First-Principles Study of Piezoelectricity in $PbTiO_3$

Gotthard Sághi-Szabó and Ronald E. Cohen
Carnegie Institution of Washington, 5251 Broad Branch Road, N.W., Washington, D.C. 20015-1305

Henry Krakauer
Department of Physics, College of William and Mary, Williamsburg, Virginia 23187-8795
(Received 6 October 1997)

The first self-consistent computations of piezoelectricity in a ferroelectric are presented. Bulk spontaneous polarization, dynamical charges (Z^*), and the full piezoelectric stress tensor of $PbTiO_3$ were determined from ground-state Berry's phase calculations using the all-electron linearized augmented plane wave method. Both the proper and total piezoelectric moduli were computed and were found to be significantly different. The theoretical piezoelectric stress moduli, $e_{15} = 3.15\ \mathrm{C/m^2}$, $e_{31} = -0.93\ \mathrm{C/m^2}$, and $e_{33} = 3.23\ \mathrm{C/m^2}$, agree well with single crystal experimental data. [S0031-9007(98)06014-1]

PACS numbers: 77.84.Dy

Ferroelectric materials are of great importance for a variety of technological applications including optoelectronics, waveguide devices, and pyrodetectors. $PbTiO_3$ (PT) is an end member of lead zirconate titanate (PZT) , which is used in many piezoelectronic devices, including acoustic and ultrasonic transducers, detectors, and actuators [1–3], but these materials are not yet fundamentally understood. $PbTiO_3$ is one of the simplest ferroelectric oxides since it has a clearly established single transition with $T_c = 766$ K from a paraelectric cubic to a ferroelectric tetragonal phase, and its electronic structure has been studied extensively [4–7]. PT is also an end member for the newly discovered relaxor-PT materials with very high electromechanical coupling properties and low dielectric loss, represented by $PbZn_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PZN-PT) and $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT) [8], which may revolutionize acoustic sensors and transducers, with important applications in medical ultrasound and acoustic measurements. PT is an obvious starting point for understanding piezoelectricity in ferroelectrics. In contrast to polycrystalline piezoelectric ceramics, morphotropic phase boundary compositions were not necessary in single crystal PZN-PT and PMN-PT materials to achieve ultrahigh piezoelectric coefficients. Using density functional theory as a method to investigate properties of infinite, periodic solids, intrinsic contributions dominating the total piezoelectric tensor of single crystal materials can be separated from extrinsic contributions (e.g., domain boundaries) existing in polycrystalline, multidomain samples. The theoretical study of the driving force behind piezoelectricity is important for the understanding and design of piezoelectric materials, especially in cases, such as PZT, when producing single crystals is difficult. In this Letter, the complete piezoelectric response and dynamical charge tensors of the technologically important ferroelectric $PbTiO_3$ are computed from first-principles within the density functional theory using the all-electron full-potential linearized augmented plane wave (LAPW) method [9]. This study is the first application of modern polarization theory using the Berry's phase approach [10,11] to compute piezoelectric response in a ferroelectric.

The total closed circuit (zero field) macroscopic polarization of a strained sample $\vec{P}^T$ can be expressed as $P_i^T = P_i^s + e_{i\nu}\epsilon_\nu$, where P_i^s is the spontaneous polarization of the unstrained sample, ϵ_ν is the strain tensor element, and $e_{i\nu}$ defines the piezoelectric tensor elements in Voigt notation. At low temperatures $PbTiO_3$ is tetragonal (crystal class *4mm*), and has a nonvanishing polarization along the (001) axis. The three independent piezoelectric tensor components are $e_{31} = e_{32}$ and e_{33}, which describe the zero field polarization induced along the z axis when the crystal is uniformly strained in the basal xy plane or along the z axis, respectively, and $e_{15} = e_{24}$ which measures the change of polarization perpendicular to the z axis induced by shear strain. This latter component is related to the induced polarization by $P_1 = e_{15}\epsilon_5$ and $P_2 = e_{15}\epsilon_4$. The total induced polarization along the crystallographic c axis can be expressed by a sum of two contributions as $P_3 = e_{33}\epsilon_3 + e_{31}(\epsilon_1 + \epsilon_2)$, where $\epsilon_1 = (a - a_0)/a_0$, $\epsilon_2 = (b - b_0)/b_0$, and $\epsilon_3 = (c - c_0)/c_0$ are strains along the a, b, and c axis, respectively, and a_0, b_0, and c_0 are lattice parameters of the unstrained reference structure. The change in total macroscopic polarization, containing both electronic and rigid ionic core contributions, is a well defined bulk property (in the absence of a macroscopic electric field $\vec{E}_{\mathrm{macro}} = 0$) and could be determined experimentally under shorted boundary conditions. Therefore the total piezoelectric constant can be calculated from finite differences of polarizations between crystals of different shapes and volumes.

