The nature of ferroelectricity under pressure

Igor A. Kornev and Laurent Bellaiche

Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Dated: October 17, 2018)

Abstract

Advances in first-principles computational approaches have, over the past fifteen years, made possible the investigation of physical properties of ferroelectric systems. In particular, such approaches have led to a microscopic understanding of the occurrence of ferroelectricity in perovskite oxides at ambient pressure. In this paper, we report ab-initio studies on the effect of hydrostatic pressure on the ferroelectricity in perovskites and related materials. We found that, unlike commonly believed, these materials exhibit ferroelectricity at high enough pressure. We also explained in details the (unusual) nature of this ferroelectricity.
I. INTRODUCTION.

ABO₃ perovskites form one of the most important classes of materials because they can exhibit a broad range of properties, e.g. superconductivity, magnetism, ferroelectricity, piezoelectricity, dielectricity and multiferroism. Such properties can be varied – and thus optimized to generate various devices with great performance and diverse functionalities – thanks to many factors. Examples of such factors are external magnetic and electrical fields, atomic substitution, chemical ordering and pressure.

In a classic paper (Samara et al., 1975), Samara et al. were able to explain the effect of hydrostatic pressure on displacive phase transitions associated with soft zone-center transverse optic (TO) and zone-boundary phonons. Among the most striking pressure effects is the decrease of the transition temperature with pressure and ultimate vanishing of ferroelectricity (Samara et al., 1975). As it was shown, the vanishing of ferroelectricity with pressure can be readily understood from the well-known soft-mode theory (Ginzburg, 2001) where the soft mode frequency depends on the short-range and Coulomb interactions. In this case, the vanishing of ferroelectricity is associated with a much more rapid increase of the short-range interactions than the long-range interactions with increasing pressure. As a result, the harmonic soft-mode frequency becomes less negative with increasing pressure. It is interesting to note that for the zone boundary modes the roles of the short-range and long-range forces are reversed, which leads to an enhancement of these modes when increasing pressure. Despite its simplicity, this model could successfully explain high pressure behavior of many compounds (Samara et al., 1975, Sani et al., 2004). [Note that “long-range” interactions denote interactions that persist even at distances where the electronic wavefunctions no longer overlap. Such long-range interactions have a distance dependency that is inversely proportional to some power of the interionic distance. “Short-range” interactions only occur when the electronic wavefunctions overlap. They typically have a distance dependency that follows an exponential form at large distances, and are inversely proportional to some power of the interionic distance at smaller distances.

The microscopic understanding of the occurrence of ferroelectricity in perovskite oxides has been substantially improved by first-principles electronic band-structure techniques. In particular, Cohen & Krakauer (Cohen, 1992; Cohen and Krakauer, 1990, 1992) showed that
a delicate balance exists between Coulomb interactions that favor ferroelectric distortions 
and the short-range repulsions that favor the undistorted high-symmetry structure. It has 
been established that the balance between different competing interactions can be tipped by 
relatively small effects that are related to covalency, namely hybridization between $p$ orbitals 
of the oxygen atoms and the $d$ orbitals of the B atoms. In fact, such covalency is essential 
for stabilizing the ferroelectric distortion or, equivalently, triggers the soft-mode instability. 
The reason for this stabilization is that the hybridization weakens the short-range repulsions. 
This fact has been elegantly demonstrated by Posternak et al. (Posternak et al., 1995) – who 
showed that the ferroelectric instability disappears in KNbO$_3$ when the interaction between 
the O 2$p$ and Nb 4$d$ states is artificially suppressed. Since then, similar conclusions have 
been drawn for other ferroelectric perovskites. Moreover, an additional Pb-O hybridization 
is the key factor to explain why PbTiO$_3$ has deeper ferroelectric double-well potentials than 
BaTiO$_3$ (Cohen and Krakauer, 1992; Kuroiwa et al., 2001). The important role of covalent 
 bonding is also clearly reflected in the anomalously large values of the Born dynamical 
charges (Ghosez et al., 1998; Zhong et al., 1994).

In this paper, we use first principles calculations to investigate many insulating per-
ovskites and related materials under hydrostatic pressure, and show that the conclusion 
about the role of the different interactions mentioned above is indeed well justified at low 
pressure but is no longer valid at high pressure (Kornev et al., 2005). More precisely, our 
study reveals (1) the absence of a cubic paraelectric phase in favor of a polar phase under 
high-enough hydrostatic pressures, and (2) the underlying physical mechanisms responsible 
for this overlooked phenomenon.

II. COMPUTATIONAL DETAILS.

The ab initio calculations are performed in the framework of the density functional 
theory, mostly within the local-density approximation (LDA) but also sometimes within 
the gradient generalized approximation (GGA) (Perdew and Yue, 1986; Perdew et al., 
1996). We have employed the pseudopotential method using the ABINIT (Gonze et al., 
2002), CUSP (Bellaiche and Vanderbilt, 2000; King-Smith and Vanderbilt, 1993), and 
PWscf (Baroni et al., 2001) packages. The calculations have been done with the extended 
norm-conserving pseudopotentials of Teter (Teter, 1993) or with the Vanderbilt-type ultra-
soft pseudopotentials \cite{Vanderbilt:1990} – always incorporating the semi-core states in the valence, unless specified otherwise. The wavefunction has been expanded in planewaves up to a kinetic energy cutoff of 120 Rydberg when using the extended norm conserving pseudopotentials and of 40 Rydberg when using the ultrasoft pseudopotentials. We use the Ceperley-Alder exchange and correlation \cite{Ceperley:1980} as parameterized by Perdew and Zunger \cite{Perdew:1981} or the Teter-Pade parametrization \cite{Goedecker:1996, Perdew:1992}. For the ground state calculations, integrals over the simple cubic Brillouin zone have been replaced by sums on a $6 \times 6 \times 6$ Monkhorst-Pack special k-point mesh \cite{Monkhorst:1976}. We determined: (i) the total energy for different volumes of the unit cell allowing for full relaxation of the cell shape and the positions of the atoms inside the unit cell, in order to determine the evolution of some phases as a function of hydrostatic pressure, (ii) the phonon spectrum of specific structures by using both finite-difference (frozen-phonon) and linear-response approaches \cite{Gonze:1992}, (iii) the Born effective charges, the dielectric constants, and (iv) the electronic band-structure and density of states. It should be noted that we checked that our results are qualitatively independent on technical details such as the used exchange-correlation functional, pseudopotential types, kinetic energy cutoff or softwares.

III. RESULTS AND DISCUSSION

A. PbTiO$_3$ under pressure

Lead titanate PbTiO$_3$ is one of the most important and best studied ferroelectric materials adopting the simple-cubic perovskite structure at high temperature. It is known that PbTiO$_3$ undergoes a single ferroelectric transition from the cubic to a tetragonal phase below 766 K. In fact, it appears to be a textbook example of a displacive ferroelectric transition \cite{Burns:1973, Lines:1977}.

Hydrostatic pressure $P$ reduces, and even annihilates for high enough value, ferroelectricity (FE) in perovskites \cite{Sanurjo:1983, Sani:2004}, according to the conventional theory. Such annihilation seems consistent with experimental X-ray diffraction studies \cite{Sani:2002, Zha:1992} and first-principles calculations \cite{Wu:2005} that reported a ferroelectric to paraelectric phase transition in lead titanate under a
“moderate” (i.e. around 10-20 GPa) pressure. On the other hand, one of our recent studies [Kornev et al., 2005] – that combines experimental techniques and ab-initio simulations – revealed that perovskites enhance their ferroelectricity as pressure increases above a critical value (which is around 30 GPa in PbTiO3).

More specifically, we performed 0 K calculations on PbTiO3 within LDA and for a wide pressure range. The calculated pressure-volume data were fitted to a Birch equation of state (Birch, 1986). Here, we present the results for 7 phases: the paraelectric cubic Pm3m state; the ferroelectric, rhombohedral R3m, and tetragonal P4mm phases; the antiferrodistortive tetragonal I4/mcm and rhombohedral R3c phases; and the tetragonal I4cm and rhombohedral R3c phases that can exhibit both polar and antiferrodistortive degrees of freedom.

Figure 1a shows the predicted pressure dependency of the difference $\Delta H = H - H_{cubic}$ between the $H_{cubic}$ enthalpy of the paraelectric cubic state and the $H$ enthalpies of the other 6 phases. For the lowest (P) pressures, only ferroelectric distortions exist in I4cm and R3c, which are thus identical to P4mm and R3m, respectively. The P4mm phase has the lowest $\Delta H$, as consistent with the fact that it is the well-known ground state of PbTiO3. Figs. 1b, c show that, as expected in perovskites [Samara et al., 1975; Sani et al., 2004], significant antiferrodistortive deformations occur in the I4cm and R3c phases when increasing $P$ above $\sim$3 GPa. The reason leading to the TiO$_6$ octahedra rotation is clear: due to the TiO$_6$ octahedra rotation, the Ti-O bonds perpendicular to the rotational axis can relax towards their equilibrium lengths, which minimizes the bond compression. In other words, the rotation relaxes the compression of the Ti-O bond perpendicular to the rotational axis. On the other hand, Fig. 1a also indicates an unexpected result, namely that increasing pressure above a critical value enhances ferroelectricity! Indeed, an increase in $P$ from 0 to $\sim$20 GPa leads to a $\Delta H$ becoming less negative in the polar phases - as consistent with the commonly-believed pressure-induced reduction of FE [Samara et al., 1975; Sani et al., 2004; Sanjurjo et al., 1983], but the $\Delta H$ –vs.-$P$ curve of these phases adopts an opposite behavior above $P_c\sim$30 GPa - revealing that PbTiO3 wants to become more and more ferroelectric after this critical pressure. We found that rhombohedral states are the most stable ones at high pressure [Kornev et al., 2005] and at 0K. The non-monotonic behavior of FE versus pressure is emphasized by the pressure dependency of the calculated c/a axial ratio in P4mm (see Fig. 2): this ratio first strongly decreases with $P$ until reaching a cubic-like value $\sim$1 in
the vicinity of $P_c$, and then it gradually increases as $P$ further increases. Our predictions are thus in sharp contrast to the common expectation that the application of hydrostatic pressure favors a cubic paraelectric crystal structure.

