Born effective charges of Barium Titanate: band by band decomposition and sensitivity to structural features

Ph. Ghosez*, X. Gonze*, Ph. Lambin† and J.-P. Michenaud*

*Unité PCPM, Université Catholique de Louvain, B-1348 Louvain-La-Neuve, Belgium
†Département de Physique, Facultés Universitaires Notre Dame de la Paix, B-5000 Namur, Belgium

(March 30, 2022)

Abstract

The Born effective charge tensors of Barium Titanate have been calculated for each of its 4 phases. Large effective charges of Ti and O, also predicted by shell model calculations and made plausible by a simplified model, reflect the partial covalent character of the chemical bond. A band by band decomposition confirms that orbital hybridization is not restricted to Ti and O atoms but also involves Ba which appears more covalent than generally assumed. Our calculations reveal a strong dependence of the effective charges on the atomic positions contrasting with a relative insensitivity on isotropic volume changes.

PACS numbers: 77.84.Dy, 77.22.Ej, 71.25.Tn
Barium Titanate (BaTiO$_3$) is a well known ferroelectric compound [1]. Its structure, cubic perovskite at high temperature, becomes tetragonal around 120$^\circ$C, orthorhombic at about 0$^\circ$C and rhombohedral near -70$^\circ$C. Although it is probably one of the most studied ferroelectric crystal [1], the mechanism of its phase transitions is still subject of controversy [2]. The character of the chemical bonding also remains questionable [3].

The Born effective charge $Z^*$ is a fundamental quantity for the study of lattice dynamics, controlling the long range Coulomb part of the force constants. An estimation of $Z^*$ for three ABO$_3$ compounds was first proposed by Axe [4] on the basis of a phenomenological theory. However, the crude hypothesis inherent in his procedure only allowed an approximate estimation of these charges and restricted his investigations to the cubic phase. New advances in “ab initio” techniques now enable one to determine $Z^*$ theoretically using perturbation theory [5] or finite difference of polarisation [6]. Accurate values have been recently reported by Resta et al. for KNbO$_3$ [7], by ourselves for BaTiO$_3$ [8] and by Zhong et al. [9] for a whole set of ABO$_3$ compounds. These studies underline the surprisingly large values already observed by Axe and generally referred to as “anomalous” charges. For BaTiO$_3$, no attempt was performed to determine how these giant charges are affected by structural details, even if this information could reveal essential for an accurate investigation of lattice dynamics. We will show that $Z^*$ are relatively insensitive to isotropic volume changes but are strongly affected by changes of positions associated to the phase transitions.

Moreover, if obtaining the values of $Z^*$ is already an important result, to understand why some charges are so large also constitutes a fundamental problem. Until now, anomalous charges in ABO$_3$ materials were explained qualitatively in the framework of a bond orbital model, following Harrison [10]. Recently, Posternak et al. [11] elegantly emphasized the role of covalency between Nb and O in KNbO$_3$ from the analysis of giant effective charges. We show here that, in a more general way, a band by band decomposition of $Z^*$ is a sensitive tool to investigate the role of covalency and ionicity without any preliminary hypothesis on the orbitals that interact. Our study helps to clarify the debate on the real nature of the chemical bonding in BaTiO$_3$ and brings out the role of the Ba atom.
We work in the framework of the Density Functional Formalism within the local density approximation [12]. The Born effective charge tensor $Z^*_{\kappa,\gamma\alpha}$ of atom $\kappa$ can be linked either to the change of polarisation $P_\gamma$ induced by the periodic displacement $\tau_{\kappa,\alpha}$, or to the force $F_{\kappa,\alpha}$ induced on atom $\kappa$ by an electric field $E_\gamma$: $Z^*_{\kappa,\gamma\alpha} = V \frac{\partial P_\gamma}{\partial \tau_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial E_\gamma} = -\frac{\partial^2 E}{\partial E_\gamma \partial \tau_{\kappa,\alpha}}$. So, it also appears as a mixed second derivative of the total energy $E$ per unit cell volume $V$, which can be evaluated using the variational approach to Density Functional Perturbation Theory [3,8]. We use the exchange-correlation energy functional and the norm-conserving pseudopotentials of ref. [8]. The Brillouin Zone was sampled with a $6 \times 6 \times 6$ $k$-point set.

The plane-wave basis set was determined by a 35 hartrees energy cutoff which guarantees a convergence better than 0.5% on $Z^*$.

