Ab initio phonon dispersion curves and interatomic force constants of barium titanate

Ph. Ghosez, X. Gonze and J.-P. Michenaud
Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain,
1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium
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Abstract

The phonon dispersion curves of cubic BaTiO$_3$ have been computed within a first-principles approach and the results compared to the experimental data. The curves obtained are very similar to those reported for KNbO$_3$ by Yu and Krakauer [Phys. Rev. Lett. 74, 4067 (1995)]. They reveal that correlated atomic displacements along $<100>$ chains are at the origin of the ferroelectric instability. A simplified model illustrates that spontaneous collective displacements will occur when a dozen of aligned atoms are coupled. The longitudinal interatomic force constant between nearest neighbour Ti and O atoms is relatively weak in comparison to that between Ti atoms in adjacent cells. The small coupling between Ti and O displacements seems however necessary to reproduce a ferroelectric instability.

Keywords: BaTiO$_3$, phonon dispersions curves, ferroelectric instability, density functional theory, linear response.
I. INTRODUCTION

Barium titanate (BaTiO$_3$) is well known to exhibit three ferroelectric phase transitions: stable at high temperature in a perovskite cubic phase, its structure becomes successively tetragonal, orthorhombic and finally rhombohedral as the temperature goes down. Many works investigated and discussed the origin of its ferroelectric phase transitions [1]. Amongst them, the most gratifying contribution was probably due to Cochran [2] who associated the ferroelectric instability with the softening of a transverse optic phonon, and emphasized the connection between the structural instability and the lattice dynamics.

Consequently to Cochran’s work, a large amount of experiments have been performed in order to confirm the existence of a soft ferroelectric mode in BaTiO$_3$. They include infrared [3,4] and Raman [5] measurements of the Γ phonon modes as well as various neutron diffraction data [6–11]. These experiments focused on the temperature behaviour of the soft phonon and were mainly concerned by the low frequency modes: only a few results are available for the higher energy vibrations.

Simultaneously, theoretical phonon dispersion curves were deduced from fits to the experimental data using different shell models. Let us mention the pseudo-ionic model developed by Gnininvi and Bouillot [12] or the rigid-shell model used by Jannot et al. [11]. These models were however not particularly suited to describe ABO$_3$ crystals, like BaTiO$_3$. Migoni, Bilz and Bäuerle [13] pointed out that the behaviour of the ferroelectric soft mode in the oxidic perovskites originates from the unusual anisotropic polarizability of the oxygen that, in turn, may be connected to hybridization between O-2p and B-d states. Consequently, a more sophisticated “polarizability model” [14] was introduced in order to include the specific physical features of ABO$_3$ compounds. The application of this model to BaTiO$_3$ was reported by Khatib et al. [15]. In their work, they obtained a full phonon band structure and investigated the temperature behaviour of the ferroelectric soft mode. However, their interesting results still remained at a semi-empirical level.

Since a few years, theoretical advances have enabled one to determine the phonon dispersion curves of solids within a truly first-principle approach. Recently, ab initio results have been reported for KNbO$_3$ [16] and SrTiO$_3$ [17]. Similarly, in this paper, we investigate the lattice dynamics of BaTiO$_3$.

Our phonon frequencies compare well with the experimental data available. Moreover, our dispersion curves are very similar to those reported for KNbO$_3$ [16], a perovskite material presenting the same sequence of phase transition as BaTiO$_3$. In particular, the wave vector of the unstable phonon modes remains located in three (110) slab region of the Brillouin zone, emphasizing a chain-structure instability in real space [16]. This behaviour is illustrated with a simplified model. The range and anisotropy of the interatomic force constants is also discussed.