The electronic part of the polarization was determined using the Berry's phase approach [10], a quantum mechanical theorem dealing with a system coupled to a slowly changing environment. One can calculate the polarization difference between two states of the same solid, under the necessary condition that the crystal remains an insulator along the path which transforms the two states into each other through an adiabatic variation of a crystal Hamiltonian parameter (λ). Expressing electronic polarization in terms of a dynamic current [12] instead of static charge separation provides well defined bulk quantities at the adiabatic limit. The magnitude of the electronic polarization of a system in state (λ) is defined only modulo $e\mathbf{R}/\Omega$, where $\mathbf{R}$ is a real-space lattice vector and Ω is the volume of the cell. In practice the eR/Ω factor can be eliminated by careful inspection, if the changes in polarization are such that $|\Delta\mathbf{P}| \ll |e\mathbf{R}/\Omega|$. The electronic polarization can be expressed as

$$P^{\mathrm{el}}(\lambda) = -\frac{2e}{(2\pi)^3}\int_{BZ} d\mathbf{k}\,\frac{\partial}{\partial\mathbf{k}'}\,\phi^{(\lambda)}(\mathbf{k},\mathbf{k}')\bigg|_{\mathbf{k}'=\mathbf{k}}, \quad (1)$$

where the integration domain is the reciprocal unit cell of the solid in state λ, and $\phi^{(\lambda)}$ are the geometric quantum phases, defined as phases of overlap-matrix determinants constructed from periodic parts of occupied valence Bloch states $\nu_n^{(\lambda)}(\mathbf{k})$ evaluated on a dense mesh of $\mathbf{k}$ points from $\mathbf{k}_0$ to $\mathbf{k}_0 + \mathbf{b}$, where $\mathbf{b}$ is the reciprocal lattice vector, as $\phi^{(\lambda)}(\mathbf{k},\mathbf{k}') = \mathrm{Im}\{\ln[\det\langle \nu_m^{(\lambda)}(\mathbf{k}) \,|\, \nu_n^{(\lambda)}(\mathbf{k}')\rangle]\}$. The electronic polarization difference between two crystal states can be expressed as $\Delta P^{\mathrm{el}} = P^{\mathrm{el}}(\lambda_2) - P^{\mathrm{el}}(\lambda_1)$. Common origins to determine electronic and core parts were arbitrarily assigned along the crystallographic axes. The individual terms in the sum do depend on the choice; however, the final results are independent of origin.

The elements of the macroscopic piezoelectric tensor can be further separated into two parts: a clamped-ion or homogeneous strain contribution evaluated at vanishing internal strain u [13], and a term that is due to an internal microscopic strain, i.e., the relative displacements of differently charged sublattices:

$$e_{i\nu} = \frac{\partial P_i^T}{\partial\epsilon_\nu}\bigg|_u + \sum_k \frac{\partial P_i^T}{\partial u_{k,i}}\bigg|_\epsilon \frac{\partial u_{k,i}}{\partial\epsilon_\nu}, \quad (2)$$

where P_i^T is the total induced polarization along the ith axis of the unit cell.

Equation (2) can be rewritten in terms of the clamped-ion part and the diagonal (in $PbTiO_3$) elements of the Born (transverse) effective charge tensor as

$$e_{i\nu} = e_{i\nu}^{(0)} + \sum_k \frac{ea_i}{\Omega} Z_{k,ii}^{*} \frac{\partial u_{k,i}}{\partial\epsilon_\nu}, \quad (3)$$

where Ω is the volume, a_i is the lattice parameter, the clamped-ion term $e^{(0)}$ is the first term of Eq. (2), and is equal to the sum of rigid core $e^{(0),\mathrm{core}}$ and valence electronic $e^{(0),\mathrm{el}}$ contributions, and subscript k corresponds to the atomic sublattices. Z^* is the transverse (Born) effective charge:

$$Z_{k,i\nu}^{*} = Z_k^{\mathrm{core}} + Z_{k,i\nu}^{*,\mathrm{el}} = \frac{\Omega}{ea_i}\frac{\partial P_i}{\partial u_{k,\nu}}\bigg|_\epsilon. \quad (4)$$

