An ab initio structure optimization technique is newly developed to determine the valley line on a total-energy surface for zone-center distortions of ferroelectric perovskite oxides and is applied to barium titanate (BaTiO$_3$) and lead titanate (PbTiO$_3$). The proposed technique is an improvement over King-Smith and Vanderbilt's scheme [Phys. Rev. B 49, 5828 (1994)] of evaluating total energy as a function of the amplitude of atomic displacements. The results of numerical calculations show that total energy can be expressed as a fourth-order function of the amplitude of atomic displacements in BaTiO$_3$ but not in PbTiO$_3$.

PACS numbers: 77.84.-s, 77.80.Bh, 63.70.+h, 02.60.Pn

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**FIG. 1:** Cubic crystal structure of perovskite oxide ABO$_3$. The cubic-tetragonal displacive transition accompanies atomic displacements $v^\tau_\alpha$ ($\tau = A, B, O_1, O_2, O_3$) indicated by arrows.

| A | 1a site |
|---|---------|
| B | 1b site |
| O | 3c site |

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$E_{\text{tot}} = E^0 + \kappa u^2 + \alpha' u^4 + \gamma'(u^2_\alpha u^2_y + u^2_\alpha u^2_z + u^2_y u^2_z)$, \hspace{1cm} (2)
FIG. 2: The total-energy surface for zone-center distortions of ferroelectric perovskite oxides are schematically illustrated with contour lines for two strains (a) \( \eta_3 = 0 \) and (b) \( \eta_3 > 0 \) in the two-dimensional subspace \((v^A_z, v^B_z)\) of the atomic-displacement space \((v^A_z, v^B_z, v^O_1, v^O_2, v^O_3)\). Thick solid lines are the valley lines for fixed \( \eta_3 \)'s. Dashed lines show the direction of the \( \Gamma_{15} \) soft-mode eigenvector at zero strain. Note that the direction is tangential to the valley line at \( v^*_z = 0 \) for \( \eta_3 = 0 \), but this is not the case for \( \eta_3 \neq 0 \).

where \( u^2 = u'^2 + u''^2 + u'^2 \), \( E^0 \) is the total energy for the cubic structure, \( \kappa \) is one-half of the eigenvalue of the soft mode, and \( \alpha' \) and \( \gamma' \) are the constants determined from coupling constants between atomic displacements and strains. Although their expression veritably describes essential properties of atomic displacements coupling with strains, it may misestimate (a) the energy gain of the lattice distortion from the cubic structure to the tetragonal equilibrium structure due to a deviation of atomic displacements from the soft-mode \( \xi \) direction as illustrated in Fig. 2 as well as (b) the total energy particularly when the amplitude of atomic displacements \( u_z \) is larger than the equilibrium value. Also, (c) \( \alpha' \) and \( \gamma' \) in eq. (2) strongly depend on coupling constants between atomic displacements and strains, but the coupling constants, \( B_{1zz} = \partial^2 E/\partial u_z \partial u_z \) for instance, are not always constant through out all the way from the cubic structure to the distorted equilibrium structure, and thus they are difficult to determine. These issues, (a)-(c), arise because King-Smith and Vanderbilt’s expression is restricted within the atomic displacements corresponding to the \( \Gamma_{15} \) soft-mode eigenvector at zero strain and also within the fourth-order function of \( u_z \), as in eq. (2). In this work, therefore, we redefine the amplitude of atomic displacements as

\[
u^*_t = \sqrt{\frac{v^2_t}{v^2_{t} + v^2_{t}' + \eta^2_3}}
\]

and evaluate the total energy as a function of \( u_\alpha \) under the condition that \( v^*_t \) and \( \eta_3 \) minimize the total energy for each \( u_\alpha \) using an \textit{ab initio} norm-conserving pseudopotential method and geometric optimization. Note that the translational displacement should be omitted both in eq. (1) and in eq. (3), i.e., the condition that

\[v^A_\alpha + v^B_\alpha + v^O_1 + v^O_2 + v^O_3 = 0\]

