Ab initio elasticity at finite temperature and stress in ferroelectrics

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Computing the temperature and stress dependence of the full elastic constant tensor from first-principles in non-cubic materials remains a challenging problem. Here we circumvent the aforementioned challenge via the generalized quasiharmonic approximation in conjunction with the irreducible derivative approach for computing strain dependent phonons using finite difference, explicitly including dipole-quadrupole contributions. We showcase this approach in ferroelectric $PbTiO_3$ using density functional theory, computing all independent elastic constants and piezoelectric strain coefficients at finite temperature and stress. There is good agreement between the quasiharmonic approximation and the experimental lattice parameters close to 0 K. However, the quasiharmonic approximation overestimates the temperature dependence of the lattice parameters and elastic constant tensor, demonstrating that a higher level of strain dependent anharmonic vibrational theory is needed.

Ferroelectric materials have been widely studied due to technological importance and interesting physics [1–5]. Many ferroelectric materials are band insulators, which are typically well described by density functional theory (DFT). For prototypical ferroelectric band insulators, the Born-Oppenheimer potential generated from appropriate exchange-correlation approximations within DFT produce temperature dependent structural phase transitions consistent with experiment [6–15], indicating an accurate representation of the vibrational free energy. However, evaluating piezoelectric properties at finite temperatures and stress requires the computation of relevant strain curvatures of the DFT based vibrational free energy at finite temperatures and stress (i.e. the elastic constants). Computing these elastic constants requires encoding or sampling the vibrational Hamiltonian as a function of strain, evaluating the vibrational free energy in some approximation as a function of strain, and evaluating the second strain derivatives of the free energy. Each of the aforementioned tasks presents substantial theoretical and computational challenges.

The standard approximation for computing finite temperature elastic constants is the quasiharmonic approximation (QHA) [16–18], yielding reasonable agreement with experimental measurements for a variety of cubic systems [19–25]. The computational cost of executing the QHA within DFT is appreciable [26], as evidenced by the sparsity of temperature dependent elastic constant computations for non-cubic systems available in the literature [27–29], and we are not aware of any published results at finite temperature and stress. The aforementioned limitations can be mitigated by using the recently developed generalized quasiharmonic approximation [30], which leverages the irreducible derivative approach to computing phonons [31, 32]. Here we showcase the power of the generalized QHA by studying the displacive ferroelectric $PbTiO_3$ (spacegroup P4mm) using DFT, computing the lattice parameters, full elastic constant tensor, and piezoelectric strain coefficients at finite temperature and stress. $PbTiO_3$ is an ideal candidate to study within

Method	a	c	$z(Ti)$	$z(O_{1,2})$	$z(O_3)$
PBEsol	3.872	4.214	0.539	0.623	0.118
SCAN	3.865	4.341	0.545	0.638	0.139
PBEsol	3.891	4.164	0.539	0.618	0.112
Mestric et al.	3.891	4.168	0.542	0.629	0.124

TABLE I. Lattice parameters and direct atomic coordinates along the z-direction. (Top) Results of DFT relaxation using the PBEsol and SCAN functionals. (Bottom) $T = 1$ K QHA results compared with measurements at $T = 12$ K [45].

the generalized QHA, as the low symmetry ferroelectric phase persists to roughly $T = 760$ K [33–35].

DFT calculations were performed using the Vienna *ab initio* simulation package (VASP) [36–39] with the projector augmented wave (PAW) method [40, 41] unless otherwise stated. The generalized gradient approximation (GGA) revised for solids (PBEsol) [42] and the strongly constrained and appropriately normed (SCAN) [43] exchange-correlation functionals were used. Convergence of the strain dependent phonons was achieved with a kinetic energy cutoff of 1000 eV and a Γ-centered **k**-point mesh of $16\times16\times16$ for the primitive unit cell with corresponding mesh densities being used for supercells. Details of the PAW potentials, finite difference calculations, and Fourier interpolation are provided in Sec. I of the supplemental material (SM) [44]. The computationally relaxed crystal structures using the PBEsol and SCAN functionals are compared with low temperature experimental measurements in Table I. Due to the significant overestimation of the c lattice parameter by the SCAN functional, computations use the PBEsol functional unless otherwise stated.