**B. Possible driving mechanism(s) for the high-pressure ferroelectric instability in PbTiO$_3$.**

In order to identify the driving mechanism(s) of the ferroelectric instability under high pressure, we decided to investigate in more details (1) the cubic paraelectric $Pm\bar{3}m$ phase and (2) the tetragonal ferroelectric $P4mm$ phase. Fig. 1b shows that the magnitude of the polarization above the turning point is smaller than that below $\simeq 10$GPa. Based on this fact, one might assume that the polarization is no longer the primary order parameter at high pressure or, equivalently, that the ferroelectric instability is driven by the coupling with other degrees of freedom, such as (i) the antiferrodistortive and (ii) elastic variables.

Possibility (i) is a primary suspect because antiferrodistortive degrees of freedom are known to increase with pressure in ferroelectric perovskites [Sani et al., 2004]. In this case, the ferroelectric instability could appear as a result of a specific interaction between the antiferrodistortive and ferroelectric distortions. However, these two degrees of freedom usually compete in perovskites [Vanderbilt and Zhong, 1998]. Furthermore, as shown in Figure 1, the ferroelectric instability exists even without taking into account the antiferrodistortive degrees of freedom. For instance, after the turning point around $\simeq 30$GPa, the $P4mm$ phase (that does not contain any rotation of the oxygen octahedra) is more stable than the cubic phase. These facts thus rule out the antiferrodistortive degrees of freedom to be the driven force for the ferroelectric instability.

Possibility (ii) is also a candidate for explaining high-pressure FE because perovskite ferroelectrics are well-known to exhibit a coupling between polarization and strain. An elastic instability may thus lead to the occurrence of a nonzero polarization. To check such hypothesis, we performed *ab initio* calculations of the elastic tensor in the cubic phase using the ABINIT package and found no elastic instability in the entire pressure range. Fig. 3 shows the pressure dependence of the elastic stiffness coefficients $c_{11}$, $c_{12}$, and $c_{44}$. The $c_{11}$ and $c_{12}$ coefficients increase linearly with increasing pressure. On the other hand, the $c_{44}$ coefficient starts to decrease gradually above the critical pressure but remains positive at
all investigated pressures (that is, up to $\simeq 150$ GPa). Furthermore, these elastic stiffness coefficients satisfy the generalized elastic stability criteria for cubic crystals under hydrostatic pressure \cite[see, for example, Ref. (Karki et al., 1997)]{Karki1997}: $c_{11} + 2c_{12} > 0$, $c_{11} - c_{12} > 0$, $c_{44} > 0$. Moreover, we found that the $P4mm$ phase without lattice relaxation is more stable at high pressure than the cubic phase. Therefore, we may now assume that the polarization is the primary order parameter even after the turning point. Elucidating the mechanisms of the high-pressure ferroelectric instability should thus involve the consideration of the soft transverse optical mode alone. (Note that we can also conclude that the electromechanical coupling that become enormous in the transition regions from the tetragonal to high pressure phases of $\text{PbTiO}_3$ \cite{Cohen2006} is not responsible for the ferroelectric instability).

C. Lattice Dynamical Properties of $\text{PbTiO}_3$ and of Related Perovskites.

It is well-known that the Born effective charges are of primary interest for the soft TO mode behavior when a competition between the Coulomb and non-classical short-range forces is important. In the following, we will denote $O_\parallel$ the oxygen atoms located between two B-atoms along the z-direction and $O_\perp$ the oxygen atoms located between two B-atoms in the perpendicular directions – when slightly displacing the atoms along the z-axis when computing the Born effective charges. Our calculations of the Born effective charges as a function of pressure in the cubic phase (see Fig. 4) show that the anomalously large values of Ti and $O_\parallel$ persist throughout the pressure range of interest, although these effective charges decrease with increasing pressure. For instance, their values are reduced by $\sim 1.4\%$ at $\sim 25$ GPa with respect to their values at 0GPa. On the other hand, the effective charges of Pb and $O_\perp$ ions increase with pressure, and deviate from their values at zero pressure by $\sim 2\%$ at $\sim 25$ GPa. Interestingly, it was demonstrated by Ghosez et al. \cite{Ghosez1996} that a change corresponding to a reduction of the order of 1% of the Ti effective charges is enough to suppress the ferroelectric instability in $\text{BaTiO}_3$. From this point of view, the tendency of the $\text{PbTiO}_3$ system to become cubic as the pressure first increases from zero is quite understandable. However, since after the turning point the Ti and $O_\parallel$ effective charges continue to decrease with pressure, one might expect that the system would continue to stay cubic which is definitely not the case. Therefore, the pressure behavior of the effective charges or, equivalently, the strengths of the Coulomb interaction alone is not sufficient to
understand high-pressure FE.

We now turn to Fig. 5a that displays the LDA-simulated pressure behavior of the zone-center transverse optical (TO) mode frequency in the cubic $Pm\bar{3}m$ phase of PbTiO$_3$. The square of such frequency is always negative, which indicates that PbTiO$_3$ has a ferroelectric instability and thus can not be cubic for any pressure at 0K. More importantly, the magnitude of this square first decreases with $P$ and then increases above the critical pressure ($P_c$) - confirming that PbTiO$_3$ has to become more and more ferroelectric above $P_c$. To understand further the high-pressure ferroelectric instability it is advantageous to divide the dynamical matrix into (1) the Coulomb part (following the formalism for the rigid ion model) that can easily be found once the Born effective charges and dielectric tensor of the system have been calculated (Giannozzi et al. 1991), and (2) the (remaining) second part – which is deduced by subtracting the first part from the total dynamical matrix. This second part thus differentiates the real material from its rigid ions picture, and gathers the (non-classical) short-range interactions. Figure 5b shows the calculated contribution of these two parts to the zone-center soft TO phonon frequency in the cubic phase of PbTiO$_3$ and BaTiO$_3$, as a function of $P$. Below $P_c$ and as commonly expected (Samara et al. 1975), the Coulomb interactions favor FE while short-range interactions tend to annihilate it - since they have a negative and positive frequency square, respectively - and the decrease of FE when increasing $P$ is driven by the cost of short-range interactions becoming predominant over the gain associated with long-range interactions. Figure 5b also reveals that FE above $P_c$ dramatically differs from the low-pressure “normal” ferroelectricity because of the reverse sign of Coulomb and short-range parts: it is now short-range effects (which are electronic in nature) that favor FE at high pressure while Coulomb interactions (that involve ions “dressed by electrons”) prefer paraelectricity!

Figure 5b indicates that the results that we present are qualitatively general for perovskite ferroelectrics and not just an artifact of studying lead-contained perovskites, since they also apply to BaTiO$_3$. This fact is further emphasized in Figures 6 that report our 0K ab-initio predictions for the eigenvalue $\lambda$ and eigenvectors ($\xi_A$, $\xi_B$, $\xi_{O\perp}$, $\xi_{O\parallel}$) of the second-derivative matrix defined in Ref. (King-Smith and Vanderbilt 1994) and associated with the soft-mode in cubic PbTiO$_3$, BaTiO$_3$ and BaZrO$_3$, as a function of pressure. (It is important to realize that the last two materials are lead-free). A negative $\lambda$ corresponds to a ferroelectric instability while the magnitude of the eigenvectors quantifies the contribution of the different
ions to FE, if any. All the data displayed in Figs. 6 are obtained by using the local density approximation (LDA) except in parts (a) and (d) for which we also report results from the use of the generalized gradient approximation (GGA). Figs. 6 undoubtedly show that all studied materials should be ferroelectric at high enough pressure, thus confirming that one has to rule out a possible suggestion that pressure-induced FE only occurs in Pb-based materials. One can further notice that $\xi_A$ has a very small magnitude at high pressure in PbTiO$_3$, BaTiO$_3$ and BaZrO$_3$. This fact clearly implies that the $A$ atoms contribute very little to high-pressure ferroelectricity. Our Figs. 6 also nicely summarize the different behaviors one can get as pressure increases in transition-metal perovskites, as a result of our discovered non-monotonic pressure behavior: the existence of FE at any pressure (PbTiO$_3$, see LDA calculation of Fig. 6(a)), the disappearance and then reentrance of FE under pressure (BaTiO$_3$, see Fig 6(b)), and the occurrence of FE at high pressure in a nominally paraelectric compound (BaZrO$_3$, see Fig. 6(c)). Moreover, Figures 6(d-f) clearly shows that the eigenvectors of $B$ and $O$ atoms have a large (and mostly material-independent!) magnitude at high pressure, which points to an “universal” microscopic explanation for high-pressure FE. Finally, such pressure-induced phenomenon is also found when performing ab-initio calculations in KNbO$_3$, NaNbO$_3$, SrTiO$_3$, CaTiO$_3$, as shown in Fig. 7, Pb(Zr,Ti)O$_3$ and some Bi-based perovskites (not shown here). Not also that the fact that the $A$ atom contributes little to high-pressure FE is clearly confirmed in Fig. 8—that shows that $A$-free WO$_3$ material also enhances its FE at high enough pressure.

