

Born effective charges of barium titanate: Band-by-band decomposition and sensitivity to structural features

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The Born effective charge tensors of barium titanate have been calculated for each of its four phases. Large effective charges of Ti and O, also predicted by shell-model calculations and made plausible by a simplified model, reflect the partly 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.

Barium titanate (BaTiO_3) is a well known ferroelectric compound.¹ Its structure, cubic perovskite at high temperature, becomes tetragonal around 120 °C, orthorhombic at about 0 °C, and rhombohedral near -70 °C. Although it is probably one of the most studied ferroelectric crystals,¹ the mechanism of its phase transitions is still a 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 proposed by Axe⁴ 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. Advances in *ab initio* techniques now enable one to determine Z^* theoretically using perturbation theory⁵ or finite difference of polarization.⁶ Accurate values have been recently reported by Resta, Posternak, and Baldereschi for KNbO_3 ,⁷ ourselves for BaTiO_3 (Ref. 8), and 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 be revealed as 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 quali-

tatively in the framework of a bond orbital model, following Harrison.¹⁰ Recently, Posternak, Resta, and Baldereschi¹¹ 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 κ can be linked either to the change of polarization P_γ induced by the periodic displacement $\tau_{\kappa,\alpha}$, or to the force $F_{\kappa,\alpha}$ induced on atom κ by an electric field \mathcal{E}_γ : $Z_{\kappa,\gamma\alpha}^* = V \partial P_\gamma / \partial \tau_{\kappa,\alpha} = \partial F_{\kappa,\alpha} / \partial \mathcal{E}_\gamma = -\partial^2 E / \partial \mathcal{E}_\gamma \partial \tau_{\kappa,\alpha}$. So, it also appears as a mixed second derivative of the total energy E per unit cell volume V , which can be evaluated from density functional perturbation theory.¹³ We choose to use the variational formulation^{5,8} of this theory. The exchange-correlation energy functional and the norm-conserving pseudopotentials are the same as in 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 hartree 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 ($a_{\text{cell}} = 4 \text{ \AA}$) and theoretically optimized ($a_{\text{cell}} = 3.94 \text{ \AA}$) lattice parameter, as well as those corresponding to a compressed cubic cell ($a_{\text{cell}} = 3.67 \text{ \AA}$) are reported in Table I. For comparison, we also computed the effective charges from the shell model parameters proposed by Khatib *et al.*¹⁴

The charges of Ba and Ti, isotropic owing to symmetry, are equal, respectively (at the theoretical volume), to +2.77

TABLE I. Born effective charges for cubic BaTiO₃.

Ions	Axe ^a	Shell model	Zhong <i>et al.</i> ^b	$a_{\text{cell}}=4.00 \text{ \AA}$	$a_{\text{cell}}=3.94 \text{ \AA}$	$a_{\text{cell}}=3.67 \text{ \AA}$	
Z_{Ba}^*	+2	2.9	1.63	2.75	2.74	2.77	2.95
Z_{Ti}^*	+4	6.7	7.51	7.16	7.29	7.25	7.23
$Z_{\text{O}_{\perp}}^*$	-2	-2.4	-2.71	-2.11	-2.13	-2.15	-2.28
$Z_{\text{O}_{\parallel}}^*$	-2	-4.8	-3.72	-5.69	-5.75	-5.71	-5.61

^aReference 4.^bReference 9.

and +7.25. For O, the values of $Z_{\text{O}_{\parallel}}^*$ (-5.71) and $Z_{\text{O}_{\perp}}^*$ (-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, King-Smith, and Vanderbilt⁹ (also at the theoretical volume) from finite difference of polarization 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 BaTiO₃. The large value of Z_{Ti}^* (7.51) proves that it implicitly includes covalency effects responsible for anomalous effective charges, as described below.

The charges on Ti and O_{||} 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 (cf. 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 $Z(u) = P(u)/u$ and a dynamic charge $Z^*(u) = \partial P(u)/\partial u$ also equal to $Z(u) + u \partial Z(u)/\partial u$. 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, $1/\bar{u} \int_0^{\bar{u}} Z^*(u) du = Z(\bar{u})$: 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 BaTiO₃, the approximate reciprocity between O_{||} (-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 asks for the identification of the relevant orbitals.

Hybridization between O $2p$ and the unoccupied metal d

orbitals is well known and was already pointed out from experiments,¹⁵ tight-binding models,¹⁰ and linear combination of atomic orbitals calculations.¹⁶ It was highlighted more recently by Cohen³ from first principles as an essential feature of ABO₃ ferroelectric compounds. In this context, it seemed realistic, following Harrison, to focus on O $2p$ -Ti $3d$ hybridization changes to explain intuitively large anomalous contributions.⁹ Posternak, Resta, and Baldereschi¹¹ went beyond this credible assumption. They showed for KNbO₃ that the anomalous contributions disappear when the interaction between the O $2p$ and Nb $4d$ orbitals is artificially suppressed.

Nothing proves that the conclusions would be the same for BaTiO₃ nor that the hybridizations are limited to these kinds of p - d interactions. Theoretical investigations, confirmed by experimental results,¹⁵ 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^* .¹⁷

At variance with 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 performed a unitary transform on the wave functions so that 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* associ-

TABLE II. Band-by-band decomposition of Z^* (see text).

