behavior of atomic displacements for 4% biaxial compressive and tensile strains:

Predicted results for the compressive strain, as functions of \( u_z \), are plotted in Fig. 7: (a) total energy; (b) lattice constants; (c) and (d) atomic displacements. Ferroelectric tetragonal equilibrium, with a 40.2 meV stabilization energy gain, is predicted at \( u_z = 0.456\text{Bohr}. \) The lattice constant \( c(u_z) \) is well fitted with a quadratic function. Normalized atomic displacements \( v^\alpha_z / u_z \) change greatly in the investigated range of \( u_z \), in contrast with BaTiO\(_3\) in which they remain almost constant with respect to the \( \Gamma_{15} \) soft-mode eigenvector in ferroelectric distortion.\(^{16}\) In the atomic displacements of the positive charge, we can find that the displacement of Ti is dominant from the paraelectric \( u_z = 0 \) state to \( u_z = 0.456 \) at which the total energy becomes minimum, whereas the displacement of Sr becomes activated instead of Ti in the region of \( u > 0.456 \), as shown in Fig. 7(c). There may be a relatedness between this Sr-Ti displacement-crossing point and the ferroelectric equilibrium structure with the minimum total energy; thus, we
Table I. Conventional atomic displacive modes: Slater mode, Last mode, and octahedron-deformation mode. The translational mode and the $\Gamma_{15}$ mode are also listed.

|       | Slater mode | Last mode | Octa. deform. mode | Trans. mode | $\Gamma_{15}$ mode |
|-------|-------------|-----------|--------------------|-------------|-------------------|
| $A$   | 0           | $4\sqrt{2}/20$ | 0                  | $1\sqrt{3}/3$ | 0                 |
| $B$   | $3\sqrt{2}/12$ | $-1\sqrt{2}/20$ | 0                  | $1\sqrt{5}/5$ | 0                 |
| $O_I$ | $-1\sqrt{2}/12$ | $-1\sqrt{2}/20$ | $1/\sqrt{3}$      | $1/\sqrt{5}$ | $1/\sqrt{2}$      |
| $O_{II}$ | $-1\sqrt{2}/12$ | $-1\sqrt{2}/20$ | $1/\sqrt{3}$      | $1/\sqrt{5}$ | $-1/\sqrt{2}$      |
| $O_{III}$ | $-1\sqrt{2}/12$ | $-1\sqrt{2}/20$ | $-2/\sqrt{6}$     | $1/\sqrt{5}$ | 0                 |

Fig. 8. Normalized atomic displacements of tetragonal SrTiO$_3$ are decomposed into three conventional modes: the Slater mode (solid line), the Last mode (dashed line), and the octahedron-deformation mode (dotted line) as functions of $u$, in Bohr.

![Normalized atomic displacements](image)

Fig. 9. Calculated results for SrTiO$_3$ under 4% biaxial tensile strain with respect to atomic displacements in tetragonal [110] direction. (a) Total energy (in meV) as a function of $u$ (in Bohr) (+'s connected with solid lines). Zero of the energy scale is placed at the total energy of the cubic structure when $u=0$. (b) Lattice constants $c$ and fixed $a$ in Bohr. (c) Atomic displacements $v'_i$. (d) Normalized atomic displacements $v'_i/u$, as functions of $u$.

mentioned that free-standing SrTiO$_3$, which have the crossing point at around $u = 0.07$, is very close to having a double well. In the negative charge, the atomic displacement of $O_I(=O_{II})$ is dominant compared with that of $O_{II}$ throughout the investigated range of $u$. To gain deeper insight into the behaviors of these atomic displacements, we analyze the presently obtained normalized atomic displacements by decomposing them into conventional three $\Gamma_{15}$ modes: the Slater mode, the Last mode, and the octahedron-deformation mode, as listed in Table I. As shown in Fig. 8, although the Slater mode is dominant throughout the entire investigated range of atomic displacements, the Last mode tends to increase while the Slater mode decreases moderately as functions of the amplitude of atomic displacements $u$. This result corresponds to the views pointed out by Schimizu and Harada that the Last mode is also important while the Slater mode plays a key role in the phase transition of SrTiO$_3$.