D. Electronic Structures under Pressure

We now resume our “detective” work and look for the microscopic origin of the observed high-pressure FE. As it was shown above, the instability is related to the non-classical short-range interactions. As a result, we will now mostly concentrate on electronic properties.

1. Influence of semicore states.

We first investigate the role played by the semicore states via Fig. 9 that shows the predicted pressure behavior of phonons in PbTiO$_3$ in the cubic phase when neglecting to incorporate the semicore states of Pb and Ti as valence electrons. Technically, the ab-initio sim-
ulations without the semicore states have been performed with the Troullier-Martins norm-conserving pseudopotentials within ABINIT. Fig. 9 indicates that the semicore states Pb $5d^{10}$ and Ti $3s^23p^6$ (1) must be included explicitly to produce the well-known ferroelectric instability at zero pressure – as consistent with previous first-principles works (Cohen and Krakauer, 1992; King-Smith and Vanderbilt, 1994) but (2) are not the reason for the existence of a turning point and of high-pressure FE (Note, however, that the magnitude of the instability is of course not the same when neglecting or incorporating these semicore states in the valence electrons). Note that the fact that Pb $5d^{10}$ orbitals are not responsible for the existence of the ferroelectric instability at high pressure could also have been guessed thanks to Fig. 8 that shows that tungsten trioxide WO$_3$ (which is a defect-perovskite structure having no A-atom) also exhibits a high-pressure FE. In fact, this latter figure, as well as Figs. (6,7), indicates that the electrons of interest for high-pressure FE should belong to the O and/or B ions.

2. **Influence of the d-states of B atoms.**

Figure 10 reports the LDA-predicted pressure behavior of the soft-mode eigenvalues of the second-derivative matrix in cubic bismuth aluminate BiAlO$_3$ and magnesium silicate MgSiO$_3$. Note that both materials, unlike the ones considered above, do not possess any B-atom having occupied d electrons. Interestingly, no turning point is observed in MgSiO$_3$ - under pressure up to 300 GPa. As a matter of fact, we found that the TO soft mode at the Γ point linearly increases with pressure in this material and become positives at around 30 GPa - which is consistent with previous studies of MgSiO$_3$ (Parlinski and Kawazoe, 2000). The same qualitative behavior is found in BiAlO$_3$ under high pressure up to 900 GPa. We thus arrive at the conclusion that the d states of the B atoms are of primary importance for understanding the physics behind the high-pressure ferroelectric instability.

3. **Electronic band structure and density of states under pressure**

To further elucidate the nature of the high-pressure ferroelectric instability and the role played by the electronic structure, we have calculated the total and atomic site projected densities of states (PDOS) of ideal cubic perovskites. Figs. 11 display some partial electronic
density of states for cubic PbTiO$_3$ under different pressures. Note that the contribution of Pb orbitals is not shown because, as discussed above, Pb was found to be relatively ferroelectric-inactive at high pressure.

Figures 11(a-c) show the low-lying states ranging between -22 and -15 eV (that solely originate from the O 2s orbitals in an ionic picture), as well as the topmost group of valence bands (that exhibits the well-known hybridization between O 2p and Ti 3d orbitals (Cohen, 1992; Cohen and Krakauer, 1990)). As it is known, the topmost states correspond mainly to $\sigma$ (bonding) and $\pi$ (non-bonding) orbitals. Moreover, the states with large Ti 3d contribution are mainly concentrated in the lower (bonding) part of the topmost region. This O 2p and Ti 3d hybridization persists throughout the pressure range of interest. The integrated PDOS of this group have a smooth and small pressure-dependency thus ruling out that high-pressure FE is caused by this $p - d$ hybridization. At the same time the Ti 3d state contribution to the low-lying O 2s-like bands has increased considerably. Thus, as the pressure increases, the admixture of Ti 3d states in the occupied bands seems to evolve differently for the occupied low-lying and topmost bands. More precisely, the evolution of O 2s - Ti 3d and O 2p - Ti 3d mixing is nicely seen in the trends displayed by the integrated (over all the occupied valence bands) PDOS (to be denoted by IPDOS), see Fig. 12(a). The IPDOS of O 2s and Ti 3d vary in a correlated way with pressure, the former decreasing and the latter increasing. On the other hand, the IPDOS of O 2p remains more or less constant, apart from the highest pressures. These tendencies are even more clearly seen in Fig. 12(b), where IPDOS are normalized with respect to their corresponding values at zero pressure. Furthermore, Fig. 12(c) reports the contributions to the IPDOS coming from the low-lying states (located between -22 and -15 eV) and from the topmost group of the valence bands. The most striking effect is that Ti 3d orbitals (and more precisely their $e_g$ parts) dramatically increase (in a nonlinear way) their mixing with the O 2s orbitals above $P_c$. The admixture of Ti 3d states in the occupied levels of the electronic structure releases O 2s - O 2s antibonding states above the Fermi level, thus optimizing the band energy. A similar behavior of integrated PDOS was found in BaTiO$_3$ under pressure, as reported in Fig. 13

A rapid relative increase of the O-s and B-d mixing can easily be understood as follows. The lobes of the Ti 3d − $t_{2g}$ orbitals point between the oxygen ligands (whereas the Ti 3d − $e_g$ orbitals point directly towards the ligands), forming the $\sigma$ bonding. Hence, the overlap with O 2s orbitals will be significant at high enough pressure for the Ti 3d − $e_g$
states, which results in local repulsion between overlapping charge densities. From one hand, this repulsive interaction will cost some energy. From the other hand, some of the repulsion is compensated by hybridization in the resulting bonding states – which in turn leads to considerable amount of O 2s state in the conduction band. Taking into account the different interatomic dependence of these two competing interactions, one might expect that the need to avoid the large local repulsion will win at some pressure, enabling atomic distortions and thus giving rise to ferroelectricity.

We would like to point out that the important role played by the small amount of 2s admixture with the $e_g$ orbitals of transition-metal cations surrounded by anions (like chlorine, bromine, fluorine, or oxygen) was also previously recognized in Ref. (Moreno et al., 1997). Moreover, recent DFT calculations (Hussermann, 2003) revealed the key role of \(s\rightarrow d\) mixing on the stability of high-pressure structures in P, As, Sb, and Bi.

E. Topological analysis of the electron density in PbTiO\(_3\).

To get more insight into the chemical bondings of PbTiO\(_3\) under pressure, we consider the topological properties of the electron density \(\rho(r)\). The total density was restored by adding atomic core electron density to the valence density obtained in pseudopotential calculations. The analysis was performed in terms of the atom-in-molecules Bader theory (Bader, 1990) which is based upon the so-called critical points, \(r_{cp}\), of the electron density. At these points, the gradient of the electronic density is null and the Hessian matrix \(\partial^2 \rho(r)/\partial x_i\partial x_j\) is characterized by its three eigenvalues, \(\lambda_k\). Interatomic interactions can be adequately described by the topological properties of the electron density at the so-called (3,-1) critical points (or bond critical points) for which the three eigenvalues of the Hessian matrix are non-zero and the algebraic sum of their signs is \(-1\). Bond critical points occur as saddle points along bond paths between pairs of bonded atoms and can be used to define atomic coordination. The characteristics of the bond critical points in PbTiO\(_3\) at 0 GPa are listed in Table 1.

As expected for cubic perovskite [see, for instance, Ref. (Zhurova and Tsirelson, 2002)], we found six (3,-1) critical points on the Ti-O lines and twelve (3,-1) critical points on the Pb-O lines at any pressure. Interestingly, all the (3,-1) critical points in PbTiO\(_3\) are characterized by the positive Laplacian of the electron density which, according to Bader (Bader,
TABLE I  Characteristics of some critical points (CP) in PbTiO$_3$ at $a = 7.35$ a.u. (zero pressure); $
abla^2 \rho(r_{cp}) = \lambda_1 + \lambda_2 + \lambda_3$, where $\lambda_1$ and $\lambda_2$ are perpendicular to the bond line curvatures of the electron density and $\lambda_3$ is parallel. Values are given in atomic units.

| $r_{cp}$ | $\rho(r_{cp})$ | $\nabla^2 \rho(r_{cp})$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | Type of CP |
|----------|----------------|------------------------|------------|------------|------------|------------|
| (0.234, 1/2, 1/2)$^a$ | 0.132 | 0.590 | -0.219 | -0.219 | 1.028 | (3,-1) |
| (0.267, 0.267)$^b$ | 0.028 | 0.078 | -0.020 | -0.022 | 0.120 | (3,-1) |

$^a$Ti-O line.  
$^b$Pb-O line.

(1990), is an indication of the closed-shell interaction between the corresponding atoms.

Analyzing the topological characteristics available in the literature, it was found (Zhurova and Tsirelson, 2002) that the bonds, typically identified as ionic, are characterized by the electron density value at the (3,-1) critical point in the range of $0.07-0.25$ e Å$^{-3}$ and a specific range of the ratio of the perpendicular and parallel curvatures of the electron density: $0.12 < |\lambda_1|/\lambda_3 < 0.17$. According to Table I, the Pb-O bond (at 0 GPa) fits well the first condition since $\rho(r_{cp}) \approx 0.1908$ e Å$^{-3}$ and closely fits the second one if we take $|(\lambda_1 + \lambda_2)/2|/\lambda_3 \approx 0.176$ rather than $|\lambda_1|/\lambda_3$. Thus, the Pb-O interaction (at zero pressure) can be considered as mostly ionic with small covalent admixture. On the other hand, the value of $\rho(r_{cp}) \approx 0.9$ e Å$^{-3}$ and the ratio $|\lambda_1|/\lambda_3 = 0.213$ at the (3,-1) critical points on the Ti-O line imply that the Ti-O bond is not ionic in nature (at zero pressure).

