FIRST-PRINCIPLES STUDY OF THE STRUCTURAL INSTABILITIES IN HEXAGONAL BARIUM TITANATE: COUPLING BETWEEN THE SOFT OPTICAL AND THE ACOUSTIC MODES

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Abstract Hexagonal BaTiO$_3$ undergoes a structural phase transition to an orthorhombic $C_{2221}$ phase at $T_0 = 222$ K. The transition is driven by a soft optical mode with $E_{2u}$ symmetry whose couplings force the appearance of a spontaneous $E_{2g}$ strain (improper ferroelastic character). Staying within the same $E_{2u}$ subspace, the system could in principle settle into a second (not observed) orthorhombic phase ($C_{mc21}$). We have carried out a first-principles investigation of these questions, studying the structure of the existing $C_{2221}$ and the virtual $C_{mc21}$ phases, and describing the spontaneous $E_{2g}$ strain in accord with the experimental observations. In addition, we show that the occurrence of $C_{2221}$ instead of $C_{mc21}$ cannot be explained by the $E_{2u}$ soft modes themselves and, therefore, must be related to their couplings with secondary order parameters. A more detailed analysis proves that the $E_{2g}$ strains do not account for the experimental preference.

Keywords: hexagonal barium titanate, structural phase transitions, first-principles

INTRODUCTION

Barium titanate has two structural polymorphs: the well known per-
ovskite type (p-BT) and its hexagonal modification (h-BT) with 30 atoms per unit cell. h-BT Undergoes two zone-center structural phase transitions: at $T_0 = 222$ K from the hexagonal $P6_3/mmc$ phase (I) to an orthorhombic $C222_1$ (II), and at $T_C = 74$ K to a monoclinic $P2_1$ phase (III).\[1\] The transition at $T_0$ presents two specially interesting features:

- It is driven by a “silent” soft optical mode of $E_{2u}$ symmetry,\[2\] coupled quadratically to the $E_{2g}$ acoustic modes (strains) $\eta_1 - \eta_2$ and $\eta_6$, which spontaneously acquire non-zero values at the transition.\[3\] In the usual terminology, the transition is then improper ferroelastic. The coupling of the $E_{2g}$ modes with the soft optical modes has been studied spectroscopically.\[4,5\]

- Depending on the direction taken by the bidimensional $E_{2u}$ order parameter, the system can find itself in structures of three different symmetries: the experimentally observed $C222_1$ and $P2_1$, as well as a second orthorhombic $Cmc2_1$ phase (II'). The preference of II over II' must ultimately be dictated by the energetics of the $E_{2u}$ instability and by its couplings with secondary order parameters.

In this paper we present a summary of the results of our investigation into the $E_{2u}$ optical instability in h-BT, including its couplings with the spontaneous $E_{2g}$ strains, and into the issue of the relative stability of the two accessible orthorhombic phases, using first-principles density-functional methods. To our knowledge, this is the first ab initio study of hexagonal BaTiO$_3$.

**TECHNICAL DETAILS**

For our calculations we have used density-functional theory within the pseudopotential approach and the local-density approximation.\[6\] We have employed Vanderbilt’s ultrasoft pseudopotentials,\[7\] which are ideally suited to deal with first-row elements and transition metals. The electron wave functions were expanded in a plane wave basis with an energy cut-off of 25 Rydberg, and the Brillouin zone sums were calculated by a $3 \times 3 \times (2(+0.5))$ Monkhorst-Pack special k-point mesh.\[8\] We checked the validity of these approximations
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by a convergence analysis. This first-principles framework has been successfully used for the investigation of structural properties in perovskite oxides.

RESULTS AND DISCUSSION

In order to proceed, the reference hexagonal structure must be determined. In I the occupied Wyckoff positions are fixed by symmetry up to five free parameters. We used the systematic procedure of Ref. [10] to relax these five $A_{1g}$ optical modes so that the forces on atoms were below $10^{-4}$ eV·bohr$^{-1}$. Our results for the fractional atomic coordinates agree with experiment [11] to within 0.6%. Due to the high computational cost of a complete analysis, we used the experimental values for the unit cell parameters ($a = 10.77$ bohr and $c/a = 2.456$).