II. TECHNICALITIES

Our calculations have been performed in the general framework of the density functional formalism [18]. The exchange-correlation energy functional was evaluated within the local density approximation, using a polynomial parametrization of Ceperley-Alder [19] homogeneous electron gas data.
We used a plane-wave pseudopotential approach. The all-electron potentials were replaced by the same extended norm conserving highly transferable pseudopotentials as in Ref. [20]. We have considered 5s, 5p and 6s as valence states to build the Ba pseudopotential, 3s, 3p, 3d and 4s valence states for the Ti pseudopotential and 2s and 2p valence states for the O pseudopotential. The electronic wave function was expanded in plane waves up to a kinetic energy cutoff of 45 Hartree (about 6200 plane waves). Integrals over the Brillouin zone were replaced by a sum on a mesh of 6X6X6 special \( k \)-points [21].

The dynamical matrix, Born effective charges and dielectric tensor were computed within a variational formulation [22] of the density functional perturbation theory [23]. First, calculations were carried out to determine the dynamical matrix on different meshes of \( q \)-points. Then, an interpolation was performed following the scheme proposed in Ref. [24,25]. This technique takes properly into account the long-range behaviour of the dipole-dipole interaction which is separated from the remaining short-range forces owing to the knowledge of the Born effective charges and the optical dielectric tensor.

An insight into the convergence reached on the phonon dispersion curves is reported in Fig. 1. The frequencies deduced from the dynamical matrix at \( q = (0.125, 0.125, 0.125) \) and \( q = (0.375, 0.375, 0.375) \) are compared to those extrapolated from two different meshes of \( q \)-points: the first mesh (M1) includes \( \Gamma (0.0, 0.0, 0.0) \), \( X (0.5, 0.0, 0.0) \), \( M (0.5, 0.5, 0.0) \) and \( R (0.5, 0.5, 0.5) \) points; the second mesh (M2) is the cubic mesh M1 to which the \( \Lambda (0.25, 0.25, 0.25) \) point was added. We obtain a very good convergence with the M2 mesh.

### III. THE PHONON DISPERSION CURVES

Our calculations are performed at the experimental lattice parameter of 4.00 Å. This choice facilitates the comparison with the experimental data. Some indications on the volume dependence of the phonon frequencies can be found in Ref. [26], where the frequencies of the \( \Gamma \) phonons at different lattice constants have been compared.

First, we present in Table I the Born effective charges and the optical dielectric constant [27], important ingredients of the present study since their knowledge allows to identify the long-range part of the interatomic force constants and makes the interpolation of phonon frequencies tractable. For Ba and Ti atoms, the effective charge tensor is isotropic. For O, the two independent components of the tensor correspond respectively to a displacement of the atom parallel \( (Z_{O\parallel}^*) \) and perpendicular \( (Z_{O\perp}^*) \) to the Ti-O bond. \( Z_{Ti}^* (+7.32) \) and \( Z_{O\parallel}^* (-5.78) \) are anomalously large [28,29] with respect to the nominal ionic charges (+4 for Ti and −2 for O). This surprising phenomenon was explained recently in connection within dynamic changes of hybridization between O-2p and Ti-3d orbitals [30,31]. This specific feature is at the origin of a large destabilizing dipole-dipole interaction, connected to the anomalous mode effective charge [26,24] and the instability of the ferroelectric mode [26].

Our computed optical dielectric constant (6.75) largely overestimates the experimental value (5.40) [32], as usual within the local density approximation. This discrepancy will essentially affect the position of the highest longitudinal optic mode: when replacing the theoretical dielectric constant by the experimental value, its frequency at the \( \Gamma \) point changes from 631 to 696 cm\(^{-1}\). At the opposite, the frequencies of the two other longitudinal modes at the \( \Gamma \) point are affected by less than 2 cm\(^{-1}\).
The calculated phonon dispersion curves are plotted along high symmetry directions in Fig. 2. The Γ-X, Γ-M and Γ-R lines are along the <100>, <110> and <111> directions, respectively. The unstable modes associated to a negative curvature of the energy hypersurface have imaginary phonon frequencies. The frequencies at the high symmetry points are reported in Table II.