In order to characterize the chemical bonds in more details (and for different pressures), we employ the recently proposed classification scheme of interatomic interactions (Espinosa et al., 2002). According to Bader (Bader, 1990) the Laplacian function $\nabla^2 \rho(r_{cp})$ is related to the potential energy density $v(r_{cp})$ (of negative value) – which represents the capacity of the system to concentrate electrons at the critical point – and the kinetic energy density $g(r_{cp})$ (of positive value) – which gives the tendency of the system to dilute electrons at the same point (Espinosa et al., 1998) – through the local form of the virial theorem $1/4 \nabla^2 \rho(r_{cp}) = 2g(r_{cp}) + v(r_{cp})$. Note that for pressure different from zero, the virial theorem should include an additional term proportional to this P pressure: in the cubic case, one should add the $+3P$ term to the lefthand side of this latter expression.

The kinetic energy can be calculated using the following expression for closed-shell in-
interactions at the bond critical points (Abramov, 1997): \[ g_{rcp} = \frac{3}{10}(3\pi^2)^{2/3}\rho_{rcp}^{5/3} + \frac{1}{6}\nabla^2\rho_{rcp}. \] The potential energy density \( v_{rcp} \) is then calculated by subtracting \( g_{rcp} \) from \( \frac{1}{4}\nabla^2\rho_{rcp} \). We also computed the total electronic energy density \( h_{rcp} \) as

\[ h_{rcp} = g_{rcp} + v_{rcp}. \]

Using the adimensional \( |v_{rcp}|/g_{rcp} \) ratio and the bond degree \( BD = h_{rcp}/\rho_{rcp} \), the atomic interactions can be divided into three classes (Espinosa et al., 1998): (i) pure closed shell for which \( |v_{rcp}|/g_{rcp} < 1 \) (and for which the \( \nabla^2\rho_{rcp} > 0 \) and \( h_{rcp} > 0 \) inequalities stand), (ii) pure shared shell for which \( 1 < |v_{rcp}|/g_{rcp} < 2 \) (and for which \( \nabla^2\rho_{rcp} < 0 \) and \( h_{rcp} < 0 \)) and (iii) transit closed shell for which \( |v_{rcp}|/g_{rcp} > 2 \) (with \( \nabla^2\rho_{rcp} > 0 \) and \( h_{rcp} < 0 \)).

Inside the ionic region (i), the bond degree parameter is an index of ionicity: the stronger the ionicity the greater the \( BD \) magnitude. In regions (ii) and (iii), the \( BD \) parameter measures the covalency degree: the stronger the covalency the greater the \( BD \) magnitude. For instance, the ionic Li-F bond is characterized by \( |v_{rcp}|/g_{rcp} \approx 0.76 \) and \( BD \approx +0.41 \) while the covalent C-O bond in CO(NH\(_2\))\(_2\) is such as \( |v_{rcp}|/g_{rcp} \approx 2.64 \) and \( BD \approx -0.29 \) (Tsirelson, 2002). Fig. 14 reports the bond degree parameter versus \( |v_{rcp}|/g_{rcp} \) ratio (as determined from our first-principles calculations) for the Ti-O and Pb-O bonds. This figure confirms that the Pb-O bond lies close to the pure closed shell region (i.e., it is mostly ionic) at 0GPa, and reveals that such bond becomes more ionic at higher pressure. On the other hand, the Ti-O bond lies close to the middle of a transit region (ii), implying that the Ti-O bond is neither purely covalent nor purely ionic. Fig. 14 also shows that the covalency degree of the Ti-O bond increases with pressure, which is consistent with our band structure calculations discussed above in subsection D.3. Interestingly, since this covalency increases with pressure, there might be a possibility for the phase transition to occur due to the drastic collapse of the oxygen ionic size (which is related to charge transfer to oxygen). For example, the Shannon ionic radius of O\(^{2-}\) is 1.23 Å (Shannon, 1976), whereas its covalent radius is 0.73 Å (Sanderson, 1962). If the size of oxygens were small compared to the allowed space then the oxygen atoms would be weakly bonded in the lattice and a multi-well potential could be expected [similar to PbTe:Ge (Murase, 1980; Weiser, 1981) and PbTe\(_{1-x}\)S\(_x\) (Abdullin et al., 1984)].
and the O ion would be unstable to the displacement from its regular high symmetry site with local distortions. This would lead to the instability of O similar to one observed for Li in LiNbO$_3$ (Parlinski et al., 2000). Indeed, although we found that the so-called Bader volumes (Bader, 1990; Gonze et al., 2002) (which are a measure of the ionic volumes) are smooth functions over the pressure interval of interest, the Bader O volume, unlike those of Pb and Ti, decreases faster under pressure than the volume of the unit cell, as shown in Fig. 15. However, our *ab initio* lattice vibration calculations show that the on-site force constant of O is positive at any pressures and, hence, the local atomic potential possesses a single minimum. We thus can rule out the drastic collapse of the oxygen ionic size as the mechanism for the high-pressure ferroelectricity.

F. Simple Tight-Binding Model

To confirm the role of the interaction between the 2s orbitals of oxygen atoms and the d orbitals of the B atoms at high pressure, we use the bond-orbital model of Harrison (Harrison, 1980) – a simplified tight-binding model, where the Hamiltonian is limited to the on-site and nearest-neighbor terms. This approximation allows an extraordinary simplification of the problem and the total energy can be rigorously calculated bond by bond. This is a very crude approximation but, surprisingly, it works very well in a wide variety of systems. In particular, it explains reasonably well the dynamical charges in ferroelectric perovskites (Ghosez et al., 1998). In this section, we shall make use of the method to clarify the role of the O 2s – B d and O 2p – B d couplings in the high pressure ferroelectric instability in perovskites. We will see that the instability at high pressure is governed by a competition between short-range covalent and overlap interactions.

Intuitively, the gradually decreasing ferroelectricity with rising hydrostatic pressure from zero to small values (i.e., before the turning point) may be attributed to the fact that the conventional mechanism responsible for triggering the ferroelectric instability at zero pressure and related to the B d – O 2p hybridization is not working well under pressure because of an increase of covalency. It is known that in the case of significantly covalent systems a paraelectric phase is of lower energy than the ferroelectric one due to the increasing of the rigidity and the stability of the metal-oxygen network (Villeszanne et al., 1998). From this point of view, it seems likely that – besides the pd covalency that appears to
prevent the ferroelectric instability at high pressure – there is an interaction that reveals itself only at high enough pressure (i.e., when the distance between atoms is sufficiently small). This gives us a clue that the interaction should be small at large interatomic distances (e.g., at zero pressure) and should increase more rapidly than covalency effects at small interatomic distances, bringing the ferroelectric instability into the system.

For a qualitative understanding of phase transformations under pressure, we recall that two energy contributions to the cohesive energy, namely the covalent and overlap energies, depend most strongly on the interatomic distance. According to the Harrison model, the (attractive) covalent interaction depends on the interatomic distance, $d$, as $\sim d^{-7/2}$ while the (repulsive) overlap interaction – which is due to nonorthogonality of wave functions on adjacent sites – behaves as $\sim d^{-7}$ and thus depends more strongly on the nearest-neighbor distance. The interplay between the short-range covalent and the overlap interactions can be nicely seen from the following arguments. The covalent energy contribution mainly represents the short-range electron-ion potential energy while the overlap energy can be predominantly ascribed to the increase of the kinetic energy of the valence electrons upon compression (Harrison, 1986). Since the resulting forces due to these two interactions (central repulsive forces and covalent forces) scale differently under pressure, one might expect that at some pressure the noncentral nature of the bonding will become negligible. Indeed, Fig. 16 shows that the high-pressure Cauchy relation between the elastic constants for hydrostatic conditions $C_{12} = C_{44} + 2P$, where $C_{12}$ and $C_{44}$ are the elastic constants calculated from first-principles, is satisfied for cubic PbTiO$_3$ in the vicinity of the the turning point ($\approx 30$GPa), which indicates an insignificant role of noncentral and many-body forces in this pressure region. This fact implies that, for instance, empirical two-body potentials could be used for calculations of elastic properties for pressures around the turning point. Away from the critical pressure the deviation from the Cauchy relation becomes significant. The latter implies that the contribution of either noncentral or many-body forces becomes more and more important at higher pressures, and it cannot be treated anymore as a small correction to the two-body potentials. Thus, we clearly see manifestation of the competing forces under pressure.

Note that a major role of competition between covalent and overlap interactions has been recognized for sp-bonded solids (Majewski and Vogl, 1985). Remarkably, a drastic softening of the transverse optical phonons across the pressure-induced phase transition
was predicted, and the physical origin of this softening was shown to be closely related to ferroelectricity (Majewski and Vogl, 1987).

