Analysis of soft optical modes in hexagonal BaTiO$_3$: transference of perovskite local distortions

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We have performed detailed first-principles calculations to determine the eigenvectors of the zone-center modes of hexagonal BaTiO$_3$ and shown that the experimentally relevant low-energy modes (including the non-polar instability) can be represented as suitable combinations of basic local polar distortions associated with the instability of the cubic perovskite phase. The hexagonal structure provides a testing ground for the analysis of the influence of the stacking of TiO$_6$ octahedra: the occurrence of relatively high-energy chains of dipoles highlights the importance of local effects related to the coherent hybridization enhancement between Ti and O ions. Our results provide simple heuristic rules which could be useful for the analysis of related compounds.

Barium titanate has two structural polymorphs: the cubic perovskite type (c-BT) and its hexagonal modification (h-BT) with six formula units per unit cell. While c-BT has been one of the best studied ferroelectric materials for decades [1], most of the work on the structural and dielectric properties of h-BT is quite recent [2]. As shown in Fig. 1, h-BT is also composed of TiO$_6$ groups, albeit with a different stacking than the perovskite form. It seems well established that the hexagonal polymorph undergoes two zone-center structural phase transitions: at 222 K from the high temperature $P6_3/mmc$ hexagonal phase to a second non-polar $C222_1$ phase, and at 74 K to a ferroelectric $P2_1$ phase. The first transition is associated with the softening of an optical mode and the second attributed to a shear strain instability; but a detailed analysis is lacking due to the absence of structural information on the two low-symmetry phases, and little is known about the microscopic origin of the instabilities.

On the other hand, the discovery of a giant LO-TO splitting in h-BT by Inoue et al. [3] suggested that its ferroelectric modes have the same origin as those of c-BT. In the cubic phase the ferroelectric instabilities can be essentially described as chains of dipoles that originate in the movement of Ti ions relative to their surrounding O$_6$ octahedra with a minor distortion of the later. Additional evidence in support of this view is provided by the successful use of polar local modes by Zhong et al. [4] in the construction of an effective Hamiltonian for c-BT. In view of the basic structural similarities between the cubic and hexagonal forms of BaTiO$_3$, it is meaningful to ask whether the local modes that describe the unstable branches in c-BT can somehow be transferred to h-BT and serve as a basis to discuss the low-energy distortions of the structure.

Here we show the results of first-principles calculations that provide for the first time structural information on the low-symmetry phases of the hexagonal polymorph of BaTiO$_3$ and reveal the microscopic nature of the modes. Our analysis proves that the structure of the experimentally found zone-center optical soft modes in h-BT is indeed characterized by the same distortions of the TiO$_6$ octahedra that are relevant in c-BT, leading to similar chains of dipoles in the hexagonal structure.

In h-BT, the experimentally found optical soft modes are: the zone-center instability that drives the phase transition at 222 K and transforms according to the $E_{2u}$ irreducible representation (irrep) of 6/mmm, and the $A_{2u}$ ferroelectric mode that softens (though remaining stable) in the temperature range of the $C222_1$ phase and is responsible for the giant LO-TO splitting. Our calculations agree with this experimental evidence. We performed a full ab-initio relaxation of the thirty-atom h-BT structure, resulting in lattice parameters $a=10.68$ and $c=26.053$ a.u. (to be compared with experimental values of 10.77 and 26.451 [5], respectively). The five free internal coordinates are also in excellent agreement with the experimentally determined ones (within 1%). After computing the force-constant matrix at Γ and diagonalizing it within the subspaces of the appropriate symmetries, we found an unstable $E_{2u}$ mode [6] and a soft but not unstable $A_{2u}$ mode. It should be noted that if the calculations are performed using the experimental lattice parameters (i.e., at a larger cell volume), the $A_{2u}$ mode is found to be unstable (and the $E_{2u}$ instability is more pronounced). The fact that the $A_{2u}$ mode is very close to being unstable could be particularly relevant for the phase transition at 74 K.

A first analysis of the eigenvectors for both soft modes reveals that the Ba contribution is small (around 10% of the total mode norm, compared to 4% in the perovskite soft mode). Moreover, we checked that if the Ba ions are frozen at their high-symmetry positions the modes are...
still soft, so we do not consider them the following discussion, and focus on the distortions of the TiO$_6$ groups.

To make the comparison to the perovskite quantitative, let us consider the polar deformations of the TiO$_6$ groups of c-BT. These are shown in Fig. 2 where we assume that the Ti ion is located at the origin of coordinates, so only the displacement patterns of the O ions need to be considered. For each spatial direction $a = x, y, z$ we have two symmetry-adapted distortions denoted by $s_{1a}$ and $s_{2a}$, and transforming according to $T_{1u}$ (vector like) irrep of $m3m$, the point group of the regular octahedra of c-BT. In terms of this basis, the tetragonal ferroelectric distortion in c-BT (along $x$ for concreteness) can be written as $0.69s_{1x} + 0.73s_{2x}$, with the distorted octahedra exhibiting point group symmetry 4mm [9]. In h-BT there are two kinds of octahedra: those centered around Ti ions at 2$a$ Wyckoff positions with 3$n$ point symmetry (denoted by TiO$_6$(1) in Fig. 1) and those arranged around Ti ions at 4$f$ Wyckoff positions with 3$n$ point symmetry (TiO$_6$(2) in the figure) [10]. The octahedra in the first set are coordinated in the same way as in c-BT, i.e., by sharing O ions with six other octahedra. Those in the second set are linked to other 1+3 octahedra by sharing one O$_3$ face and single O ions respectively.