First we investigate the Born effective charges in the cubic structure. Ab-initio values, obtained at the experimental ($a_{cell}=4\AA$) and theoretically optimized ($a_{cell}=3.94\AA$) lattice parameter, as well as those corresponding to a compressed cubic cell ($a_{cell}=3.67\AA$) are reported in Table I. In comparison, we also computed the effective charges from the shell model parameters proposed by Khatib et al. [13].

The charges of Ba and Ti, isotropic owing to symmetry, are equal respectively (at the theoretical volume) to +2.77 and +7.25. For O, the values of $Z^*_{O\parallel}$ (-5.71) and $Z^*_{O\perp}$ (-2.15) refer respectively to a displacement of the oxygen ion along the Ti-O direction or perpendicular to it. Our results are in good agreement with those obtained by Zhong et al. [9] (also at the theoretical volume) from finite difference of polarisation and globally reproduce the values deduced by Axe [4]. The accordance with the shell model is only qualitative and illustrates the limited precision obtained within such an empirical description. We note however that this shell model was not designed to reproduce the dielectric properties of BaTiO$_3$. The large value of $Z^*_T$ (7.51) proves that it implicitly includes covalency effects responsible for anomalous effective charges, as described below.

The charges on Ti and O$_\parallel$ are surprisingly large in the sense that they reach about twice the value they would have in a pure ionic picture: they reveal the presence of a large dynamic contribution superimposed to the static charge. As the latter quantity is ill defined,
determining the dynamic contribution is an ambiguous task. So, in the following, we prefer to speak in terms of anomalous contributions that we define as the additional charge with respect to the well known, ionic value (cfr. first column of Table I).

The physical possibility of obtaining anomalous charges can be understood within a very simplified model. Let us just consider a diatomic molecule XY with an interatomic distance \( u \) and a dipole moment \( P(u) \). The dipole moment enables us to define a static charge \( Z(u) = \frac{P(u)}{u} \) and a dynamic charge \( Z^*(u) = \frac{\partial P(u)}{\partial u} \) also equal to \( Z(u) + u \frac{\partial Z(u)}{\partial u} \). As the distance between X and Y is modified from 0 to some \( \bar{u} \) (the distance corresponding to a complete transfer of electrons from X to Y), the dipole moment evolves continuously from \( P(0) = 0 \) (since there is no dipole for that case) to \( P(\bar{u}) \). Interestingly, \( \int_0^{\bar{u}} Z^*(u)du = [P(\bar{u}) - P(0)] = \bar{u} Z(\bar{u}) \). So, \( \frac{1}{\bar{u}} \int_0^{\bar{u}} Z^*(u)du = Z(\bar{u}) \): the mean value of \( Z^*(u) \) from 0 to \( \bar{u} \) is equal to \( Z(\bar{u}) \). This result guarantees that, if \( Z(u) \) changes with \( u \), \( Z^*(u) \) has to be greater than \( Z(\bar{u}) \) for some \( u \) between \([0, \bar{u}]\). The difference between \( Z(u) \) and \( Z^*(u) \) can be large if \( Z(u) \) changes rapidly with \( u \).

In BaTiO\(_3\), the approximate reciprocity between O\(_\perp\) (-3.71) and Ti (+3.25) anomalous contributions suggests that they correspond to a global transfer of charge from O to Ti when the Ti-O distance shortens. In the framework of the bond orbital model proposed by Harrison \([10]\), the charge redistribution is attributed to a change in the hopping integral produced by dynamic modification of orbital hybridizations. Matching this bond orbital model to the real material ask for the identification of the relevant orbitals.

Hybridization between O 2\(p\) and the unoccupied metal \(d\) orbitals is well known and was already pointed out from experiments \([14]\), tight-binding models \([10]\) and LCAO calculations \([15]\). It was highlighted more recently by Cohen \([3]\) from first-principles as an essential feature of ABO\(_3\) ferroelectric compounds. In this context, it seemed realistic, following Harrison, to focus on O 2\(p\)-Ti 3\(d\) hybridization changes to explain intuitively large anomalous contributions \([3]\). Posternak et al. \([11]\) went beyond this credible assumption. They showed for KNbO\(_3\) that the anomalous contributions disappear when the interaction between the O 2\(p\) and Nb 4\(d\) orbitals is artificially suppressed.
Nothing proves that the conclusions would be the same for BaTiO$_3$ neither that the hybridizations are limited to this kind of $p$-$d$ interactions. Theoretical investigations, confirmed by experimental results \[14\], suggest that Ba also plays a major role in forming the valence band structure. Now, we propose a more detailed investigation, based on a band by band analysis of $Z^*\ [18]$. 