should be satisfied. Although, below room temperature, BaTiO\(_3\) exhibits tetragonal–orthorhombic (\(C_{14}^{1}\))–rhombohedral (\(C_{3v}^{1}\)) structure transitions and the total energy can be defined as a function of \( u_\alpha, u_y, \) and \( u_z \), we restrict our argument, in this paper, only to the cubic–tetragonal distortion: \( E_{\text{tot}} = E_{\text{tot}}(u_\alpha = 0, u_y = 0, u_z) \) and we optimize the strains \( \eta_1 = \eta_2 \) and \( \eta_3 \) while \( \eta_4, \eta_5, \) and \( \eta_6 \) are kept at zero. Minimization of total energy under the constant-\( u_z \) constraint, i.e., on the constant-\( u_z \) sphere, is carried out iteratively. Suppose that at the previous iteration indexed \( k \) we calculated a gradient \( \textbf{g} \), i.e., forces exerted on atoms, and a symmetric Hessian matrix \( B \), i.e., the second derivative of total energy \( B_{\sigma\tau} = \partial^2 E_{\text{tot}}/\partial v^2_{\sigma} \partial v^2_{\tau} \) at displacement vector \( v_{z,k} \). In the neighborhood of \( v_{z,k} \), total energy has the form

\[
E_{\text{tot}}(v_z) = \frac{1}{2} t(v_z - v_{z,k})B(v_z - v_{z,k}) + \frac{1}{2}(v_z - v_{z,k})\textbf{g} + E_{\text{tot}}(v_{z,k}) \tag{5}
\]

where \( t \)’s indicate the transpose of vectors. We first minimize eq. (5) on a plane that includes \( v_{z,k} \) and is perpendicular to \( \textbf{n} = v_{z,k}/|v_{z,k}| \), i.e., on a plane that touches the constant-\( u_z \) sphere at \( v_{z,k} \). This constraint can be expressed as

\[
t(v_z - v_{z,k})\textbf{n} = 0 \tag{6}
\]

The method of Lagrange multipliers specifies that the gradients of eq. (5) and eq. (6) must be proportional. Thus, a trial displacement \( v'_{z,k+1} \) for the next iteration \( k + 1 \) can be determined by solving

\[
B(v_z - v_{z,k}) + g = \lambda n \tag{7}
\]

where \( \lambda \) is a Lagrange multiplier. We can determine the Lagrange multiplier \( \lambda = \frac{1}{2} \textbf{n}B^{-1}g/n\textbf{B}^{-1}\textbf{n} \), and now we obtain

\[
v'_{z,k+1} = v_{z,k} - B^{-1}(g - \frac{1}{2} \frac{n\textbf{B}^{-1}g}{n\textbf{B}^{-1}\textbf{n}}) \tag{8}
\]

but \( |v'_{z,k+1}| \) may be slightly different from \( u_z \). Hence, we use

\[
v_{z,k+1} = \frac{v'_{z,k+1}}{|v'_{z,k+1}|}u_z \tag{9}
\]

as a trial displacement for the next iteration. The strains \( \eta_1 = \eta_2 \) and \( \eta_3 \), i.e., lattice constants \( a \) and \( c \), are optimized simultaneously in the iterations. We continue...
this iterative scheme of optimizing the atomic and lattice structure until the differences in total energies become less than \(10^{-7}\) Hartree twice successively.

In the case of chemical reactions of molecules, a reaction path can be defined as the steepest-descent path from a transition structure down to reactants and down to products, i.e., the valley line \(\mathcal{E}\). Although there are some techniques to determine the chemical reaction path \(\mathcal{E}\), we expect our optimization technique to be accurate enough and to give a simple approximation for the \(ABO_{3}\) perovskite oxides.

We use the ABINIT package \(\mathcal{E}\) for all \textit{ab initio} calculations. Bloch wave functions of electrons are expanded into plane waves with a cut-off energy of 60 Hartree, using Teter’s extended norm-conserving pseudopotentials \(\mathcal{E}\). The pseudopotentials include O 2s and 2p, Ti 3s, 3p, 3d and 4s, Ba 5s, 5p and 6s, and Pb 5d, 6s and 6p as valence electrons. Bloch wave functions are sampled on an \(8 \times 8 \times 8\) grid of \(k\)-points in the first Brillouin zone. The grid is reduced to 40 irreducible \(k\)-points under \(C_{4v}\) symmetry. The exchange-correlation energy is treated within the local density approximation (LDA). As the parametrized correlation energy, we use Teter’s rational polynomial parametrization \(\mathcal{E}\), which reproduces the results obtained by Ceperley and Alder \(\mathcal{E}\). The electronic states are calculated by the iterative scheme to reach a tolerance of convergence that requires differences of forces to be less than \(5 \times 10^{-7}\) Hartree/Bohr twice successively.