We begin by showcasing the computed phonons in the supercell $\hat{S}_{BZ} = 4\hat{1}$ (see Fig. 1 (a)), achieving good agreement to previous computations [46]. The dipole-dipole contribution to Fourier interpolated phonons is included [30, 47, 48] shown as the red lines, where the dielectric tensor and Born effective charges were calcu-

lated from density functional perturbation theory [49, 50] within VASP. Along the path from the Γ point to the R point, there are interpolated imaginary phonon frequencies caused by a deficiency in the Fourier interpolation, which was elucidated in previous work [51]. Supplementing the interpolation with the dipole-quadrupole interactions has demonstrated the ability to remove these spurious imaginary frequencies from the interpolation [51]. Our Fourier interpolation of the phonons including the dipole-dipole and the dipole-quadrupole contributions shown as the blue lines does not contain any spurious imaginary frequencies, consistent with results in Ref. [51]. Computation of the dipole-quadrupole contribution has been implemented analogously to the dipole-dipole contribution, where dynamical quadrupoles were computed [52] using density functional theory implemented in the (ABINIT) package [53, 54] using the PBEsol optimized norm-conserving Vanderbilt pseudopotential (ONCVPSP) [55]. Our results illustrate that both dipole-dipole and dipole-quadrupole corrections to the Fourier interpolation can straightforwardly be utilized in our irreducible derivative approaches, which are based on the finite difference method.

We now present selected generalized Gruneisen parameters,

$$\gamma_{i,\mathbf{q}\ell} = -\frac{1}{\omega_{\mathbf{q}\ell}}\frac{\partial \omega_{\mathbf{q}\ell}}{\partial \epsilon_i}, \tag{1}$$

which encapsulate the first order strain dependence of the phonons along a given strain (see Fig. 1 (b) and (c)). Computation of the full elastic constant tensor within the QHA requires the phonons to be computed as a function of all symmetrically distinct strains, whereas thermal expansion computations only use strains associated with changes in volume. Thus, panel b shows the A_1° Gruneisen parameter associated with expansion along the z-axis, where the symmetrized representations of the identity strains are denoted as $\epsilon_{A_1^\square} = \frac{1}{\sqrt{2}}(\epsilon_{xx}+\epsilon_{yy})$ and $\epsilon_{A_1^\circ} = \epsilon_{zz}$. Integration of the density of states yields averaged Gruneisen parameters of $\bar{\gamma}_{A_1^\square}$=1.78 and $\bar{\gamma}_{A_1^\circ}$=0.28. Panel c shows the B_1 Gruneisen parameter, where $\epsilon_{B_1} = \frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy})$. Symmetry selection rules and first order perturbation theory require the Gruneisen parameter to be zero along various directions in reciprocal space.

Having computed the strain dependence of the phonons, we apply the generalized quasiharmonic approximation to compute the a and c lattice parameters at finite temperature and stress (see Fig. 2). We compare with experimental measurements at various temperatures under unstressed conditions [33, 45, 56–58]. The a and c lattice parameters are in good agreement within the experimental measurements, as there is at most 0.5% difference between various measurements at any given temperature. Computation of the lattice parameters at

FIG. 1. Phonons and specific Gruneisen parameters computed from DFT (diamonds) within the $4\hat{1}$ and $2\hat{S}_C$ supercells, respectively, and Fourier interpolated (lines). Left panels show values along high symmetry directions, and right panels show the density of states. (a) Computed phonons which are Fourier interpolated with dipole-dipole (red) or dipole-dipole and dipole-quadrupole (blue) contributions. Gruneisen parameters computed with strains transforming like the (b) A_1° and (c) B_1 irreducible representations.