Band	Cubic (3.94 Å)			Cubic (3.67 Å)		Tetragonal
	Z_{Ba}^*	$Z_{\text{O}_{\perp}}^*$	$Z_{\text{O}_{\parallel}}^*$	Z_{Ti}^*	Z_{Ti}^*	
Core	10.00	6.00	6.00	12.00	12.00	12.00
Ti 3s	0.01	0.00	0.02	-2.03	-2.07	-2.05
Ti 3p	0.02	-0.02	0.21	-6.22	-6.43	-6.26
Ba 5s	-2.11	0.02	0.01	0.05	0.09	0.05
O 2s	0.73	-2.23	-2.51	0.23	0.27	0.25
Ba 5p	-7.38	0.58	-0.13	0.36	0.64	0.34
O 2p	1.50	-6.50	-9.31	2.86	2.73	1.48
Total	2.77	-2.15	-5.71	7.25	7.23	5.81

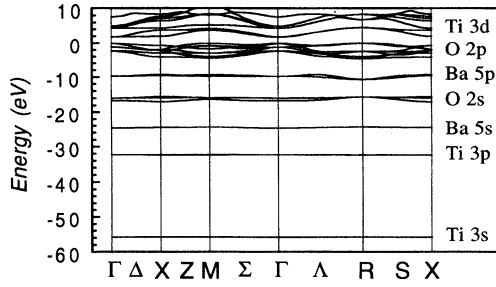


FIG. 1. Electronic band structure of cubic BaTiO₃ ($a_{\text{cell}}=3.94$ Å).

ated 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 nonhybridized orbitals. As covalency develops, different orbitals mix adding anomalous contributions from several bands.

Results for the theoretical cubic structure are reported in Table II. 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 expected, the main Z_{Ti}^* anomalous charge is localized on the O 2p bands (+2.86). It can be understood by a hybridization between O 2p and Ti 3d 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 Ti 3s contribution is close to -2. This result *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 *not* small. Nevertheless, they are partially compensated by Ba 5p (-1.38) and Ba 5s (-0.11) anomalous contributions. This result gives tangible proof of the hybridization of Ba 5p orbitals already suggested from the experiment.¹⁵

TABLE III. Eigenvalues of the Born effective charge tensors of Ba and Ti at the experimental volumes.

Phase	$Z_{\text{Ti},11}^*$	$Z_{\text{Ti},22}^*$	$Z_{\text{Ti},33}^*$	$Z_{\text{Ba},11}^*$	$Z_{\text{Ba},22}^*$	$Z_{\text{Ba},33}^*$
Cubic	7.29	7.29	7.29	2.74	2.74	2.74
Tetragonal	6.94	6.94	5.81	2.72	2.72	2.83
Orthorhombic	6.80	6.43	5.59	2.72	2.81	2.77
Rhombohedral	6.54	6.54	5.61	2.79	2.79	2.74

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

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 Posternak, Resta, and Baldereschi for KNbO₃, 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 BaTiO₃: it clearly establishes that the covalent character is not restricted to the Ti-O bond.

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 KNbO₃ (Ref. 7) and PbTiO₃,⁹ 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 BaTiO₃ (Ref. 9) also suggests a reduction of Z^* in this phase.

We computed the Born effective charge tensors for the three 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 and 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 points in the Ti-O direction: we identify this highest contribution as O_{\parallel} while the others are referred as O_{\perp} , by analogy with the cubic phase.

Although the charges of Ba and O_{\perp} remain globally the same in the four phases, for Ti and O_{\parallel} , stronger modifica-

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

Phase	O_{\perp}						O_{\parallel}		
	$Z_{O1,11}^*$	$Z_{O2,11}^*$	$Z_{O3,11}^*$	$Z_{O1,22}^*$	$Z_{O2,22}^*$	$Z_{O3,22}^*$	$Z_{O1,33}^*$	$Z_{O2,33}^*$	$Z_{O3,33}^*$
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	-5.45
Rhombohedral	-1.97	-1.97	-1.97	-1.98	-1.98	-1.98	-5.05	-5.05	-5.05

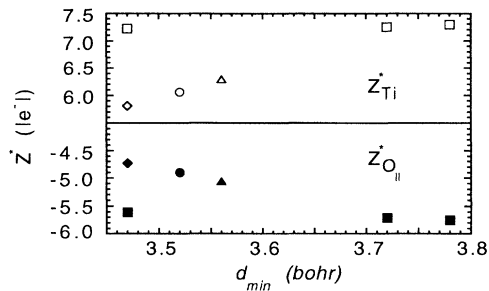


FIG. 2. Born effective charge of Ti (opened symbols) and O (filled symbols) in the direction of the shortest Ti-O bond length d_{\min} with respect to this interatomic distance for the cubic (square), tetragonal (lozenge), orthorhombic (circle), and rhombohedral (triangle) phases.

tions are observed. Changing the Ti position by 0.076 \AA (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 \AA in which the Ti-O distance is *the same* as 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 II. While in the cubic structure at 3.67 \AA 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 $2p$ bands ($+1.48$ instead of $+2.86$) while the other contributions remain equivalent to those of the cubic phase at 3.94 \AA . Analysis from the cubic structure at 3.67 \AA reveals that the O $2p$ contribution is not significantly affected by hydrostatic pressure; on the other hand, the anomalous parts of the Ba $5p$, 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 four phases. Effective charges are a sensitive tool for analyzing dynamic changes of orbital 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.

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