Due to the low (as compared to the case of c-BT) symmetry of the octahedra in h-BT, their distortions associated to general $E_{2u}$ and $A_{2u}$ modes can be decomposed in a relatively large number of symmetry-adapted displacement patterns. Among all the possible ones, we restrict ourselves to those of c-BT type and check if they can actually account for the structure of the soft modes [11]. For instance, a general $A_{2u}$ distortion leads the crystal to a phase with space group $P6_3mc$, in which the TiO$_6$(1) groups reduce their point symmetry to 3$n$ (see Table 1). As shown in Fig. 1b, c-BT distortions in the $s_{1x} = s_{iy} = s_{iz}$ component combination (Ti ions move towards O$_3$ faces as in the rhombohedral phase of c-BT) produce this symmetry breaking. In the case of an $E_{2u}$ distortion, TiO$_6$(1) reduces its point symmetry to 2, and the appropriate c-BT mode has the form $s_{iz} = -s_{iy}$ (orthorhombic), as shown in Fig. 1c.

For the two soft modes of h-BT, we considered separately the various classes of octahedra, computed from our ab-initio eigenvectors the displacement of the O ions relative to the Ti ion, and performed a projection of the resulting distortion field into the c-BT type symmetry-adapted modes. The results (last column of Table 1) present two main features: First, almost 100% of the total structural change associated with both soft modes can be described in terms of the c-BT type polar distortions (normalization is chosen in such a way that, for instance, for the first row in Table 1 we have $(0.62^2 + 0.78^2) \times 100 = 99.3\%$). Second, the components $s_{1}$, $s_{2}$ are always similar in magnitude to those of c-BT ($0.69:0.73$) and present a positive $s_{1}/s_{2}$ ratio, which implies that the O$_6$ octahedral cage moves almost rigidly relative to the Ti ion also in h-BT. We have also computed the Born effective charge associated with the ferroelectric $A_{2u}$ soft mode and found it unusually large ($Z^* = 11.29$), further confirming the relation with the (rhombohedral) ferroelectric instability of c-BT (for which $Z^* = 9.956$) [12].

We have proved then that at a local level the soft modes in h-BT can be described by the same distortion vectors that determine the c-BT polar instability. In the crystal as a whole, these local polar distortions lead to chains of dipoles, which points at the $E_{2u}$ instability and the softness of the $A_{2u}$ mode of h-BT as being caused by Coulomb destabilizing forces, as it happens in the cubic perovskite. The ferroelectric $A_{2u}$ soft mode, polarized along $z'$, is roughly depicted in Fig. 1. In the $E_{2u}$ distortion the chains of dipoles lay on the $x'y'$ plane and alternate in orientation with a zero net polarization (the resulting C222$_1$ phase could be informally considered anti-ferroelectric rather than paraelectric).

From first-principles studies of the c-BT phase it is known that parallel dipole chains are very weakly coupled, so that a transverse modulation of a chain-like instability is not energetically relevant, and, therefore, unstable TO normal modes exist almost in the whole Brillouin Zone (BZ) [13]. [The only exception are $k$ points near $k_R = \pi(1,1,1)$, for which we have an anti-phase modulation of the Ti displacements (Ti$\rightarrow$O$\leftarrow$Ti$-$O) in the three spatial directions, so the long-range destabilizing forces are always canceled.] If this view is taken to its logical conclusion, we could expect to find more zone-center soft modes in h-BT, corresponding to the other possible distributions of chains of dipoles. Table 1 enumerates all the possibilities. Apart from the already discussed $A_{2u}$ and $E_{2u}$ modes, our ab-initio calculations show that there is one $E_{1g}$ mode that is indeed rather low in energy, while the ferroelectric $E_{1u}$ and the $E_{2g}$ modes that are dominated by the movement of Ti ions are quite hard. In order to explain this result, let us remark that for the $E_{2u}$ and $A_{2u}$ soft modes the distortion is such that if an O ion is approached by one of its two Ti neighbors the second Ti ion moves away from it. This reflects the hybridization of the Ti 3$d$ and O 2$p$ electronic states, which has been shown to be essential for the occurrence of the c-BT ferroelectric instability [14]. It can be checked that any other zone-center arrangement of the chains of dipoles results in either two Ti ions approaching one O ion (for example, if the two Ti ions in one of the O$_3$--Ti--O$_3$--Ti--O$_3$ groups depicted in Fig. 1 move in the same way in the $x'y'$ plane, there is at least one oxygen of the shared face that is approached by both) or in the second titanium not moving away from an oxygen. In the former case ($E_{1u}$ and $E_{2g}$) the effect of the hybridization is lost and the corresponding modes are hard. In the latter ($E_{1g}$ and $B_{1g}$), the hardening is not as strong. Thus, we conclude that the particular stacking of the TiO$_6$ groups in h-BT causes (through this local effect) the relatively high energy of some chain-like dis-
tortions. We can then formulate two “rules of thumb” for the characterization of a given locally polar distortion as low-energy: First (R1): “There need to be chains of dipoles (without regard for their transverse modulation)”. Second (R2): “The distribution of such chains must lead to a coherent hybridization enhancement between Ti and O ions, where the word coherent means that the destabilizing effect is lost when two Ti ions approach the same O ion”. These heuristic rules could be used to predict the occurrence of locally polar soft modes at other \( k \) points of the BZ of h-BT, as well as in other structures with TiO\(_6\) octahedra as basic building blocks.