In what follows we work with a symmetry-adapted Taylor expansion of the potential energy of the system around the reference structure, as a function of the above mentioned relevant variables: the $E_{2u}$ soft optical and the $E_{2g}$ acoustic modes. It is convenient to decompose this expansion into:

$$E - E_1 = E_{\text{optical}} + E_{\text{strain}} + E_{\text{coupling}},$$

where $E_1$ is the energy of the reference structure I.

As a pre-requisite for the study of $E_{\text{optical}}$, we needed to check that the $ab\text{ initio}$ methods predict the experimentally observed instability. We solved the associated eigenvalue problem (there are seven zone center $E_{2u}$ symmetry modes) and indeed found only one instability with spring constant $-0.743$ eV·bohr$^{-2}$. (We consider the Fourier transform of the so called force-constant-matrix and not the dynamical matrix.) The corresponding (degenerate) eigenvectors determine the unstable two-dimensional subspace. Using as coordinates the respective amplitudes in polar form ($Q_1 =: r\cos\varphi$ and $Q_2 =: r\sin\varphi$), we can write:

$$E_{\text{optical}} = \frac{1}{2}A_2r^2 + \frac{1}{4}A_4r^4 + \frac{1}{6} [A_6 + A_6'(6\varphi)]r^6,$$
where $\varphi = \{0, \pm \pi/3, \pm 2\pi/3, \pi\}$ and $\varphi = \{\pm \pi/6, \pm \pi/2, \pm 5\pi/6\}$ correspond to II and II' respectively, while for a general $\varphi$ the system is in III. Eq. (2) shows that the sign of $A'_6$ determines the relative stability of the orthorhombic minima (with $A_2 < 0$).\footnote{For the energetic analysis of the monoclinic phases, higher order terms should be considered.}

![Graph](image)

FIGURE 1: Potential energy well of the $E_{2u}$ instability of I, in the $\varphi = 0$ direction (corresponding to II). The ab initio data is fitted to a quartic and $E_1$ is set to zero.

Figure (I) shows $E_{\text{optical}}$ as a function of $r$ with $\varphi = 0$, the case of II. (The data for II' are identical at the scale of the figure). In order to model these data, two facts must be taken into account. First, quadratic ($A_2$) and quartic ($A_4$) terms are symmetry-forced to be the same in both phases. Second, the fitted $A_2$ must be in good accord with the previously obtained eigenvalue. We determined: $A_2 = -0.72 \pm 0.02$ eV·bohr$^{-2}$ and $A_4 = 2.56 \pm 0.07$ eV·bohr$^{-4}$, with the energy minima in $|r_{\text{min}}| = 0.52 \pm 0.01$ bohr ($E_{\text{min}} = -50 \pm 4$ meV). We could obtain no convincing fitting for the $O(r^6)$ term and thus concluded that the quartic approximation constitutes the best model to describe the $E_{2u}$ instabilities, i.e., the soft modes themselves cannot account for the differences between the II and II' minima, so their couplings with secondary order parameters must be responsible for the experimental observation of II.

This calculation constitutes a prediction of the structural parame-
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ters of the orthorhombic $C22_1$ phase, which to our knowledge has not yet been determined experimentally. (Further details about the structure will be published elsewhere.)

Turning to the pure elastic energy term in Eq.(2), it is convenient to use polar coordinates also for the $E_{2g}$ strains ($\eta_1 - \eta_2 =: \rho \cos \phi$ and $\eta_6 =: \rho \sin \phi$), and write:

$$E_{\text{strain}} = C_2 \rho^2 + C_3 \cos(3\phi) \rho^3. \quad (3)$$

For a general $\phi$ the system is distorted to III (due to $\eta_6$), while for $\phi = \{0, \pi\}$ it goes to $Cmcm$, which is a supergroup of both II and II', so $\eta_1 - \eta_2$ is the only secondary order parameter we take into account. We studied the response of the system to this strain with the optical phonon amplitudes set to zero (and imposing $\eta_1 + \eta_2 = 0$, so that only deformations with $E_{2g}$ symmetry are considered), and concluded that the best model reduces to $C_2 = 130 \pm 2$ eV. (The $O(\rho^3)$ term cannot be reliably fitted.)