Contrariwise to the total effective charge tensor, the band by band decomposition depends not only on the Hilbert space of occupied valence states but also on the particular valence eigenfunctions. In order to identify the contribution of each band we worked in the “diagonal gauge” \[17\] in which the matrix of the first-order eigenenergies with respect to atomic displacements is diagonal. This is equivalent to associate Wannier functions with each separate set of bands for calculating the polarization \[6,18\].

For a reference configuration in which the contribution to the charge of a given atom is -2 for each band associated to its own orbitals and 0 for the other bands, each Wannier function is centered on a given atom. Within the recent theory of the polarization \[6,18\], the anomalous charge associated to a particular band for a given ion (defined as the additional part with respect to our reference value) reflects how the center of the Wannier function of this band moves with respect to the ion. In a purely ionic crystal, each band would be composed of non hybridized orbitals. As covalency develops, different orbitals mix adding anomalous contributions from several bands.

Results for the theoretical cubic structure are reported in Table I. The first line brings together the charge of the nucleus and the core electrons included in the pseudopotential. The other contributions come from the valence electron levels. Sets of bands were identified by the name of the main atomic orbital which generated this energy level in the solid (Fig. 1). Their dominant character was confirmed by partial density plots. As a check of the coherency of our decomposition, the sum of the contributions of each fully occupied band, obtained independently, is -2 (within ±0.01, the accuracy of our calculation).

As expected, the main $Z^*_T$ anomalous charge is localized on the O 2$p$ bands (+2.86). It can be understood by an hybridization between O 2$p$ and Ti 3$d$ orbitals. Interestingly, there
are also smaller but non-negligible anomalous charges from the Ti 3p (-0.22), O 2s (+0.23) and Ba 5p (+0.36) bands. The different positive contributions correspond to a displacement of the center of the Wannier function of the O and Ba bands in the direction of Ti when this atom moves. The Ti3s contribution is close to -2. This result \textit{a posteriori} justifies the inclusion of deeper levels as part of ionic pseudopotentials.

For $Z_{Ba}^{*}$, the decomposition is more surprising: the small global anomalous effective charge (+0.77) that could be typical of a more ionic character appears partially fortuitous. The anomalous charges of O 2s (+0.73) and O 2p (+1.50) bands are \textit{not} small. Nevertheless, they are partially compensated by Ba 5p (-1.38) and Ba 5s (-0.11) anomalous contributions. This result gives a tangible proof of the hybridization of Ba 5p orbitals already suggested from the experiment [14].

Concerning oxygen, even if O$_{∥}$ and O$_{⊥}$ are defined respectively for a displacement of O in the Ti and Ba direction, it seems only qualitative to associate $Z_{O_{∥}}^{*}$ with $Z_{Ti}^{*}$ and $Z_{O_{⊥}}^{*}$ with $Z_{Ba}^{*}$. The O 2p anomalous contributions to Ti and O$_{∥}$ do not compensate. Moreover, O 2p contribution to $Z_{Ba}^{*}$ not only comes from O$_{⊥}$ but has equivalent contributions coming from O$_{∥}$.

Within this analysis, several bands appear as a complex mixing of orbitals coming from the different ions. In this context, and contrasting with the conclusion of Posternack \textit{et al.} for KNbO$_3$, a correct understanding of the Born effective charge goes here beyond the simple model of Harrison. Our result clarifies the mixed ionic-covalent character of BaTiO$_3$: it clearly establishes that the covalent character is not restricted to the Ti-O bond as generally assumed.

Until now, calculations of $Z^{*}$ essentially focused on the cubic phase [8,9]. On the basis of an investigation of these charges in the experimental tetragonal structure of KNbO$_3$ [7] and PbTiO$_3$ [4], it was argued that they are quite insensitive to structural details. This result is surprising if we remember that anomalous contributions to $Z^{*}$ are closely connected to orbital hybridizations, these in turn, being strongly affected by phase transitions [3]. In addition, the theoretical overestimation of the spontaneous polarization for the rhombohedral structure...
of BaTiO$_3$ also suggests a reduction of $Z^*$ in this phase.