Let us now proceed further by approximating, in Ti-based perovskites, the total effect of the coupling (i) between the oxygen $2s$ states and the $d$-orbitals of the Ti atom, and (ii) between the oxygen $2p$ states and the $d$-orbitals of the Ti atom, via the following expressions:

$$E_{sd\,\text{bond}} = 2V_3(sd) - 2[V_2(sd)^2 + V_3(sd)^2]^{1/2} + E_{sd\,\text{rep}}$$

$$E_{pd\,\text{bond}} = 6V_3(pd) - 6[V_2(pd)^2 + V_3(pd)^2]^{1/2} + E_{pd\,\text{rep}}$$

where the (polar energies) $V_3$ are the average of the cation and anion energy, and are given by $V_3(sd) = (e_d - e_s)/2$ and $V_3(pd) = (e_d - e_p)/2 -$ with $e_s = -29.14$ eV, $e_p = -14.13$ eV, and $e_d = -11.04$ eV (which are the energies of the $2s$ and $2p$ states of the oxygen atom and of the $3d$ states of the titanium atom, respectively (Harrison, 1980). The second terms $[...]^{1/2}$(which are the covalent energies) are connected with the bond formation energy and are responsible for lowering the energy of the bonding state. Based upon a second-moment approximation (Wills and Harrison, 1983), these covalent energies are given by $V_2(sd)^2 = \sum_j V_{s\sigma}(r_j)^2$ and $V_2(pd)^2 = \sum_j (V_{p\sigma}(r_j)^2 + 2V_{pd\pi}(r_j)^2)/3$, where the last sum is over the 6 nearest neighbors to Ti and where the so-called Harrison’s two-center interactions, $V_{ldm}$, can be taken to be of the form (Harrison, 1980):

$$V_{ldm} = \eta_{ldm} \frac{\hbar^2}{\mu} \frac{r_d^{3/2}}{r_j^{3/2}}$$

where $r_j$ is the interatomic distance between $Ti$ and the $j^{th}$ nearest-neighbor $O$, $\mu$ is the free-electron mass, $r_d = 1.029$ Å for titanium, $m = \sigma, \pi$, and $\eta$’s take the following values: $\eta_{s\sigma} = -3.16$, $\eta_{s\pi} = -2.95$, and $\eta_{sd\sigma} = 1.36$ (Harrison, 1980).

The third terms of Eq. (1), $E_{sd\,\text{rep}}$ and $E_{pd\,\text{rep}}$, are related to the overlap interactions. A repulsion comes from the shift in the energy of each electron due to the nonorthogonality of the $s, d$ and $p, d$ states on adjacent sites, with the average shifts being given by (Harrison and Straub, 1987):

$$\delta \varepsilon_{sd} = -\sum_j V_{s\sigma}(r_j)S_{s\sigma}(r_j)$$

$$\delta \varepsilon_{pd} = -1/3 \sum_j [V_{p\sigma}(r_j)S_{p\sigma}(r_j) + 2V_{pd\pi}(r_j)S_{pd\pi}(r_j)]$$
The overlap repulsion for a given bond, is equal to this shift times the number of electrons in these states. In the approximations adopted here we use the extended Hückel theory (Hoffmann, 1963) to derive the overlap elements, as proposed by van Schilfgaarde and Harrison (van Schilfgaarde and Harrison, 1986). It is plausible to take the overlap elements to be proportional to the corresponding off-diagonal hopping elements and inversely proportional to the on-site atomic orbital energies:

\[ S_{\alpha dm}(r) = \frac{2K_{\alpha d}}{e_{\alpha} + e_{d}}, \]

where \( \alpha = s, p \) and \( m = \sigma, \pi \). For the Wolfsberg-Helmholz parameter \( K_{ad} \), the weighted formula \( K_{ad} = \kappa + \frac{(e_{\alpha} - e_{d})^2}{(e_{\alpha} + e_{d})^2} + \frac{(1 - \kappa)(e_{\alpha} - e_{d})^4}{(e_{\alpha} + e_{d})^4} \) (Ammeter et al., 1978) could be used. In general, the Wolfsberg-Helmholz parameter \( K_{ad} \) can be given by the distance-dependent form (Calzaferri and Rytz, 1996). For the sake of simplicity and following Refs. (Baranowski, 1984; Harrison, 1983; Majewski and Vogl, 1987), we assume that \( K \) takes a different value for each row of the Periodic Table, i.e., the \( K \) of Carbon (\( K_C = 1.63 \)) for Oxygen and the \( K \) of Ge (\( K_{Ge} = 1.07 \)) for Titanium (Harrison, 1999) and take the average as \( K = (K_C K_{Ge})^{1/2} \).

Following this scheme, the covalent or polar bonding character of a given bond (e.g., \( sd \) or \( pd \)) can now be addressed. For each bond, the bond polarity, \( \alpha_p \), of the compound can be obtained from \( \alpha_p^2 = V_2^2/(V_2^2 + V_3^2) \) and a complementary quantity, the covalency coefficient, \( \alpha_c \), is defined through the relation \( \alpha_c^2 = 1 - \alpha_p^2 \). The tight-binding model demonstrates the strong reduction of the polarity of the \( sd \) and \( pd \) bonds under pressure, as shown in Fig. 17. On the other hand, the model predict a considerable increase of the \( sd \) \( O - Ti \) chemical bond covalency under pressure (i.e., when the interatomic distance decreases) – which is consistent with the first-principles population analysis reported in Section III.D.3. Indeed, as it can be clearly seen from Fig. 17 the \( sd \) bond covalency depends more strongly on the nearest-neighbor distance than the \( pd \) bond covalency, and therefore the first one may predominantly determine the behavior of perovskites in the vicinity of the turning point.

In the Harrison bond-orbital formalism, the frequency of the \( q = 0 \) optical phonon can be easily obtained (Harrison, 1980). Consider a perovskite structure viewed along a \( \langle 100 \rangle \) direction with a relative displacement \( u_j = u_{Ti} - u_{Oj} \) of the \( Ti \) and \( O \) atoms from their equilibrium positions in a \( \langle 100 \rangle \) direction when the atoms oscillate according to a \( \Gamma \)-point soft mode. Accordingly, the change in length of the indicated bond \( Ti - O \) is \( \delta d_j \), leading to a change in the bonding energy of \( \delta E_{sd \, bond} \) and \( \delta E_{pd \, bond} \). These changes in the bonding energy may be viewed as the frozen-phonon energy obtained as the difference of the respective energy
relative to its equilibrium value, $\delta E_{\alpha d\ bond} = E_{\alpha d\ bond}(u_j) - E_{\alpha d\ bond}(0)$. For the evaluation of the $sd$ and $pd$ contributions to the frozen-phonon energy, usual harmonic fit function can be used, i.e. $2 \delta E_{\alpha d\ bond} = \omega_{\alpha d}^2 \sum_j M_j u_j^2$, where $M_j$ are the atomic masses, and $\omega_{\alpha d}$ are the contributions from $sd$ and $pd$ interactions to the total frequency. [As an alternative to the above method, an analytic expression for these changes can be obtained by expanding Eq. 1 in a Taylor series with respect to the displacements and then truncating the series to the second order in the displacements.]

Let us consider the frequency of the $q = 0$ optical mode in which the $Ti$ and $O$ atoms move out of phase with the relative displacements which reproduce a high-pressure eigenvector of the soft mode obtained from first-principles (see, e.g., Fig.6). Since above the turning point the relative displacement of each of the 4 transverse oxygens $u_\perp$ is greater than that of each of the 2 longitudinal oxygens $u_\parallel$, $2u_\perp > u_\parallel$, we have chosen the following displacement pattern along the $z$ axis for the 6 oxygen ions: $[0.4u, 0.4u, u, u, u, u]$ with $u = 0.002$. Denoting $d$ as half of the cubic lattice constant We now see that one neighbor distance becomes $d - 0.4u$ (between the Ti atom and the top O atom), one becomes $d + 0.4u$ (between the Ti atom and the bottom O atom) and four become $(d^2 + u^2)^{1/2}$ (between the Ti atom and 4 transverse O atoms).

The results of the frozen-phonon calculations are shown in Fig. 18. At large interatomic distances both $sd$ and $pd$ contributions stabilize the paraelectric state, since they both have a positive $\delta E$. The curves of $\delta E_{sd\ bond}$ and $\delta E_{pd\ bond}$ have maximums which lies at around 2 Å and 1.8 Å, respectively. One thus finds a maximum at around 1.85 Å for the sum of two contributions. [Note that the experimental equilibrium interatomic distance in, for instance, SrTiO₃ is 1.95 Å and the turning point is around 1.85 Å according to our first-principles calculations.] These estimates are compatible with the assumption that the repulsion overlap energy does not become important until the turning point. The most striking result is that the model predicts a strong phonon softening upon compression since Fig. 18 shows that both $\delta E_{sd\ bond}$ and $\delta E_{pd\ bond}$, that first increase with pressure and reach a maximum at around the turning point, then decrease rapidly under compression and become negative at $\approx 1.83$ Å and $\approx 1.6$ Å, respectively. The interatomic distance at which the sum of both contributions becomes negative is $\approx 1.64$ Å, to be compared with our ab-initio result of $\approx 1.78$ Å for SrTiO₃. [It should be emphasized that an exact agreement with ab-initio calculations cannot be expected, on account of the approximations made in
the tight-binding model, especially the neglect of long-range interaction. Interestingly, it is the $sd$ contribution which first destabilizes the paraelectric phase under the influence of pressure. Therefore, the phonon frequency is reduced under pressure after the turning point as much as this destabilization is not compensated for by the other energy contributions. Moreover and interestingly, as the system is further compressed the $pd$ contribution also contributes to the destabilizing of the paraelectric phase. The present tight-binding model thus predicts a striking softening of a $\Gamma$-point phonon mode under compression, and clearly explains the strong preference of perovskites to form ferroelectrically distorted structures at high pressure due to an *electronically driven* structural instability (i.e., electron-phonon coupling). In particular, this simple model reveals the predominant role played by the costly-in-energy overlap between the $2s$ orbitals of oxygen and the $3d$ orbitals of Ti on the high-pressure FE of perovskites.