Piezoelectric response includes contributions that appear in linear response for finite distortional wave vectors $\mathbf{q}$, termed proper, and contributions which formally appear at $\mathbf{q} = 0$, termed improper [14]. *Improper* macroscopic polarization changes arise from the rotation or dilation of the spontaneous polarization (P_i^s). The proper polarization of a ferroelectric or pyroelectric material is given by $P_i^P = P_i^T - \sum_j(\epsilon_{ij}P_j^s - \epsilon_{jj}P_i^s)$. Proper piezoelectric constants $e_{i\nu}^P$ can be expressed as

$$e_{31}^P = \frac{\partial P_3^T}{\partial\epsilon_1} + P_3^s, \qquad e_{15}^P = \frac{\partial P_1^T}{\partial\epsilon_5} - P_3^s, \quad (5)$$

and $e_{33}^P = e_{33}^T$, that is the improper part of e_{33}^T is zero. The difference between proper and total polarizations is due only to the homogeneous part, which can be expressed for e_{31} ($e_{31}^{P,\mathrm{hom}}$) as

$$e_{31}^{P,\mathrm{hom}} = e_{31}^{\mathrm{hom}} + P_3^s = \frac{\partial P_3^{\mathrm{el},T}}{\partial\epsilon_1} + P_3^{\mathrm{el},s}. \quad (6)$$

One can derive a similar expression for $e_{15}^{P,\mathrm{hom}}$. The homogeneous part appears as a pure electronic term only in the expression for the *proper* piezoelectric modulus. It is evident that the proper and total piezoelectric constants differ only in materials with nonzero polarization in the unstrained crystal.

The first term in Eq. (3) can be evaluated from polarization differences as a function of strain, with the internal parameters kept fixed at their values corresponding to zero strain. The second term, which arises from internal microscopic relaxation [15,16], can be calculated after determining the elements of the dynamical transverse charge tensors and variations of internal coordinates u_i as a function of strain. Transverse charges in general are the mixed second derivatives of a suitable thermodynamic potential with respect to atomic displacements and electric field. They measure the change in polarization induced by unit displacement of a given atom at zero electric field to linear order. In a polar insulator transverse charges indicate the extent of polarization changes induced by relative sublattice displacements. While many ionic oxides have Born effective charges close to their static value [17], ferroelectric perovskites display anomalously large dynamical charges [18–20].

Total energy calculations were performed within the general gradient approximation (GGA) using the full-potential *ab initio* LAPW method with local orbital (LO) extension [9]. The Perdew-Burke-Ernzerhof 1996 [21] exchange-correlation parametrization was used in the calculations. The value of $RK_{\max}$ was set to 8.3, LAPW sphere radii of 2.0, 1.7, and 1.6 a.u. were used for Pb, Ti, and O, respectively. Pb *5d, 6s, 6p*, Ti *3s, 3p, 3d, 4s*, and O *2s* and *2p* orbitals were treated as valence orbitals. Atomic core states were calculated relativistically, ignoring spin-orbit coupling, while valence states were treated semirelativistically. The special points method [22] was applied for Brillouin-zone samplings with a

TABLE I. Structural parameters of tetragonal $PbTiO_3$. Internal coordinates along the z direction (u) are given in terms of the c lattice constant.

	GGA [a]	LDA [b]	LDA [c]	Exp [d]
a(a.u.)	7.356	7.247	7.380	7.373
c/a	1.073	1.122	1.063	1.065
u_{Pb}	0.000	0.000	0.000	0.000
u_{Ti}	0.530	0.542	0.549	0.538
u_{O_1,O_2}	0.610	0.634	0.630	0.612
u_{O_3}	0.105	0.134	0.125	0.117

[a]Constant volume is from Ref. [24].
[b]Optimized c/a at constant volume, local density approximation (LDA), all-electron basis set.
[c]Reference [7] constant volume and c/a, LDA, ultrasoft pseudopotentials with plane-wave basis.
[d]Reference [25], room temperature data.

$4 \times 4 \times 4$ **k**-point mesh. The **k**-space integrations in the Berry's phase calculations were made on a uniform $4 \times 4 \times 20$ **k**-point mesh. The results of the calculations were checked for convergence with respect to the number of **k** points and the plane wave cutoff energy. Analytical forces were calculated using the formulation of Yu *et al.* [23].

The tetragonal structure of $PbTiO_3$ is completely defined by the a lattice constant, the c/a ratio, and by three internal coordinates u_i. Table I contains the optimized internal parameters in the five atom unit cell at experimental volume and optimized c/a together with other theoretical and experimental results. Full, unconstrained optimization of structural parameters using the GGA resulted in an unreasonably large value, $c/a = 1.09$. Therefore the volume of the $PbTiO_3$ unit cell was kept at its experimental value, and an optimum set of c/a and u_i parameters which minimize the total energy was determined under this constraint. This configuration served as the reference state in further polarization calculations.