Our result can be compared to the experimental data [3,6–11]. However, a complication arises from the fact that all the experimentally observed vibrational excitations have a real frequency while the computed unstable modes are obtained with an imaginary frequency. As the soft mode can be clearly identified by its symmetry, the associated experimental frequencies were removed from the comparison, for clarity. In the low frequency region, the presence of this additional soft mode may have slightly modified the frequency of the other modes. In spite of these difficulties we observe a good correspondence between our theoretical frequencies and the experimental data, specially for the acoustic modes for which a large variety of data are available.

The ferroelectric phase transitions are driven by the unstable phonon modes. We are therefore mainly concerned by the analysis of these specific phonons. Two transverse optic modes are unstable at the Γ point: they correspond to a displacement of the Ti atom against the oxygen cage. The associated displacement eigenvector is equal to $\delta(Ba) = -0.002$, $\delta(Ti) = -0.096$, $\delta(O_1) = +0.158$, $\delta(O_2) = \delta(O_3) = +0.071$ [34]. These two modes remain unstable all along the Γ-X line, with very little dispersion. One of them stabilizes along the Γ-M and X-M lines. Examination of the eigenvectors reveals that the unstable mode at the M (0.5, 0.5, 0.0) point is polarized along the $z$-direction: its displacement eigenvector is equal to $\delta(T_{iz}) = -0.130$, $\delta(O_{1z}) = +0.106$ [34]. Both of the unstable modes become stable when deviating from the three Γ-X-M planes to the R-point.

These features were also observed for KNbO$_3$ [16] and point out a marked 2D character of the instability in the Brillouin zone. This behaviour is more easily visualized in Fig. 3 where we show the frequency isosurface of the lowest unstable phonon branch corresponding to $\omega = 0$. The region of instability, $\omega^2(q) < 0$, lies between three pairs of flat surfaces, that are parallel to the faces of the Brillouin zone cube. In other words, the unstable modes are contained in three perpendicular interpenetrating slab-like regions of finite thickness containing the Γ point.

As highlighted by Yu and Krakauer [16], this behaviour corresponds to chain instabilities in real space. At the M-point, we have seen that there is a single unstable mode polarized along the z-axis and dominated by the Ti$_z$ and O$_{1z}$ displacements. At this wave vector ($q_z = 0$), the Ti and O$_1$ atoms will be coherently displaced all along an infinite <001> chain. Going now from M to the R-point, the coherency of the displacement will gradually disappear and a finite length of correlation will be reached for which the phonon becomes stable. The finite thickness of the slab region of instability therefore corresponds to a minimum correlation length of the displacement required to observe an unstable phonon mode. From Fig. 3, the length of the shortest unstable chain can be estimated to 4 $a_{cell} / \AA = 16 \AA$ [35]. Note finally, the small dispersion of the unstable mode in the Γ-X-M plane suggests a small correlation of the displacements between the different Ti–O chains.
IV. THE INTERATOMIC FORCE CONSTANTS

In cubic BaTiO$_3$, we will see that the single displacement of a particular atom never leads to an instability: When one atom is displaced, a force is induced and brings it back in its initial position (see Tables III - V: the self-force on Ti and O is positive). However, its atomic displacement will simultaneously induce forces on the other atoms. It is only the additional displacement of some other atoms in this force field that can lower the total energy and produce an instability. The amplitude and the range of the interatomic force constants (IFC) associated to this mechanism can be analysed in order to clarify the chain instability pointed out in the previous Section. Moreover, the specific role of the dipole-dipole interaction (DD) can be separated from that of the short-range forces (SR) following the scheme proposed in Ref. [25]. Our conventions on the interatomic force constants $C_{\alpha,\beta}(\kappa, \kappa')$ are such that the force $F_{\alpha}(\kappa)$ induced on atom $\kappa$ by the displacement $\Delta \tau_{\beta}(\kappa')$ of atom $\kappa'$ is given by: $F_{\alpha}(\kappa) = -C_{\alpha,\beta}(\kappa, \kappa') \cdot \Delta \tau_{\beta}(\kappa')$.