**G. Electronically Driven Instability**

According to the above simple tight-binding model, it is the electrons and their interactions with ions (i.e., electron-phonon coupling) that are responsible for the high-pressure ferroelectric instability of perovskites. In this section, the electron-ion interaction will be considered in more details. More precisely, we shall be interested in the electronic contribution into the ferroelectric soft mode within DFT and within the adiabatic approximation.

Note that the adiabatic approximation consists in (a) neglecting the phonon contributions to the electronic density response and (b) approximating the dynamical response by a static one (Geilikman, 1973; Sham, 1974). In the adiabatic approximation, the electrons are considered to remain in the instantaneous (electronic) ground state when the lattice vibrates. Consequently, the effect of electrons on the adiabatic phonon frequencies is due to the fact that the change in the charge density induced by the displacements of nuclei screens the external perturbation (and the linear-response equations must be solved self-consistently) (Savrasov, 1996).

To refresh readers’ memory, let us remind some basic equation of density-functional theory (DFT). Within the framework of DFT, the total energy can be expressed in terms of the Kohn-Sham eigenvalues $\epsilon_i$:  

\[ E = \sum_i \epsilon_i \]
\[ E = \sum_i f_i \epsilon_i - \frac{e^2}{2} \int dr dr' \frac{n(r)n(r')}{|r - r'|} + E_{xc}[n(r)] - \int n(r)v_{xc}(r)dr + E_N(R). \]  

where \( f_i \) is the occupancy of the state \( i \), and \( n(r) \) is the density of the valence electrons. The first term is the band structure energy:

\[ \sum_i f_i \epsilon_i = \sum_i f_i \langle i | -1/2 \nabla^2 + V_{SCF}(r) | i \rangle \]  

where an effective potential (also called self-consistent, SCF, potential) is:

\[ V_{SCF}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r - r'|}dr' + v_{xc}(r), \]  

and \( v_{xc}(r) \equiv \delta E_{xc}/\delta n(r) \) is the exchange-correlation potential and \( V_{ext}(r) \) is the external (ionic) potential acting on the electrons. \( E_N(R) \) is the electrostatic interaction between different nuclei:

\[ E_N(R) = \frac{e^2}{2} \sum_{i \neq j} \frac{Z_i Z_j}{|R_i - R_j|}. \]  

Note that, in general, the bare ion-ion contribution into phonon modes can stabilize as well as destabilize the paraelectric state. The destabilizing nature of this contribution is a trivial consequence of Earnshaw’s theorem (Earnshaw, 1842; Feynman and Sands, 1975) that states that a static system of electric charges can not have a position of stable equilibrium. As a result, the crystals stability is ensured by the electron contribution to the force constants. Although it is possible that the ion-ion contribution to a ferroelectric soft mode destabilizes this mode, it is not necessarily the case—implying that the ferroelectric soft mode can be stable in a lattice of bare ionic charges (Kvyatkovskii and Maksimov, 1988). This particular situation occurs in the case of the ferroelectric soft mode in perovskites under pressure, since we numerically found that the ionic term in the force constants (which arises from the ion-ion Ewald term (Giannozzi et al., 1991) with the bare ionic (pseudo)charges (for example, \( Z_{Pb} = 14, Z_{Ti} = 12, Z_{O} = 6 \)) is positive in the pressure range of interest.

Next, we are interested in the electronic contribution to the phonon spectrum. The total second-order change in the electronic energy \( E_{el}^{(2)} \) can be written as (Johnson, 1969; Sham, 1969).

\[ E_{el}^{(2)} = E_{el1}^{(2)} + E_{el2}^{(2)} \]
\[= \sum_{i \neq j} f_i \langle i|\delta V_{\text{ext}}|j\rangle \langle j|\delta V_{\text{ext}}|i\rangle \frac{(\epsilon_i - \epsilon_j)}{\epsilon_i - \epsilon_j} + \sum_i f_i \langle i|\delta V_{\text{ext}}^{(2)}|i\rangle \]

\[= 1/2 \int d\mathbf{r} \delta n(\mathbf{r}) \delta V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r} n^0(\mathbf{r}) \delta V_{\text{ext}}^{(2)}(\mathbf{r})\]  (8)

where \(n^0(\mathbf{r})\) is the electronic density of the unperturbed crystal, \(\delta n(\mathbf{r})\) is the change in the electron density due to the ionic displacements, \(\delta V_{\text{ext}}(\mathbf{r})\) is the change in the “bare” potential experienced by the electron system to first order in the ionic displacements, and \(\delta V_{\text{ext}}^{(2)}(\mathbf{r})\) the second order change. Therefore, the expression for the electronic contribution to the adiabatic force constant matrix consists of a negative-definite contribution \(E^{(2)}_{\text{el1}}\) (the first term in Eq. 8) and a positive-definite contribution \(E^{(2)}_{\text{el2}}\) (the second term in Eq. 8) (Kvyatkovskii and Maksimov, 1988).

Let us now consider the negative-definite contribution \(E^{(2)}_{\text{el1}}\) to the adiabatic force constant matrix in more details (Geilikman, 1975; Kvyatkovskii and Maksimov, 1988). This contribution describes how a first order change in the external Hamiltonian leads to a first order change in the density matrix, which acts back at the Hamiltonian.

Let us first consider the change in density \(\delta n(\mathbf{r})\) induced by a change in the external potential \(\delta V_{\text{ext}}(\mathbf{r})\). Within DFT, one can define the non-interacting electron polarizability, \(\chi_0(\mathbf{r}, \mathbf{r}')\), as the charge-density response to a variation of the total potential:

\[\delta n(\mathbf{r}) = \int d\mathbf{r}' \chi_0(\mathbf{r}, \mathbf{r}') \delta V_{\text{SCF}}(\mathbf{r}').\]  (9)

The expression for \(\chi_0(\mathbf{r}, \mathbf{r}')\) has the well known form (Pick et al., 1970; Sham, 1969, 1974):

\[\chi_0(\mathbf{r}, \mathbf{r}') = \sum_{i,j} \frac{f_i - f_j}{\epsilon_i - \epsilon_j} \psi_i^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}').\]  (10)

where the sums over \(i\) and \(j\) extend to both occupied and empty states. Clearly, only terms involving virtual transitions from occupied or partially occupied to empty or partially empty states contribute because of the difference \(f_i - f_j\) in the numerator.

Recall the relationship between the bare and the self-consistent perturbing potential:

\[\delta V_{\text{SCF}}(\mathbf{r}) = \delta V_{\text{ext}}(\mathbf{r}) + \int d\mathbf{r}' K(\mathbf{r}, \mathbf{r}') \delta n(\mathbf{r}'),\]  (11)

where:

\[K(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta n(\mathbf{r}) \delta n(\mathbf{r}')}\]  (12)

Combining Eqs. (8–11), one can rewrite the the negative-definite contribution as follows:
are the electron-phonon matrix-elements. The sum has to be carried out, in principle, for overlap effects. An important feature of this expression noted in Refs. (Varma and Weber, 1973, 1979) is the negative-definite contribution of the band structure energy \( E_{el}^{(2)} \) to the dynamical matrix can be written in the form

\[
E_{el}^{(2)} = 1/2 \int dr \delta n(r) \delta V_{ext}(r) - 1/2 \int dr' \delta V_{SCF}(r) \chi_0(r, r') \delta V_{SCF}(r') - 1/2 \int dr \delta n(r) K(r, r') \delta n(r') \quad (13)
\]

Substituting the results (12) and (13) in Eq. (8) we obtain

\[
E_{el}^{(2)} = 1/2 \int dr \delta V_{SCF}(r) \chi_0(r, r') \delta V_{SCF}(r') + \int dr \delta n(r) \delta V_{ext}(r) \left[ \frac{e^2}{|r - r'|} + \frac{\delta^2 E_{xc}}{\delta n(r) \delta n(r')} \right] \delta n(r') \quad (14)
\]

The first two terms in Eq. (14) are due to the variation of the band energy term in the total energy (the first term in Eq. (11)) and the third term in Eq. (14) is due to the variation of the Hartree energy and the exchange-correlation energy.

The total electronic contribution (see Eq. 8) to the interatomic force constant tensor \( \Phi_{\alpha \beta}^{\lambda \mu} \) between the atoms at \( r_l \) and \( r_{l'} \) can be linked to the second-order change in the electronic energy with respect to collective ionic displacements in the usual way as

\[
2E_{el}^{(2)} = \sum_{l, l'} \Phi_{\alpha \beta}^{\lambda \mu} \delta n_{\alpha \beta}(r_l, r_{l'}) = \sum_{l, l'} \delta n_{\alpha \beta}(r_l, r_{l'})\delta V_{SCF}(r_l, r_{l'})
\]

where \( \delta n_{\alpha \beta}(r_l, r_{l'}) \) is the displacement of the \( l \)th ion in the \( \alpha \)-direction from its equilibrium position \( R_l \).