Piezoelectric constants were determined by using both the direct and the indirect Eq. (3) methods. In the direct approach, absolute macroscopic polarization values were computed at a reference structure $P^{\rm ref}$ and at several strained structures P^{ϵ}, with equilibrium internal parameters determined at each strain value. Applied strain values were typically in the $\pm 1\%$ range. The slope of the $(P^{\epsilon} - P^{\rm ref})$ vs strain curve at small strains (linear regime) yielded directly the piezoelectric constants. The $\partial u_i/\partial \epsilon_\nu$ values (Table II) were used together with the corresponding dynamical charge tensor elements to evaluate the individual microscopic strain contributions. Born effective charges were obtained from changes of macroscopic polarization induced by small displacements of atomic sublattices (Table III). Our results satisfy the acoustic sum rule, $\sum_j Z^*_{j,ii} = 0$, indicating that the calculations are relatively fully converged with respect to computational conditions. The clamped-ion contribution to the piezoelectric moduli in Eq. (3) was determined from slopes of polarization vs strain curves. During this set of calculations, internal parameters were kept fixed at those determined for the experimental volume structure with optimized 1.073 c/a ratio. No significant difference (less than 0.5%) was found between moduli calculated by the two methods, indicating that the linear approximation used to describe the piezoelectric response of $PbTiO_3$ is valid for the applied magnitude of strains.

TABLE II. Internal displacement gradients [a] as a function of strain.

i	ν	$\frac{\partial u_{Pb,i}}{\partial \epsilon_\nu}$	$\frac{\partial u_{Ti,i}}{\partial \epsilon_\nu}$	$\frac{\partial u_{O_1,i}}{\partial \epsilon_\nu}$	$\frac{\partial u_{O_2,i}}{\partial \epsilon_\nu}$	$\frac{\partial u_{O_3,i}}{\partial \epsilon_\nu}$
z	3	0.360	0.216	−0.133	−0.133	−0.310
$z,(z)$	1, (2)	0.165	−0.073	−0.122	0.160	−0.130
$z,(z)$	4, (5)	−0.082	−0.024	0.052	0.045	0.009
$y,(x)$	4, (5)	0.150	0.021	−0.107	−0.020	−0.044

[a]$\sum_k \frac{\partial u_{k,i}}{\partial \epsilon_\nu} = 0$.

Table IV contains the computed total and proper piezoelectric moduli, and two sets of experimental data of the full piezoelectric stress tensor. Our theoretical value for the total e_{33} modulus is 3.23 C/m^2. The clamped ion contribution is -0.88 C/m^2, whereas the contribution from internal macroscopic strain is much larger with an opposite sign, 4.11 C/m^2. These values and our *proper* e_{15} and e_{31} moduli are in good agreement with the single-crystal data reported by Li *et al.* [26]. However, there is a significant spread between various measurements [27]. Methods used in this work give results for the intrinsic piezoelectric properties of an infinite single-domain perfect material, while values reported by Ikegami *et al.* [28] are based on experimental data obtained on a poled ceramic sample with small amounts of dopants. In the latter case, significant extrinsic contributions to piezoelectric constants can be expected in addition to the intrinsic contribution. It is however not uncommon that extrinsic contributions are of the same magnitude as the intrinsic part [29].

Spontaneous polarization was computed in $PbTiO_3$ at the optimized external and internal structural parameters. Our theoretical value of 0.88 C/m^2 agrees well with the measured value [30] of 0.75 C/m^2 (295 K). Experiments generally give reduced results due to cracking and charge leaking [25].

TABLE III. Born effective charges for $PbTiO_3$.

Atom	Z^*_{xx}	Z^*_{yy}	Z^*_{zz}
Pb	3.74/*3.90* [b]	3.74	3.52
Ti	6.20/*7.06* [b]	6.20	5.18
O_1 [a]	$-2.61_\perp$/*−2.56*	$-5.18_\parallel$/*−5.83* [b]	−2.16
O_3	−2.15	−2.15	−4.38

[a]O_1 is on the xz face of the unit cell, $\perp$ marks the direction perpendicular to Ti-O bond in the xy plane, $\parallel$ indicates atomic displacement along the Ti-O bond.
[b]Reference [18], LDA pseudopotential results at experimental structural parameters.