We computed the Born effective charge tensors for the 3 ferroelectric phases at the experimental unit cell parameters [19], with relaxed atomic positions [20]. In this paper, we only comment on the eigenvalues of these tensors (Tables III-IV) that already allow a pertinent comparison with the cubic phase. The $Z^*_{33}$ eigenvalues of Ba and Ti correspond to an eigenvector aligned along the ferroelectric axis. In the case of O, the eigenvector associated to the highest eigenvalue approximately point in the Ti-O direction: we identify this highest contribution as $O_{\parallel}$ while the others are refer as $O_{\perp}$, by analogy with the cubic phase.

Although the charges of Ba and $O_{\perp}$ remain globally the same in the 4 phases, for Ti and $O_{\parallel}$, stronger modifications are observed. Changing the Ti position by 0.076 Å (2% of the unit cell length) when going from the cubic to the rhombohedral phase, reduces the anomalous part of $Z^*_{Ti}$ by more than 50% along the ferroelectric axis (Table III). The amplitude of $Z^*_{Ti}$ and $Z^*_O$ in the direction of the shortest Ti-O bond length $d_{min}$ of each phase is plotted in Fig. 2 with respect to the interatomic distance $d_{min}$. For the different phases at zero pressure, the anomalous parts decrease with $d_{min}$. The comparison with a compressed cubic phase at 3.67 Å in which the Ti-O distance is the same that the shortest Ti-O bond length in the tetragonal structure shows nevertheless that the evolution of $Z^*_{Ti}$ cannot be explained in terms of the Ti-O distance only but is critically affected by the anisotropy of the Ti environment.

This is clear from the band by band decompositions of $Z^*_{Ti}$ in Table IV. While in the cubic structure at 3.67 Å every Ti-O distance is equivalent to the others, in the tetragonal phase, along the ferroelectric axis, a short Ti-O bond length is followed by a larger one which breaks the Ti-O chain in this direction and inhibits the giant current associated to the large effective charges. This appears at the level of the O 2$p$ bands (+1.48 instead of +2.86) while the other contributions remains equivalent to those of the cubic phase at 3.94 Å. Analysis from the cubic structure at 3.67 Å reveals that the O 2$p$ contribution is not significantly affected by hydrostatic pressure; on the other hand, the anomalous parts of the Ba 5$p$, Ba
5s and Ti 3p bands are modified by about 50 % due to the compression.

In this work, we were able to compute the Born effective charges of BaTiO$_3$ in its 4 phases. Effective charges are a sensitive tool for analysing dynamic changes of orbitals hybridizations, especially if a band by band decomposition is performed. In our description Ba appears more covalent than generally assumed. The charges of Ti and O are strongly affected by atomic displacements but quite insensitive to hydrostatic pressure.

We thank Z. Levine, D. C. Allan for sharing some of their routines and J.-M. Beuken for informatic support. X.G. and Ph.L. acknowledge financial support from the FNRS-Belgium. We are grateful to Corning Inc. (M.P. Teter and D.C. Allan) for the availability of the PlaneWave code for ground-state calculations. We used IBM-RS 6000 work stations from common projects between IBM-Belgium, UCL-PCPM and FUNDP.
REFERENCES

[1] M. E. Lines and A.M. Glass, “Principles and Applications of Ferroelectrics and Related Materials.”, Clarendon Press, Oxford (1977).

[2] K. Laabidi et al., Europhys. Lett. 26, 309 (1994).

[3] R. E. Cohen, Nature 358, 136 (1992).

[4] J. D. Axe, Phys. Rev. 157, 429 (1967).

[5] X. Gonze, D.C. Allan and M.P. Teter, Phys. Rev. Lett. 68, 3603 (1992).

[6] R.D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).

[7] R. Resta, M. Posternak and A. Baldereschi, Phys. Rev. Lett. 70, 1010 (1993).

[8] Ph. Ghosez, X. Gonze and J.-P. Michenaud, Ferroelectrics 153, 91 (1994).

[9] Zhong, R.D. King-Smith and D. Vanderbilt, Phys. Rev. Lett. 72, 3618 (1994).

[10] W. A. Harrison, “Electronic Structure and the Properties of Solids, Dover, New-York (1980).

[11] M. Posternak, R. Resta and A. Baldereschi, Phys. Rev. B 50, 8911 (1994).

[12] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).

[13] D. Khatib, R. Migoni, G. E. Kugel and L. Godefroy, J. Phys.: Condens. Matt. 1, 9811 (1989).

