VOLUME 62, NUMBER 24 PHYSICAL REVIEW LETTERS 12 JUNE 1989

Piezoelectric Properties of III-V Semiconductors from First-Principles Linear-Response Theory

Stefano de Gironcoli[(a)]
Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-34014 Trieste, Italy

Stefano Baroni
Scuola Internazionale Superiore di Studi Avanzati (SISSA), Strada Costiera 11, I-34014 Trieste, Italy

Raffaele Resta[(b)]
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), Ecole Polytechnique Fédérale de Lausanne, CH-1015, Lausanne, Switzerland

(Received 7 November 1988)

We present a novel *ab initio* approach to piezoelectricity. The piezoelectric tensor is given by the stress induced by a homogeneous electric field. The perturbation is treated self-consistently by linear response, thus avoiding both supercells and numerical differentiation. We calculate the piezoelectric constants of nine III-V semiconductors; as a byproduct we also provide the first systematic study of zone-center phonons, internal strain parameters, effective charges, and dielectric constants. Our results agree very well with experiments where available, and allow predictions where they are not.

PACS numbers: 77.60.+v, 71.10.+x

Piezoelectricity is a property of many materials which display a macroscopic electric polarization upon application of a uniaxial stress.[1] Despite the fact that the basic phenomenology has been known for several decades, the piezoelectric effect has long escaped a proper theoretical understanding. In particular, only rather recently has a definite proof based on microscopic arguments been given that piezoelectricity is a *bulk* property of crystals and is therefore independent of the shape of the sample.[2]

Piezoelectricity is a *macroscopic* property of materials. Because of the long range of the Coulomb interaction, its proper description using *microscopic* ingredients is therefore possibly only in the long-wavelength limit which is incompatible with the Born–von Kármán boundary conditions generally adopted to perform first-principles calculations. This is a major obstacle which is usually overcome using large *supercells* in order to recover the macroscopic limit. We are aware of only two papers where the piezoelectric properties of real materials are investigated from first principles.[3,4] The first[3] deals with GaAs within the plane-wave pseudopotential scheme, and predicts a value for the piezoelectric constant which is about one-half of the experimental one. The second[4] investigates piezoelectricity in copper halides using a localized basis set and a molecular-cluster-embedding method. This calculation is not entirely consistent since it does not provide the value of the dielectric constant used to determine piezoelectric properties: The quality of the results is therefore difficult to assess. It is the crucial role of macroscopic electrostatics which makes piezoelectricity such a difficult problem, where most of the present-day first-principles machinery performs inefficiently.

In this Letter we present a novel approach. We calculate the piezoelectric constant from the stress induced by an applied electric field, at vanishing macroscopic strain. The linear response to the applied perturbation is obtained by a recently introduced self-consistent Green's-function method.[5] This approach allows us to perform analytically the long-wavelength limits necessary to handle homogeneous electric fields and directly yields the first-order correction to the crystal wave functions. The stress tensor[6] is then explicitly linearized with respect to these corrections. This procedure allows one to determine, to linear order, the dependence of the stress upon the applied electric field and, hence, the piezoelectric constant. Our procedure does not require the use of supercells; it can be (and actually is) worked out using modern norm-conserving pseudopotentials; and, last but not least, it directly yields the desired linear relation between polarization and strain without the need of any numerical differentiation.

The piezoelectric tensor γ is defined by the relation

$$\bar{f}(\mathbf{E},\alpha)=\bar{f}_0+\frac{\Omega}{2}\sum_{\alpha\beta\gamma\delta}\alpha_{\alpha\beta}\alpha_{\gamma\delta}\lambda_{\alpha\beta;\gamma\delta}-\frac{\Omega}{8\pi}\sum_{\alpha\beta}E_\alpha E_\beta\epsilon_{\alpha\beta}-\Omega\sum_{\alpha\beta\gamma}\gamma_{\alpha;\beta\gamma}E_\alpha\alpha_{\beta\gamma}\,, \tag{1}$$

where $\bar{f}$ is the ($T=0$) free energy per unit cell up to second order in the independent variables $\mathbf{E}$ (electric field) and α (strain), and Ω is the volume of the unit cell; λ and ϵ are the elastic constants and dielectric tensors, respectively. The stress tensor σ and the free-charge field $\mathbf{D}$ are the conjugate variables of α and $\mathbf{E}$:

$$\sigma_{\gamma\delta}=-\frac{1}{\Omega}\frac{\partial\bar{f}}{\partial\alpha_{\gamma\delta}}=-\sum_{\alpha\beta}\lambda_{\alpha\beta;\gamma\delta}\alpha_{\alpha\beta}+\sum_{\alpha}\gamma_{\alpha;\gamma\delta}E_\alpha\,; \tag{2a}$$

$$D_\alpha=-\frac{4\pi}{\Omega}\frac{\partial\bar{f}}{\partial E_\alpha}=\sum_\beta\epsilon_{\alpha\beta}E_\beta+4\pi\sum_{\gamma\delta}\gamma_{\alpha;\gamma\delta}\alpha_{\gamma\delta}\,. \tag{2b}$$