In summary, first-principles calculations of the character of the zone-center modes of hexagonal BaTiO\(_3\) support the physically appealing idea that the experimentally relevant soft modes (including the non-polar instability) can be represented as combinations of local polar distortions transferred directly from the cubic perovskite form of the compound. Our results lead also to heuristic rules that provide insight into the influence of the arrangement of TiO\(_6\) octahedra on the low-energy dynamics of a structure [15].

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[5] We use the term soft to refer to instable modes as well as low-energy (though maybe stable) modes.

[6] We have used the local-density approximation and the pseudopotential approach with Vanderbilt’s ultrasoft pseudopotentials. The electron wave functions were expanded in a plane wave basis with an energy cut-off of 25 Rydberg, and the BZ sums were calculated by a \( 3 \times 3 \times (2(+0.5)) \) Monkhorst-Pack special \( k \)-point mesh.

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[8] A complete ab-initio study of the energy surface corresponding to the \( E_{2u} \) instability can be found in J. Íñiguez, A. García, and J.M. Pérez-Mato, to appear in Ferro-electrics.

[9] A rhombohedral distortion (3\( m \)) would be represented by equal amplitudes of the three components of \( \hat{s}_1 \), and \( \hat{s}_2, \) (maintaining the same (0.69, 0.73) mix), and an orthorhombic one (222) by equal amplitudes for two of the components and zero for the third.

[10] In this case, the octahedra exhibit a polar distortion even in the \( P6_3/mmc \) phase of h-BT: both Ti ions in a \( O_3-Ti-O_3-Ti-O_3 \) set are displaced along \( z' \) towards the \( O_3 \) faces on the side (which agrees with the R2 heuristic rule in the text), producing two opposite local dipoles and no net polarization.

[11] It can be proven (by group-theoretical considerations) that polar distortions located at both 2\( a \) and 4\( f \) Wyckoff positions produce zone-center modes of the desired symmetries.

[12] Born effective charges are calculated following the Berry’s phase approach as in W. Zhong, R.D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. 72, 3618 (1994).

[13] Ph. Ghosez, E. Cockayne, U. V. Waghmare, and K.M. Rabe, Phys. Rev. B 60, 836 (1999). For example, the modulation given by \( \mathbf{k}_X = \frac{\pi}{a}(1,0,0) \) is compatible with chains of dipoles polarized along \( y \) and \( z \) directions, so two (degenerate) instabilities exist at \( \mathbf{k}_X \).

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[15] A more detailed account of the work presented here, as well as other results (such as the existence of a previously unreported zone-center soft Rigid Unit Mode) will be presented elsewhere.
Table I. Symmetry breakings of the h-BT phase TiO\(_6\) groups associated to the \(A_{2u}\) and \(E_{2u}\) soft modes. The fourth column shows the combinations of symmetry-adapted c-BT type distortions that are compatible with the symmetry reduction (it applies to both \(s_1\) and \(s_2\)). The last column shows the projections of the normalized total distortion of the TiO\(_6\) groups onto the \(\hat{s}_{i,\alpha}\) modes of the second column, in the form \(s_{x,1};s_{y,2}\). The \(E_{2u}\) mode removes all symmetry elements from the TiO\(_6\) (2) octahedra, and any combination of \(s_{\alpha}\) is possible. For this case we have listed in the last column the \(s_{x,1};s_{y,2}\) projections along each of the three spatial directions as well as the modulus.

Table II. Symbolic description of the possible zone-center chains of dipoles in h-BT, classified in terms of irreps of \(6/mmm\). The layers of Ti ions are represented along the \(z'\) direction as in Fig. 1. (Ti(1) and Ti(2) refer to Ti ions in TiO\(_6\) (1) and TiO\(_6\) (2) groups respectively). Arrows indicate the orientation of the dipoles (horizontal ones symbolize any direction in the \(x'y'\) plane), and those set in the same type are symmetry related. The superscript \(f\) marks the ferroelectric modes. Displacement patterns that violate \(R2\) (see text) are marked with an asterisk. The bottom line shows the mode force constants in atomic units (for \(B_{1g}\) an unambiguous assignment cannot be made).