a given temperature T and stress $\boldsymbol{\sigma}$ is achieved through the Biot strain function,

$$\tilde{\boldsymbol{\epsilon}}(T,\boldsymbol{\sigma}), \quad \text{where} \quad \tilde{\boldsymbol{\sigma}}(T,\tilde{\boldsymbol{\epsilon}}(T,\boldsymbol{\sigma})) = \boldsymbol{\sigma}. \tag{2}$$

where definitions and notation are equivalent to Ref. [30] (see Eqs. 21-26). The phonons are computed on a grid of strains and compared with a Taylor series expansion of the phonons in strain, where convergence of the thermal expansion is achieved when including first, second,

FIG. 2. The a (panel a) and c (panel b) lattice parameters computed with the QHA (lines) under unstressed (blue) and stressed (red) conditions compared with previous experimental measurements (diamonds) [33, 45, 56–58].

and third strain derivatives within the Taylor series (see Sec. I of the SM [44]). The crystal structure predicted at $T = 1$ K by the QHA differs from the values obtained from DFT relaxations due to zero point motion, and are compared with experimental measurements at $T = 12$ K [45] (see Table I). The predicted shift in lattice parameters due to zero-point motion yields remarkable agreement with the values obtained from experiment, however there are discrepancies in the predicted direct atomic coordinates. The change in lattice parameters with temperature is overestimated by the quasiharmonic approximation which is well known for anharmonic materials [59, 60]. Under the application of $\sigma_{A_1^\square} = -0.95$ GPa and $\sigma_{A_1^\circ} = -0.15$ GPa, the a and c lattice parameter computations agree with experimental measurements at room temperature.

Having computed the lattice parameters, we now discuss the strain curvature of the free energy at finite temperature and stress. There are three experimentally rel-

evant quantities related to the free energy curvature at finite stress [61]: the free energy curvature C_{ij}, the elastic wave propagation coefficient S_{ij}, and the stress-strain coefficient B_{ij}. Additionally, elastic constants in ferroelectrics can be measured under boundary conditions of constant electric field E or constant electric displacement field D. The relation between the two boundary conditions is given by [62],

$$C_{ij}^D(T, \boldsymbol{\sigma}) = C_{ij}^E(T, \boldsymbol{\sigma}) + \sum_{\alpha\beta} \big(e_{\alpha i}(T, \boldsymbol{\sigma}) \times$$
$$e_{\beta j}(T, \boldsymbol{\sigma})((\hat{\epsilon}^{\infty,S}(T, \boldsymbol{\sigma}))^{-1})_{\alpha\beta} \big), \qquad (3)$$

where $\hat{\epsilon}^{\infty,S}$ is the relaxed-ion dielectric tensor at fixed strain and $e_{\alpha i}$ is the relaxed-ion piezoelectric stress coefficient [62–65]. Our evaluation of $\hat{\epsilon}^{\infty,S}$ and $e_{\alpha j}$ at finite temperature T and stress $\boldsymbol{\sigma}$ is achieved by using the value at the strain corresponding to $\tilde{\epsilon}(T, \boldsymbol{\sigma})$.

We compute the elastic constant tensor at finite temperature and stress, and compare with experimental values measured under unstressed conditions [66–68] (see Fig. 3). The elastic constants which were not measured at multiple temperatures are shown in Sec. II of the SM [44]. There is good agreement within the experimental values at room temperature, where the largest disagreement is a 4% difference in the measured C_{44}^D values. At room temperature, the QHA with PBEsol yields good agreement for C_{11}^E and C_{44}^E, however C_{33}^D and C_{44}^D are overestimated and C_{66} is underestimated. The change in the predicted elastic constants with temperature is greater than the change observed in experiment, likely due to an overestimation of the thermal expansion with temperature (see Fig. 2) and due to the neglect of explicit phonon interactions within the QHA [59, 60]. The change in the constant D-field elastic constants with temperature is significantly greater than the change seen in experimental measurements, and is due to the temperature dependence of e_{ij} and $\hat{\epsilon}_{ij}^{\infty,S}$. These relaxed-ion quantities depend on the Γ-point dynamical matrix, and therefore the temperature dependence is overestimated due to the aforementioned volume and anharmonic effects.