The presently calculated ratios of lattice constants \(c/a\) and the amplitudes of atomic displacements \(u_{z}\) for the tetragonal equilibrium structures are \(c/a = 1.0029\) and \(u_{z,eq} = 0.0975\) Bohr for BaTiO\(_{3}\) and \(c/a = 1.0284\) and \(u_{z,eq} = 0.6087\) Bohr for PbTiO\(_{3}\). The experimentally observed values are \(c/a = 1.0086\) and \(u_{z,eq} = 0.2638\) Bohr for BaTiO\(_{3}\) \(\mathcal{E}\) and \(c/a = 1.0649\) and \(u_{z,eq} = 0.9076\) Bohr for PbTiO\(_{3}\) \(\mathcal{E}\). Thus, calculations underestimate the experimental values. Calculated energies gained through cubic to tetragonal distortions are 0.386 meV in BaTiO\(_{3}\) and 37.5 meV in PbTiO\(_{3}\). Although energy gain and experimentally observed transition temperature (408 K = 35.2 meV for BaTiO\(_{3}\) and 763 K = 65.8 meV for PbTiO\(_{3}\)) cannot be compared directly, the energy gains also seem to be underestimated. These underestimations are because the large sensitivity to volume makes the volume errors in LDA unusually important \(\mathcal{E}\). Nevertheless, we believe that calculations using LDA clarify some trends of displacive transitions of perovskite oxides.

Figure 3 shows the obtained results for BaTiO\(_{3}\). We can see that total energy is well expressed as a fourth-order function of the amplitude of atomic displacements \(u_{z}\) (Fig.\(\mathcal{E}\)). Lattice constants \(a\) and \(c\) are also well fitted with the quadratic function of \(u_{z}\) (Fig.\(\mathcal{E}\)). These results suggest that for the compound with the small spontaneous distortion the \textit{direction} of atomic displacements remains almost equal to the soft-mode eigenvector \(\xi\) through out the speculate range of atomic displacements, as shown in Fig.\(\mathcal{E}\)), and thus the total energy can be well expressed within the fourth order expansion.

In PbTiO\(_{3}\), on the contrary, total energy cannot be expressed as a fourth-order function of \(u_{z}\), as shown in Fig.\(\mathcal{E}\). We can see in Fig.\(\mathcal{E}\) that lattice constant \(c\) is not well fitted by the quadratic function of \(u_{z}\). These are due to the deviation of atomic displacements from the soft-mode \(\xi\) direction as \(u_{z}\) becomes larger (Fig.\(\mathcal{E}\)); from \(u_{z} = 0\) to around \(u_{z} = 0.6087\), at which the total energy becomes minimum, the normalized displacement of \(A=Pb\) increases and that of \(B=Ti\) decreases. Then, beyond \(u_{z} = 0.6087\), that of \(O_{3}\) decreases while that of \(O_{1}\) slightly increases. This result is the first clarification of the non-fourth-order behavior of the total-energy surface, though it was predicted for the compounds with the largest spontaneous distortion \(\mathcal{E}\), but has been difficult to formalize with coupling between atomic displacements and strains.

![Graph showing total energy and displacement](image-url)
calculations show that total energy can be expressed as a fourth-order function of the amplitude of atomic displacements $u_z$ in BaTiO$_3$ but not in PbTiO$_3$. (c) Our new optimization technique can automatically evaluate the total energy as a function of $u_z$ and coupling between atomic displacements and strains, i.e., the quadratic or nearly quadratic $u_z$-dependences of strains. This is an advantage of our technique compared with King-Smith and Vanderbilt’s scheme.

Computational resources were provided by the Center for Computational Materials Science, Institute for Materials Research, Tohoku University.

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