[14] V. V. Nemoshkalenko and A. N. Timoshevskii, Phys. Stat. Sol. b127, 163 (1985); L. T. Hudson, R. L. Kurtz, S. W. Robey, D. Temple and R. L. Stockbauer, Phys. Rev. B 47, 1174 (1994).

[15] F. M. Michel-Calendini, H. Chermette and J. Weber, J. Phys. C: Sol. St. Phys. 13, 1427 (1980).
[16] Ph. Ghosez, X. Gonze and J.-P. Michenaud, proceedings of the “Third Williamsburg Workshop on First Principles Calculations for Ferroelectricity” (1994).

[17] X. Gonze, unpublished.

[18] D. Vanderbilt and R. D. King-Smith, Phys. Rev. B 48, 4442 (1993).

[19] A. W. Hewat, Ferroelectrics 6, 215 (1974); G. H. Kwei, A. C. Lawson, S. J. L. Billinge and S.-W. Cheong, J. Phys. Chem. 97, 2368 (1993).

[20] Ph. Ghosez, X. Gonze, Ph. Lambin and J. P. Michenaud, unpublished.
FIGURES

FIG. 1. Electronic band structure of cubic BaTiO$_3$ ($a_{celt}$=3.94Å).

FIG. 2. Born effective charge of Ti (opened symbols) and O (filled symbols) in the direction of the shortest Ti-O bond length $d_{min}$ with respect to this interatomic distance for the cubic (square), tetragonal (lozenge), orthorhombic (circle) and rhombohedral (triangle) phases.
### TABLE I. Born effective charges for cubic BaTiO$_3$.

| Ions     | Axe [4] | Shell Model | Zhong et al. [9] | $a_{cell}=4.00\AA$ | $a_{cell}=3.94\AA$ | $a_{cell}=3.67\AA$ |
|----------|---------|-------------|------------------|---------------------|---------------------|---------------------|
| $Z_{Ba}^*$ | +2      | 2.9         | 1.63             | 2.75                | 2.74                | 2.95                |
| $Z_{Ti}^*$ | +4      | 6.7         | 7.51             | 7.16                | 7.29                | 7.23                |
| $Z_{O_{\perp}}^*$ | -2      | -2.4        | -2.71            | -2.11               | -2.13               | -2.28               |
| $Z_{O_{\parallel}}^*$ | -2      | -4.8        | -3.72            | -5.69               | -5.75               | -5.71               |
TABLE III. Eigenvalues of the Born effective charge tensors of Ba and Ti at the experimental volumes.

| phase          | $Z_{Tt,11}^*$ | $Z_{Tt,22}^*$ | $Z_{Tt,33}^*$ | $Z_{Ba,11}^*$ | $Z_{Ba,22}^*$ | $Z_{Ba,33}^*$ |
|----------------|---------------|---------------|---------------|---------------|---------------|---------------|
| cubic          | 7.29          | 7.29          | 7.29          | 2.74          | 2.74          | 2.74          |
| tetragonal     | 6.94          | 6.94          | 5.81          | 2.72          | 2.72          | 2.82          |
| orthorhombic   | 6.80          | 6.43          | 5.59          | 2.72          | 2.81          | 2.77          |
| rhombohedral   | 6.52          | 6.52          | 5.58          | 2.79          | 2.79          | 2.74          |

TABLE IV. Eigenvalues of the Born effective charge tensors of O at the experimental volumes.

| phase          | $Z_{O1,11}^*$ | $Z_{O2,11}^*$ | $Z_{O3,11}^*$ | $Z_{O1,22}^*$ | $Z_{O2,22}^*$ | $Z_{O3,22}^*$ | $Z_{O1,33}^*$ | $Z_{O2,33}^*$ | $Z_{O3,33}^*$ |
|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| cubic          | -2.13         | -2.13         | -2.13         | -2.13         | -2.13         | -2.13         | -5.75         | -5.75         | -5.75         |
| tetragonal     | -1.99         | -1.95         | -1.95         | -1.99         | -2.14         | -2.14         | -4.73         | -5.53         | -5.53         |
| orthorhombic   | -1.91         | -1.91         | -1.97         | -2.04         | -2.04         | -2.01         | -4.89         | -4.89         | -5.44         |
| rhombohedral   | -1.97         | -1.97         | -1.97         | -1.97         | -1.97         | -1.97         | -5.03         | -5.03         | -5.03         |
Ghosez et al., Fig. 1
Ghosez et al., Fig. 2

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.png}
\end{figure}