We proceed with the computation of the piezoelectric strain coefficients as a function of temperature and stress, and compare with existing experimental values measured under unstressed conditions [67–69] (see Fig. 4). The piezoelectric strain coefficients d_{ij} are constructed using the elastic constant tensor and the piezoelectric stress coefficients [62, 70],

$$d_{\alpha i}(T, \boldsymbol{\sigma}) = \sum_j ((\hat{B}^E(T, \boldsymbol{\sigma}))^{-1})_{ij} e_{\alpha j}(T, \boldsymbol{\sigma}), \qquad (4)$$

where $\hat{B}_{ij}^E$ denotes the stress-strain coefficient under a constant electric field. The experimentally measured values of the piezoelectric strain coefficients [67–69] show quantitative inconsistency, as the values vary as much as

FIG. 3. Selected elastic constants under constant E fields or D fields computed with the QHA (lines) under unstressed (solid) and stressed (dashed) conditions compared with previous experimental measurements (markers) [67, 68]. The axial and shear elastic constants are shown in panels a and b, respectively.

50% for d_{33} and 20% for d_{31}. Our quasiharmonic predictions of the d_{33} and d_{31} overestimate the experimental measurements, and the discrepancy can be explained by differences in the $C^{E}_{A^{\square}_1 A^{\circ}_1}$ and C^{E}_{33} elastic constants. We compute values of $d_{33} = 201.6$ pC/N and $d_{31} = -41.1$ pC/N using Eq. 4, in good agreement with our QHA predictions, by using the experimental values from Ref. [67] and substituting the values of $C^{E}_{A^{\square}_1 A^{\circ}_1}$ and C^{E}_{33} to the room temperature computed values of 108.3 GPa and 56.2 GPa, respectively. The temperature dependence of the d_{31} piezoelectric coefficient agrees with the only temperature dependent experimental measurement [69] from low temperatures up to room temperature, where the QHA predictions increase rapidly.

In summary, we have demonstrated the application of the generalized quasiharmonic approximation to a non-cubic crystal, ferroelectric PbTiO$_3$, under conditions of

FIG. 4. Piezoelectric strain coefficients $-d_{31}$, d_{33}, and d_{15} computed with QHA (lines) under unstressed (blue) and stressed (red) conditions compared with existing experimental measurements (circles) [67–69] are shown in panels a, b, and c, respectively.

finite temperature and stress. The irreducible derivative approach to computing phonons from finite difference yields the strain dependent phonons, where dipole-quadrupole effects are successfully incorporated in the Fourier interpolation. The thermal expansion, elastic constants, and piezoelectric strain coefficients are computed at finite temperature and stress. The temperature dependence of the thermal expansion and elastic constants at zero stress are over estimated by the quasiharmonic approximation, illustrating the need to solve the vibrational Hamiltonian of PbTiO$_3$ using a strain-dependent theory which explicitly accounts for phonon

interactions. Our observed limitations of the QHA are not unexpected, as discrepancies of the QHA are well known in various anharmonic materials [59, 60]. Advances in the computation of finite temperature vibrational properties from DFT using more sophisticated approximations than the QHA have been achieved [71–76], however we are not aware of the application of any of these theories to the computation of the elastic constant tensor at finite temperature. These more advanced theories can be straightforwardly applied as a function of strain to compute thermal expansion and elastic constants at finite temperature and stress using the general formalism outlined previously [30], which will be the subject of future work.

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