TABLE IV. Piezoelectric stress tensor elements (C/m^2) of tetragonal $PbTiO_3$.

	e_{15}	e_{31}	e_{33}
Homogeneous	2.87	−2.60	−0.88
Proper homogeneous	1.99	−1.72	−0.88
Internal strain	1.16	0.79	4.11
Total	4.03	−1.81	3.23
Proper total	3.15	−0.93	3.23
Exp[a]	3.92	−0.98	3.35
Exp[b]	2.96	0.46	6.50
Exp[c]	4.4	2.1	5.0
Exp[c]	4.8	−0.67	4.1

[a]Reference [26].
[b]Reference [28].
[c]Reference [27], two sets of velocity rms deviations.

These results demonstrate that the Berry's phase approach within the all-electron LAPW + LO formalism can be effectively used to predict values of piezoelectric tensor elements even in computationally difficult materials such as $PbTiO_3$. The computed intrinsic piezoelectric moduli are found to be in relatively good agreement with experimental data measured on single crystal material. The large piezoelectric response in this material is mainly due to the large relative displacement of cationic and anionic sublattices induced by the macroscopic strain. This effect is further amplified in tetragonal solid $PbTiO_3$ by the anomalously large elements of Born dynamic charge tensors.

This work was supported by the Office of Naval Research under ONR Grants No. N00014-97-1-0052 (R. E. C.) and N00014-97-1-0049 (H. K.). Computations were performed on the CRAY J90/16-4096 computer at the Geophysical Laboratory, Carnegie Institution of Washington supported by Grant No. NSF EAR-9304624. The authors thank Michel Posternak, Andrea Dal Corso, David Singh, Raffaele Resta, and Richard Martin for helpful discussions.

[1] K. Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academic Publishers, Boston, 1996).
[2] T. Tanaka, Ferroelectrics **40**, 167 (1982).
[3] L. M. Sheppard, Cer. Bull. **71**, 85 (1992).
[4] R. E. Cohen and H. Krakauer, Phys. Rev. B **42**, 6416 (1990).
[5] R. E. Cohen, Nature (London) **358**, 136 (1992).
[6] K. M. Rabe and U. V. Waghmare, J. Phys. Chem. Solids **57**, 1397 (1996).
[7] A. Garcia and D. Vanderbilt, Phys. Rev. B **54**, 3817 (1996).
[8] S.-E. Park and T. R. Shrout, T. Appl. Phys. **82**, 1804 (1997).
[9] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic Publishers, Boston, 1994).
[10] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).
[11] R. Resta, Rev. Mod. Phys. **66**, 899 (1994).
[12] R. Resta, Ferroelectrics **136**, 51 (1992).
[13] S. de Gironcoli, S. Baroni, and R. Resta, Phys. Rev. Lett. **62**, 2853 (1989).
[14] R. M. Martin, Phys. Rev. B **5**, 1607 (1972).
[15] A. Dal Corso, M. Posternak, R. Resta, and A. Baldereschi, Phys. Rev. B **50**, 10 715 (1994).
[16] M. Posternak, A. Baldereschi, A. Catellani, and R. Resta, Phys. Rev. Lett. **64**, 1777 (1990).
[17] M. Posternak, A. Baldereschi, H. Krakauer, and R. Resta, Phys. Rev. B (to be published).
[18] W. Zhong, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **72**, 3618 (1994).
[19] R. Resta, M. Posternak, and A. Baldereschi, Phys. Rev. Lett. **70**, 1010 (1993).
[20] G. Sághi-Szabó, R. E. Cohen, and H. Krakauer (to be published).
[21] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **72**, 3865 (1996).
[22] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **16**, 1748 (1977).
[23] R. Yu, D. Singh, and H. Krakauer, Phys. Rev. B **43**, 6411 (1991).
[24] G. Shirane and R. Pepinsky, Acta Crystallogr. **9**, 131 (1956).
[25] *Ferroelectrics: Oxides, Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology*, edited by T. Mitsui and E. Nakamura (Springer-Verlag, Berlin, 1996), Group III, Vol. 28, Pt. a.
[26] Z. Li, M. Grimsditch, X. Xu, and S.-K. Chan, Ferroelectrics **141**, 313 (1993).
[27] A. G. Kalinichev, J. D. Bass, B. N. Sun, and D. A. Payne, J. Mater. Res. **12**, 2623 (1997).
[28] S. Ikegami, T. Ueda, and T. Nagata, J. Acoust. Soc. Am. **50**, 1060 (1971).
[29] Q. M. Zhang, H. Wang, N. Kim, and L. E. Cross, J. Appl. Phys. **75**, 454 (1993).
[30] V. G. Gavrilyachenko *et al.*, Sov. Phys.-Solid State **12**, 1203 (1970).