Taking into account that \( \delta V_{SCF}(r) = 1/2 \sum_l \delta V_{SCF}(r_l)/\delta R_l \cdot u_l \), the negative-definite contribution of the band structure energy \( E_{el}^{(2)} \) to the dynamical matrix can be written in the form (Varma and Weber, 1973)

\[
\Phi_{\alpha \beta}^{\lambda \mu}(q) = \frac{1}{N_c} \sum_{\lambda \mu, k} \frac{f_{k+q \lambda'} - f_{k \lambda}}{\epsilon_{k+q \lambda'} - \epsilon_{k \lambda}} g_{k+q \lambda, k \lambda}^{\alpha \lambda} g_{k+q \lambda', k \lambda}^{\beta \lambda} \quad (15)
\]

where \( N_c \) the number of unit cells in the crystal, and \( g_{k \lambda \lambda', k \lambda}^{\lambda \lambda'} = (\delta V_{SCF}(r) / \delta R_{\lambda q}) (k \lambda) \) are the electron-phonon matrix-elements. The sum has to be carried out, in principle, over all bands \( \lambda, \lambda' \) and all \( k \) points \( k \), \( k' \) that can be connected via the phonon wave vector \( q \). Interestingly, simplifying the electron-phonon matrix-elements within nonorthogonal tight-binding representation as (Varma and Weber, 1977, 1979) \( g_{k \lambda \lambda', k' \lambda'} \propto (\partial \epsilon_{k \lambda} / \partial k [A_k^{\dagger} S_k A_k^{\dagger},]_{\lambda \lambda'} - \partial \epsilon_{k' \lambda'} / \partial k' [A_{k'}^{\dagger} S_{k'} A_{k'}^{\dagger},]_{\lambda \lambda'}) \) – where \( S \) is the overlap and \( A \) the eigenvector matrix – we clearly see the dependence of the electron-phonon interaction on the overlap effects. An important feature of this expression noted in Refs. (Varma and Weber, 1973, 1979).
is the fact that the electron-phonon coupling is large where the electron velocities are large and therefore the density of states are small. Indeed, we numerically checked these facts in our first principles calculations.

Interestingly, Eq. (15) is in fact the electron-phonon coupling in the so-called Fröhlich model (Fröhlich, 1954) – which thus proves that such coupling is naturally included in the adiabatic approximation within DFT (Geilikman, 1975; Kvyatkovskii and Maksimov, 1988). (Note that the electron-phonon coupling is responsible for the ferroelectric instability in the vibronic theory of ferroelectricity (Kristoffel and Konsin, 1988), i.e., the existence of the pseudo Jahn-Teller effect due to the existence of two closely situated filled $p$ and $d$ empty bands in perovskites-like structures (Sinha and Sinha, 1964)).

Eq. (15) has been used to calculate the electron-phonon contribution to the ferroelectric soft mode at the $\Gamma$ point in PbTiO$_3$ and NaNbO$_3$. More precisely, we obtained the eigenvalues of the LDA-determined $\Phi_{ll}^{\alpha\beta}(q)$ matrix corresponding to the LDA-determined eigenvectors of the total dynamical matrix. The resulting eigenvalue $\omega_{ep}^2$ corresponding to the soft TO mode is negative for any pressure and shown in Fig. 19 and clearly behaves in a nonmonotonic way with pressure. Interestingly, this nonmonotonic behavior varies in a correlated way with the soft-mode total frequency (see Figs. 6, 7, 8) under pressure – which thus confirms that the electron-phonon coupling is the leading mechanism for the high-pressure ferroelectricity.

IV. CONCLUDING REMARKS.

In summary, our results reveal that, unlike commonly thought, ferroelectricity is not suppressed by high pressure in insulating perovskites. Instead, ferroelectricity is found to enhance as pressure increases above a critical value. Moreover, this unexpected high-pressure ferroelectricity is different in nature from conventional ferroelectricity because it is driven by an original electronic effect rather than by long-range ionic interactions. Depending on the energetic difference between ferroelectric and paraelectric phases at atmospheric pressure, such phenomenon can lead to various overlooked/original effects, e.g. (i) the disappearance and then re-entrance of ferroelectricity under pressure; (ii) the occurrence of FE at high pressure in a nominally-paraelectric compound; and (iii) the existence of FE at any pressure (see Figure 6). We thus hope that this article, and its numerous details, will stimulate the
investigation of novel effects in “smart” materials under pressure.

We would like to thank S. Prosandeev and I. Ponomareva for useful discussions. This work is supported by ONR grants N00014-01-1-0365, N00014-04-1-0413 and N00014-01-1-0600, by NSF grants DMR-0404335, and by DOE grant DE-FG02-05ER46188.