Let us first investigate the IFC with respect to a reference Ti atom along a Ti-O chain (Table III). As previously mentionned, we note that the self-force on the Ti atom is large and positive (+0.15215 Ha/Bohr$^2$). We observe also that the longitudinal IFC with the first neighbour O atom is surprisingly small (+0.00937 Ha/Bohr$^2$); moreover, it is positive. The analysis of the DD and SR contributions points out that these characteristics are the result of a destabilizing DD interaction, sufficiently large to compensate the SR forces. It is this close compensation which allows the displacement of Ti against the O atoms. Another insight on this balance of forces was already reported in Ref. [26]. Consequently to the very small total IFC, the Ti and O displacements might be relatively decoupled.

At the opposite, the DD forces induced on the next Ti atom are negative: they will combine with the SR forces in order to produce sizeable coupling ($-0.06721$ Ha/Bohr$^2$). This mechanism is at the origin of the chain correlation of the Ti atomic displacements. By contrast, the transverse force on the first Ti neighbour is very small and confirms the small correlation of the displacements from chain to chain.

The decay of the Ti–Ti and O–O longitudinal IFC with the interatomic distance can also be investigated. The results are reported in Table IV and V. It is seen that the longitudinal IFC are anisotropic: they propagate essentially along the Ti–O chain. This appears clearly for the SR part. For O, the DD contribution is also highly anisotropic due to the anisotropy of the Born effective charges. The anisotropy of the IFC is inherent to the chain correlation previously mentionned in this paper.

V. THE CHAIN-STRUCTURE INSTABILITY

From the knowledge of the IFCs previously reported, we can also investigate the energy surface of BaTiO$_3$ and illustrate the chain correlation highlighted in Section III. Let us consider that we have a bulk cubic crystal with the atoms frozen at their equilibrium position $\tau_{\kappa_0}$. Then, we allow displacements of Ti and O atoms belonging to a [100] single Ti–O chain of finite but increasing size. The total energy of this system will be given by:

$$E(\tau_k) = E(\tau_{\kappa_0}) + \sum_{\kappa,\kappa'} C_{1,1}(\kappa, \kappa') \Delta \tau_{\kappa} \Delta \tau_{\kappa'}$$
where $C$ is the interatomic force constant matrix and the sum on $\kappa$ and $\kappa'$ is restricted to the Ti and O atoms that are allowed to move. With the help of this equation, we can track the appearance of an instability in terms of the length of the chain of displaced atoms. An instability will correspond to a specific displacement pattern that lowers the total energy of the system: it will be associated to a negative eigenvalue of the restricted force constant matrix.

In Fig. 4, we report the evolution of the lowest eigenvalue of the force constant matrix with respect to the length of the chain of moving atoms. Displacing only a single atom, the force induced on the Ti is larger than that on the O atom. With 3 atoms, we observe, at the opposite, that the Ti-terminated chain (Ti–O–Ti) is more stable than the O-terminated one (O–Ti–O): it points out the important role of the Ti–Ti interaction. The difference between Ti and O terminated chains will disappear progressively with the chain length. It is seen that an instability takes place for a chain longer than 10 atoms (5 unit cells). This is in close agreement with the correlation length estimated in the previous Section. It suggests that the behaviour of BaTiO$_3$ is already well reproduced when considering an isolated Ti–O chain of displacements. It confirms that the correlation between the different chains may play a minor role.

Going further and freezing all the O atoms in such a way that only the Ti atoms are allowed to move along the chain, we can repeat the previous investigations. For this case, however, we do not observe any instability even for an infinite chain of correlated Ti displacements. This result aims to prove that the relatively weak coupling between Ti and O displacements still remains an important feature in the appearance of the structural instability.

VI. CONCLUSIONS

In summary, we have reported first-principles linear response calculations of the phonon dispersion curves of cubic BaTiO$_3$. Our results are in good agreement with the experimental data. Moreover, they are very similar to those reported for KNbO$_3$, a cubic perovskite material presenting a sequence of phase transitions analogous to BaTiO$_3$. In particular it was seen that a ferroelectric instability takes place when correlated atomic displacements are allowed along $<100>$ chains of finite length. This has been investigated with a simplified model and the length of the shortest unstable chain estimated to a dozen of atoms. The interatomic force constants are anisotropic and propagate essentially along the Ti-O chains. Their analysis has emphasized the correlation of the Ti displacements. It has shown that the Ti and O atomic displacements are only weakly coupled. This small coupling remains however an important ingredient to reproduce the ferroelectric instability.