Finally, we examined the coupling between the $E_{2u}$ soft optical and the $E_{2g}$ acoustic degrees of freedom, considering:

$$E_{\text{coupling}} = E_{\text{coupling}}^{(1)} + E_{\text{coupling}}^{(2)}$$

$$E_{\text{coupling}}^{(1)} = \alpha_{12} \cos(2\varphi + \phi) \rho r^2$$

$$E_{\text{coupling}}^{(2)} = \left\{ \alpha_{14} \cos(2\varphi + \phi) + \beta_{14} \cos(4\varphi + \phi) \right\} \rho r^4$$

$$+ \left\{ \alpha_{22} + \beta_{22} \cos[2(\varphi - \phi)] \right\} \rho^2 r^2$$

$$+ \left\{ \alpha_{24} + \beta_{24} \cos[2(\varphi - \phi)] + \gamma_{24} \cos[2(2\varphi - \phi)] \right\} \rho^2 r^4. \quad (4)$$

The first term $E_{\text{coupling}}^{(1)}$ is the simplest form of coupling usually considered in the literature, and indeed it provides us with a very good fit of the ab-initio energies in the presence of $E_{2g}$ distortions (for both the II and II' phases). Figure (2) shows the main result of including this minimal strain coupling into the energy analysis: the minima shift their positions and get deeper. As table (1) shows, the configurations of minimum energy are located at $|r_{min}| = 0.55 \pm 0.01$ bohr, and the associated spontaneous strain is $\rho_{min} = (5.6 \pm 0.2) \times 10^{-3}$ with $\phi = 0$ and $\pi$ for II and II' respec-
tively. We found no experimental measurement of the $\alpha_{12}$ parameter; nevertheless, its sign is correct as compared with results in Ref. 14. The location of the wells provides us with a more complete (this time including strain) prediction of the structure of the orthorhombic phase.

![Energy map of II](image)

**FIGURE 2:** $(r, \rho)$ Energy map of II. We show the equi-energy lines of a model in which only the $A_2$, $A_4$ and $C_2$ terms (with the values of the text) are present (dashed) and those corresponding to the fit in table (solid). Energies are given in meV and $E_I$ is set to zero.

However, as the well depths are within this minimal model identical for both II and II', we still have found no reason for Nature’s preference for the first. To further analyze this issue, we included $E^{(2)}_{\text{coupling}}$ in Eq. (1) in our fitting procedure and found that only the $O(\rho^3 r^4)$ terms improve the model. We got $\alpha_{24} + \beta_{24} + \gamma_{24} = 7.3 \pm 0.2$ eV·bohr$^{-4}$ for II and $\alpha_{24} - \beta_{24} + \gamma_{24} = 7.9 \pm 0.2$ eV·bohr$^{-4}$ for II', but the difference is so small that it produces no definite distinction between the two minima. Thus, it can be concluded that neither the $E_{2u}$ instability itself nor its coupling with $E_{2g}$ strains justify the existence of II instead of II'.

**CONCLUSIONS**

We have presented a first-principles study on the stability of hexag-
TABLE 1: Best fits for Eq.(1) when only a minimal coupling ($\alpha_{12}$ term) is considered in the model. We present the fits corresponding to II and II$'$ separately (so that the fulfillment of symmetry restrictions can be observed), plus a final result (II & II$'$) including aggregate data for the two phases. In all cases, parameters $A_2$ and $A_4$ were fixed to the values in the text. The quality of the fits is highly sensitive to small variations in $C_2$, so we left it free (the obtained results are within the error of our initial estimation).

We have shown that first-principles calculations are able to predict the experimentally observed zone center $E_{2u}$ soft optical and the $E_{2g}$ acoustic modes.

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