References

Abdullin, K., A. Lebedev, A. Gas'kov, V. Demin, and V. Zlomanov, 1984, JETP Lett. 40(6), 998.
Abramov, Y., 1997, Acta Cryst. A53, 264.
Ammeter, J. H., H. B. Buergi, J. C. Thibeault, and R. Hoffmann, 1978, J. Am. Chem. Soc. 100, 3686.
Bader, R., 1990, Atoms in molecules. A quantum theory (Oxford University Press, Oxford, UK).
Baranowski, J. M., 1984, J. Phys. C: Solid State Phys. 17, 6287.
Baroni, S., A. Dal Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti, P. Focher, A. Pasquarello, K. Laasonen, A. Trave, et al., 2001, (www.pwscf.org).
Bellaiche, L., and D. Vanderbilt, 2000, Phys. Rev. B 61(12), 7877.
Birch, F., 1986, J. Geophys. Res. 91(B5), 4949.
Burns, G., and B. Scott, 1973, Phys. Rev. B 7(7), 3088.
Calzaferri, G., and R. Rytz, 1996, J. Phys. Chem. 100, 11122.
Ceperley, D., and B. Alder, 1980, Phys. Rev. Lett. 45(7), 566.
Cohen, R., 1992, Nature 358(6382), 136.
Cohen, R., and H. Krakauer, 1990, Phys. Rev. B 42(10), 6416.
Cohen, R., and H. Krakauer, 1992, Ferroelectrics 136(1-4), 65.
Cohen, R., and Z. Wu, 2006, in APS March Meeting (Baltimore, MD).
Earnshaw, S., 1842, Trans. Camb. Phil. Soc. 7, 97.
Espinosa, E., I. Alkorta, J. Elguero, and E. Molins, 1998, Chem. Phys. Lett. 285, 170.
Espinosa, E., I. Alkorta, J. Elguero, and E. Molins, 2002, J. Chem. Phys. 117, 5529.
Feynman, R., R.P. and Leighton, and M. Sands, 1975, The Feynman Lectures on Physics, volume 2 (Addison-Wesley).
Frohlich, H., 1954, Advances in Physics 3(11), 325.
Geilikman, B., 1975, Sov. Phys. Usp. 18, 190.
Ghosez, P., X. Gonze, and J. Michenaud, 1996, Europhysics Letters 33(9), 713.
Ghosez, P., J.-P. Michenaud, and X. Gonze, 1998, Phys. Rev. B 58(10), 6224.
Giannozzi, P., S. de Gironcoli, P. Pavone, and S. Baroni, 1991, Phys. Rev. B 43(9), 7231.
Ginzburg, V., 2001, Phys-Usp. 44, 1037.
Goedecker, S., M. Teter, and J. Hutter, 1996, Phys. Rev. B 54(3), 1703.
Gonze, X., D. Allan, and M. Teter, 1992, Phys. Rev. Lett. 68(24), 3603.
Gonze, X., J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstaete, G. Zerah, F. Jollet, M. Torrent, A. Roy, et al., 2002, Computational Materials Science 25(3), 478.
Harrison, W., 1980, Electronic structure and the properties of solids : the physics of the chemical bond (W. H. Freeman and Company, San Francisco).
Harrison, W., 1999, Electronic Structure and the Properties of Solids (River Edge, NJ : World Scientific, Singapore).
Harrison, W. A., 1983, Phys. Rev. B 27, 3592.
Harrison, W. A., 1986, Phys. Rev. B 34(4), 2787.
Harrison, W. A., and G. K. Straub, 1987, Phys. Rev. B 36(5), 2695.
Hoffmann, R., 1963, The Journal of Chemical Physics 39(6), 1397.
Hussermann, U., 2003, Chem. Eur. J. 9, 1472.
Johnson, F. A., 1969, Proc. R. Soc. London Ser. A 310, 79, 89, 101, 111.
Karki, B. B., G. J. Ackland, and J. Crain, 1997, J. Phys.: Condens. Matter 9(41), 8579.
King-Smith, R., and D. Vanderbilt, 1994, Phys. Rev. B 49, 5828.
King-Smith, R. D., and D. Vanderbilt, 1993, Phys. Rev. B 47(3), 1651.
Kornev, I. A., L. Bellaiche, P. Bouvier, P.-E. Janolin, B. Dkhil, and J. Kreisel, 2005, Physical Review Letters 95(19), 196804.
Kristoffel, N., and P. Konsin, 1988, Phys. Status Solidi B 149(1), 11.
Kuroiwa, Y., S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata, and M. Sakata, 2001, Phys. Rev. Lett. 87(21), 217601.
Kvyatkovskii, O. E., and E. G. Maksimov, 1988, Sov. Phys. Usp. 31, 1.
Lines, M. E., and A. M. Glass, 1977, Principles and Applications of Ferroelectrics and Related Materials (Clarendon Press).
Majewski, J., and P. Vogl, 1985, Phys. Rev. Lett. 57(11), 1366.
Majewski, J., and P. Vogl, 1987, Phys. Rev. B 35, 9666.
Monkhorst, H. J., and J. D. Pack, 1976, Phys. Rev. B 13(12), 5188.
Moreno, M., J. A. Aramburu, and M. T. Barriuso, 1997, Phys. Rev. B 56(22), 14423.
Murase, K., 1980, J. Phys. Soc. Jpn. 49, 725.
Parlinski, K., and Y. Kawazoe, 2000, Eur. Phys. J. B 16(1), 49.
Parlinski, K., Z. Q. Li, and Y. Kawazoe, 2000, Phys. Rev. B 61(1), 272.
Perdew, J., and Y. Wang, 1992, Phys. Rev. B 45(23), 13244.
Perdew, J., and W. Yue, 1986, Phys. Rev. B 33, 8800.
Perdew, J., and A. Zunger, 1981, Phys. Rev. B 23(10), 5048.
Perdew, J. P., K. Burke, and M. Ernzerhof, 1996, Phys. Rev. Lett. 77(18), 3865.
Pick, R., M. H. Cohen, and R. Martin, 1970, Phys. Rev. B 1, 910.
Posternak, M., R. Resta, and A. Baldereschi, 1995, Phys. Rev. B 50(12), 8911.
Samara, G. A., T. Sakudo, and K. Yoshimitsu, 1975, Phys. Rev. Lett. 35(26), 1767.
Sanderson, R., 1962, Chemical Periodicity (Reinhold, New York).
Sani, A., M. Hanfland, and D. Levy, 2002, J. Phys.: Cond. Matt. 44, 10601.
Sani, A., B. Noheda, I. A. Kornev, L. Bellaiche, P. Bouvier, and J. Kreisel, 2004, Phys. Rev. B 69(2), 020105.
Sanjurjo, J., E. Lopez-Cruz, and G. Burns, 1983, Phys. Rev. B 28, 7260.
Savrasov, S. Y., 1996, Phys. Rev. B 54(23), 16470.
van Schilfgaarde, M., and W. A. Harrison, 1986, Phys. Rev. B 33(4), 2653.
Sham, L. J., 1969, Phys. Rev. 188(3), 1431.
Sham, L. J., 1974, Theory of lattice dynamics of covalent crystals (American Elsevier Publishing Company, Inc., North-Holland, Amsterdam), volume 1 of Dynamical Properties of Solids, chapter 5, p. 301.
Shannon, R., 1976, Acta Cryst. A32, 751.
Sinha, K. P., and A. P. B. Sinha, 1964, Indian Journal of Pure and Applied Physics 2(3), 91.
Teter, M., 1993, Phys. Rev. B 48(8), 5031.
Tsirelson, V. G., 2002, Acta Cryst. B58, 632.
Vanderbilt, D., 1990, Phys. Rev. B 41, 7892.
Vanderbilt, D., and W. Zhong, 1998, Ferroelectrics 207(1-2), 181, ISSN 0015-0193.
Varma, C. M., and W. Weber, 1977, Phys. Rev. Lett. 39(17), 1094.
Varma, C. M., and W. Weber, 1979, Phys. Rev. B 19(12), 6142.
Villesuzanne, A., C. Elissalde, M. Pouchard, and J. Ravez, 1998, Eur. Phys. J. B 6(3), 307.
Weiser, K., 1981, Phys. Rev. B 23(6), 2741.
Wills, J. M., and W. A. Harrison, 1983, Phys. Rev. B 28, 4363.
Wu, Z., and R. E. Cohen, 2005, Physical Review Letters 95(3), 037601 (pages 4).
Zha, C., A. Kalinichev, J. Bass, C. Suchicital, and D. Payne, 1992, J. Appl. Phys. 72(8), 3705.
Zhong, W., R. D. King-Smith, and D. Vanderbilt, 1994, Phys. Rev. Lett. 72(22), 3618.
Zhong, W., D. Vanderbilt, and K. Rabe, 1995, Phys. Rev. B 52(9), 6301.
Zhurova, E. A., and V. G. Tsirolelson, 2002, B58, 567.
FIG. 1 First-principles prediction of the pressure behavior of (a) $\Delta \mathcal{H}$ (see text) for all the considered phases (the phase corresponding to a minimal $\Delta \mathcal{H}$ at a given $P$ is thus the most stable one for this pressure), (b) the Cartesian components (along the pseudo-cubic $\langle 001 \rangle$ axes) of the polar local soft-mode (Zhong et al., 1995) - which is directly proportional to the spontaneous polarization - for the P4mm, I4cm, R3m and R3c phases, and (c) the rotational angle of the oxygen octahedra with respect to the pseudo-cubic $\langle 111 \rangle$ direction for the R3c and R3c rhombohedral phases and with respect to the pseudo-cubic $\langle 001 \rangle$ direction for the I4cm and I4/mcm tetragonal phases.
FIG. 2 The LDA-predicted pressure behavior of the $c/a$ distortion at 0K for the P4mm phase in PbTiO$_3$. 
FIG. 3 The pressure dependence of the elastic stiffness coefficients $c_{11}$ (squares), $c_{12}$ (dots), and $c_{44}$ (triangles) of the cubic phase of PbTiO$_3$, as predicted by LDA.
FIG. 4 Pressure evolution of the normalized Born effective charges for Pb, Ti, O⊥ and O∥ in the cubic phase of PbTiO₃. The normalization is done with respect to the Born effective charges at zero pressure obtained with ABINIT for Pb, Ti, O⊥, and O∥ in the cubic Pm3m phase – that are 3.915, 7.14, -2.61 and -5.85, respectively.
FIG. 5 Pressure behavior of phonons in PbTiO$_3$ (solid symbols) and BaTiO$_3$ (open symbols). Panel (a) displays the square of the zone-center TO phonon frequency in the cubic phase within LDA at 0K. Panel (b) shows the contributions from the Coulomb interactions (squares) within the rigid ions model and non-Coulomb interactions (triangles) to this square.
FIG. 6 LDA-predicted pressure behavior of the soft-mode eigenvalue and eigenvectors of the second-derivative matrix in cubic PbTiO$_3$ (panels (a) and (d)), BaTiO$_3$ (panels (b) and (e)) and BaZrO$_3$ (panels (c) and (f)). The GGA results are also shown for PbTiO$_3$ in panels (a) and (d), and suggest that PbTiO$_3$ may be paraelectric within a small pressure range. O$_3$ is the oxygen atom located between two (slightly displaced) B-atoms along the [001] direction.
FIG. 7 LDA-predicted pressure behavior of the soft-mode eigenvalue and eigenvectors of the second-derivative matrix in cubic KNbO$_3$, NaNbO$_3$, SrTiO$_3$, CaTiO$_3$ and PbZrO$_3$. 
FIG. 8 LDA-predicted pressure behavior of the soft-mode frequency square in cubic WO$_3$. 
FIG. 9 LDA-predicted pressure behavior of the soft-mode frequency square in the cubic phase of PbTiO$_3$, when excluding the 5d semicore states of Pb and 3s and 3p semicore states of Ti from the valence electrons (unlike the 6s and 6p states of Pb, the 3d and 4s states of Ti and the 2s and 2p states of oxygen that are kept in the valence).
FIG. 10 LDA-predicted pressure behavior of the soft-mode eigenvalues of the second-derivative matrix in cubic bismuth aluminate BiAlO$_3$ and magnesium silicate MgSiO$_3$. 
FIG. 11 Electronic-related properties of PbTiO$_3$ under pressure. Panels (a), (b) and (c) display the partial electronic density of occupied states in the cubic phase at 3.6, 40 and 103 GPa, respectively, for the O 2s, O 2p and Ti 3d orbitals. The zero in energy is chosen at the top of the valence band, $E_f$. 
FIG. 12 Integrated DOS of PbTiO$_3$ under pressure in the cubic state. Panel (a) displays the integrated PDOS for Ti 3$d$ and O 2$p$ and 2$s$ states; panel (b) displays the normalized integrated PDOS for the same states; panel (c) displays the contributions to the normalized integrated PDOS coming from the low-lying O 2$s$ and Ti 3$d$ $e_g$ states (located between -22 and -15 eV) and from the topmost group of the valence O 2$p$ and Ti 3$d$ bands.
FIG. 13 Integrated PDOS of BaTiO$_3$ under pressure in the cubic state. The inset shows the variation of the integrated PDOS of Ti $3d$ $e_g$ and Ti $3d$ $t_{2g}$ versus pressure.
FIG. 14 The bond degree parameter $BD = h(r_{cp})/\rho(r_{cp})$ vs. $|v(r_{cp})|/g(r_{cp})$ ratio for the Ti-O (squares) and Pb-O (triangles) bonds. The arrows indicate the direction of pressure increase. Vertical dashed lines indicate the regions of stability for the three classes of atomic interactions (see text).
FIG. 15 (a) Pressure evolution of the ionic Bader volumes for Pb, Ti and O and the unit cell volume $V_{\text{CELL}}$ in the cubic phase of PbTiO$_3$. (b) The pressure dependence of the normalized volumes. (The normalized volumes are equal to unity at 0 GPa.)
FIG. 16 LDA-predicted deviations from the Cauchy relation \( \delta = C_{12} - C_{44} - 2P \) as a function of pressure for the cubic phase of PbTiO\(_3\).
FIG. 17 The Ti3d-O2s and Ti3d-O2p bonds polarity and covalency of a perovskite as a function of the interatomic Ti-O distance $d$ in the ideal cubic phase. (Note that the pressure increases as $d$ decreases).
FIG. 18 Change in bonding energy (solid lines) within the bond-orbital model of Harrison. This change is directly proportional to the soft-mode frequency square within this model. The contributions of the \(sd\) and \(pd\) bonds to that total change are also indicated via dashed lines. \(d\) is the Ti-O distance in the ideal cubic phase.
FIG. 19 Normalized electron-phonon contribution $\omega_{ep}^2$ to the ferroelectric soft mode at the $\Gamma$ point in the cubic state of PbTiO$_3$ and NaNbO$_3$. Normalization has been done such as to obtain values of $-1$ at 0 GPa.