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The values presented here are slightly different from those reported by us elsewhere due to the different convergence reached in the calculation.

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The eigendisplacement vector $\eta$ was normalized such that $\langle \eta | M | \eta \rangle = 1$, where $M$ is such that $M = M_\kappa \delta_{\kappa, \kappa'}$ and $M_\kappa$ is the mass of atom $\kappa$ in atomic mass units.

The length of the shortest unstable chain is slightly different from that reported for KNbO$_3$. Changes in material properties could explain this difference although part of it could be due to the different $k$-point and $q$-point convergence achieved in Ref. [16]: as observed in Fig. [1], the use of a finer mesh of $q$-points could still slightly decrease the size of the zone of instability of BaTiO$_3$. 

$\epsilon_\infty$ was obtained by extrapolating to zero frequency index of refraction measurements [G. Burns and F. H. Dacol, Solid State Comm. 42, 9 (1982)] at different wavelengths using a one-oscillator Sellmeier equation.
FIGURES

FIG. 1. Convergence achieved on the calculated phonon dispersion curves of cubic BaTiO$_3$ along the Γ-R line. The open symbols correspond to $q$-points included in the M1 (circle) and M2 (circle+square) meshes used to extrapolate the curves (M1: dotted lines; M2: full lines). The filled symbols are associated to points not included in the mesh: they illustrate that a satisfactory convergence is obtained with the M2 mesh.

FIG. 2. Calculated phonon dispersion curves of cubic BaTiO$_3$ at the experimental lattice constant. The theoretical result shows a reasonable agreement with the experimental data: (●) Ref. [3], (○) Ref. [6], (+) Ref. [7], (□) Ref. [8], (×) Ref. [9], (∇) Ref. [10], (△) Ref. [11].

FIG. 3. Zero-frequency isosurface of the lowest unstable phonon branch over the Brillouin zone. Γ is located at the center of the cube. The mode is unstable in the region between the nearly flat surfaces.

FIG. 4. Lowest eigenvalue of the restricted force constant matrix associated to atomic displacements along a finite Ti-O chain of increasing size.
TABLES

TABLE I. Born effective charges and optical dielectric constant of cubic BaTiO$_3$ at the experimental volume [27].

|       | Experiment | Present | Zhong et al.$^c$ |
|-------|------------|---------|-----------------|
| $Z_{Ba}^*$ | $+2.9^a$ | $+2.74$ | $+2.75$ |
| $Z_{Ti}^*$ | $+6.7^a$ | $+7.32$ | $+7.16$ |
| $Z_{O\perp}^*$ | $-2.4^a$ | $-2.14$ | $-2.11$ |
| $Z_{O\parallel}^*$ | $-4.8^a$ | $-5.78$ | $-5.69$ |
| $\epsilon_{\infty}$ | $5.40^b$ | $6.75$ | $-$ |


$^a$ Reference [28]

$^b$ Reference [32]

$^c$ Reference [29]

TABLE II. Computed phonon frequencies (cm$^{-1}$) of cubic BaTiO$_3$ at Γ, X, M and R. Symmetry labels follow the convention of Ref. [33].