For SrTiO$_3$ under the 4% tensile strain, the calculated results of total energy, lattice constants and atomic displacements in the $x$-direction as functions of the amplitude of atomic displacements, $u = \sqrt{u_x^2 + u_y^2}$, are shown in Fig. 9. In this case, a ferroelectric monoclinic equilibrium structure is stabilized by a 48.6 meV energy gain at $u = 0.443$ Bohr. For the atomic displacements in the $x$-direction, Ti in the positive charge and $O_I(=O_{II}$ in the $y$-direction) and $O_{III}$ in the negative charge are dominant from the paraelectric state $u = 0$ state to $u = 0.443$ at which the total energy becomes minimum, whereas the $x$-direction displacements of Sr and $O_I(=y$-direction of $O_I$) become active in the region of $u > 0.443$, as shown in Fig. 9(c). The lattice constant $c$ decreases slightly at small $u$, then, after the alternation of the dominance in displacements from $v'^{O_{II}}$ to $v'^{O_I}$ at $u \sim 0.725$ Bohr, it begins to increase. We analyze the charge density distribution at each amplitude of atomic displacements $u$ for the tensile-strained SrTiO$_3$. Shown in Fig. 10 are the pseudo-valence charge density maps in the (001) cross sections and a projection at the following three points; [A] the paraelectric state at $u = 0$, [B] the monoclinic equilibrium state at $u = 0.443$ Bohr, and [C] the large displacement state at $u = 0.870$ Bohr, which are indicated on the total-energy surface shown in Fig. 9(a). In the process from the paraelectric state to the monoclinic equilibrium state, we can find that Ti comes close to O$_I$ and O$_{II}$ while Sr and O$_{III}$ mutually approach each other, as shown in Figs. 10[A] and 10[B]. In other words, the closeness of Ti-O$_I$, O$_{II}$ and that of Sr-O$_{III}$ play the dominant role for ferroelectric structural distortion in SrTiO$_3$ under an induced 4% tensile strain. In the region of the large amplitude of atomic displacements $u > 0.443$, however, the displacements in which O$_I$ and O$_{II}$ come close to Sr are enhanced while the closenesses of Ti-O$_I$, O$_{II}$ and that of Sr-O$_{III}$ are each saturated, as shown in Figs. 9(c) and 10[C]. From these results, the displacements of O$_I$ and O$_{II}$ are shifted in the direction in which they approach Sr because the Ti-O$_I$, O$_{II}$ closeness displacement is saturated by the rigid-sphere-like ionic repulsion between them; thus, in the atomic displacements in the $x$-direction of
as shown in Fig. 9(c), Sr in the positive charge and $O_{II}$ in the negative charge are displaced dominantly. The increase in lattice constant $c$ produces open spaces for the closing of $Sr-O_{II},O_{II}$. Hence, $SrTiO_3$ can be regarded as a typical ionic crystal. The ferroelectricity can be hypothesized to originate from the movement of the rigid-sphere-like ions into open spaces as induced by the biaxial tensile strain.

4. Summary

In this study, we investigated the effect of the in-plane biaxial compressive and tensile strains of $SrTiO_3$ on its ferroelectric distortion by determining the total-energy surface accurately with our structure optimization technique. (a) We confirmed that the ferroelectric distortion is induced strongly and Curie temperature is raised by applying the biaxial compressive or tensile strains to $SrTiO_3$. (b) From the results of the normalized atomic displacements, it is clarified that the ferroelectric distortion of $SrTiO_3$ is strongly influenced by the atomic displacements corresponding to the hard mode as well as to the soft mode. (c) By analyzing the obtained normalized displacements for a biaxial compressive strain of 4%, we showed that the Slater mode plays a dominant role while the Last mode is also important in the ferroelectric phase transition of $SrTiO_3$. (d) The behavior of atomic displacement associated with ferroelectric distortion was clarified by analyzing the charge density distribution in each amplitude of the atomic displacements for the 4% biaxial tensile strain.

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