| $q$-point | label | frequency | label | frequency |
|----------|------|-----------|------|-----------|
| Γ        | $\Gamma_{15}$ (TO) | 219 | i | $\Gamma_{25}$ | 281 |
|          | $\Gamma_{15}$ (A) | 0 | | $\Gamma_{15}$ (LO) | 445 |
|          | $\Gamma_{15}$ (LO) | 159 | | $\Gamma_{15}$ (TO) | 453 |
|          | $\Gamma_{15}$ (TO) | 166 | | $\Gamma_{15}$ (LO) | 631 |
| X        | $X_5$ | 189 | i | $X_3$ | 322 |
|          | $X_{5\prime}$ | 104 | | $X_{5\prime}$ | 330 |
|          | $X_{2\prime}$ | 146 | | $X_5$ | 421 |
|          | $X_5$ | 194 | | $X_1$ | 517 |
|          | $X_1$ | 260 | | $X_{2\prime}$ | 627 |
| M        | $M_{3\prime}$ | 167 | i | $M_5$ | 344 |
|          | $M_{2\prime}$ | 103 | | $M_2$ | 354 |
|          | $M_{5\prime}$ | 104 | | $M_{5\prime}$ | 435 |
|          | $M_3$ | 208 | | $M_1$ | 456 |
|          | $M_{5\prime}$ | 270 | | $M_4$ | 683 |
|          | $M_{3\prime}$ | 333 | |
| R        | $R_{15}$ | 128 | | $R_{25\prime}$ | 386 |
|          | $R_{25}$ | 182 | | $R_{15}$ | 414 |
|          | $R_{12\prime}$ | 314 | | $R_{2\prime}$ | 717 |
### TABLE III. Longitudinal (∥) and transverse (⊥) interatomic force constants (Ha/Bohr²) with respect to a reference Ti atom (Ti(0)) along the Ti-O chain of cubic BaTiO₃.

| Atom | Total force | DD force | SR force |
|------|-------------|----------|----------|
| Ti(0) | +0.15215 | −0.27543 | +0.42758 |
| O∥(1) | +0.00937 | +0.23247 | −0.22310 |
| Ti∥(2) | −0.06721 | −0.03680 | −0.03041 |
| O∥(3) | +0.01560 | +0.00861 | +0.00699 |
| Ti∥(4) | −0.00589 | −0.00460 | −0.00129 |
| O⊥(1) | −0.02114 | −0.04298 | +0.02184 |
| Ti⊥(2) | +0.00751 | +0.01840 | −0.01089 |

### TABLE IV. Ti-Ti longitudinal interatomic force constants (Ha/Bohr²) with respect to a reference Ti atom at (.5, .5, .5).

| coordinate | distance | IFC | DD part | SR part |
|------------|----------|-----|---------|---------|
| (.5, .5, .5) | 0.0000 | +0.15215 | −0.27543 | +0.42758 |
| (-.5, .5, .5) | 7.5589 | −0.06721 | −0.03680 | −0.03041 |
| (-.5, -.5, .5) | 10.6899 | −0.01114 | −0.01301 | +0.00187 |
| (-.5, -5, -.5) | 13.0924 | −0.00643 | −0.00780 | +0.00065 |
| (-1.5, .5, .5) | 15.1178 | −0.00589 | −0.00460 | −0.00129 |

### TABLE V. O-O longitudinal interatomic force constants (Ha/Bohr²) with respect to a reference O atom at (.5, .5, 0).

| coordinate | distance | IFC | DD part | SR part |
|------------|----------|-----|---------|---------|
| (.5, .5, 0) | 0.0000 | +0.12741 | −0.35322 | +0.48062 |
| (.5, 0, .5) | 5.3450 | −0.02838 | −0.03367 | +0.00529 |
| (-.5, .5, 0) | 7.5589 | −0.00190 | −0.00314 | +0.00124 |
| (.5, .5, -1) | 7.5589 | −0.03212 | −0.02295 | −0.00918 |
| (-.5, 0, .5) | 9.2577 | −0.00183 | −0.00111 | −0.00179 |
| (-.5, -.5, 0) | 10.6899 | −0.00290 | −0.00340 | −0.00078 |
| (-.5, 1, -.5) | 10.6899 | −0.00415 | −0.00340 | −0.00078 |
| (.5, -1, -.5) | 11.9517 | −0.00254 | −0.00246 | −0.00008 |
| (-.5, -5, -1) | 13.0924 | −0.00113 | −0.00129 | +0.00016 |
Smallest eigenvalue of the force constant matrix (a.u.) vs. Chain length (atom)

- [Ti-O]_n-Ti chain
- [Ti-O]_n chain
- [O-Ti]_n-O chain