Equation (2b) can be equivalently cast into the usual form;[2]

$$P_\alpha = \sum_{\gamma\delta} \gamma_{\alpha;\gamma\delta}\alpha_{\gamma\delta} + \sum_{\beta}\chi_{\alpha\beta}E_\beta\,, \tag{2c}$$

where **P** is the electric polarization and χ the polarizability tensor. Equations (2) define the piezoelectric tensor as the stress induced in the unstrained material ($\alpha = 0$) by a unit electric field or, equivalently, as the polarization induced by a unit strain maintaining the sample short circuited ($\mathbf{E} = 0$).

The simplest crystal structure which displays the piezoelectric effect is zinc blende, where γ has as the only dependent component γ_{14}. The most convenient geometry for calculating it is to consider an electric field along the (111) direction: $\mathbf{E} = E(111)$. According to Eqs. (2), the stress induced by such a field is $\sigma_{\alpha\beta} = \sigma_4(1-\delta_{\alpha\beta})$. The piezoelectric constant is then given by $\gamma_{14} = \sigma_4/E$; the sign of γ_{14} is fixed assuming that the positive (111) direction goes from cation to anion. In the zinc-blende structure, a homogeneous stress along (111) is in general coupled to an internal (*microscopic*) strain, i.e., a relative displacement of the two sublattices. The actual value of the internal strain is the one which minimizes $\bar{f}$ at a given value of the independent variables α and **E**. In the Born-Oppenheimer approximation, the macroscopic strain results from two distinct contributions: a purely electronic one, given by $\gamma_{14}^{(0)}E$ and calculated at vanishing internal strain, and one which is due to the relative displacement of the two sublattices;[6] the latter contribution is linear in E as well. At vanishing macroscopic strain, the stress induced by an electric field along (111) is thus,

$$\sigma_4 = \gamma_{14}^{(0)}E - \zeta u \Phi/a^2\,, \tag{3}$$

where ζ is the *internal strain parameter*,[7] u is the (111) bond-length variation, a is the lattice constant, and $\Phi = \mu\omega_{\mathrm{TO}}^2$ is the harmonic force constant associated with u (μ is the ionic reduced mass, and ω_{TO} the transverse-optic phonon frequency). The equilibrium value of u is obtained from the condition that the forces acting on individual ions in an unstrained crystal in the presence of the macroscopic field **E** vanish:

$$u = -eZ^*E/\Phi\,, \tag{4}$$

where Z^* is the Born effective charge of the cation. The final result can be expressed[2] in terms of the adimensional quantity $\bar{\gamma}_{14}$:

$$\bar{\gamma}_{14} \equiv \frac{a^2}{e}\gamma_{14} = \frac{a^2}{e}\gamma_{14}^{(0)} + Z^*\zeta\,. \tag{5}$$

According to Eq. (5), in order to calculate the piezoelectric constant $\bar{\gamma}_{14}$, one has to calculate the stress induced by an applied electric field at vanishing nuclear displacement ($u = 0$), and the one induced by a bond-length variation u [i.e., by a TO phonon at Γ polarized along (111)], at vanishing electric field. We thus consider two *independent* perturbations acting on the crystal: (i) an electric field oriented along (111) and (ii) a TO phonon also polarized along (111). Since a zone-center TO phonon is lattice periodic, the perturbation (ii) would be accessible as well to standard techniques for electronic ground-state calculations; matters are different for perturbation (i), which involves a macroscopic electric field. In the latter case the perturbing potential lacks translational symmetry, and the standard techniques can be used only at the price of introducing large supercells.[8] The main advantage of linear-response theory in this respect is its capability of coping with long-wavelength perturbations (such as a macroscopic electric field) without any need of supercells. Basically this is due to the fact that the theory uses only off-diagonal matrix elements of the perturbing potential between eigenstates of the unperturbed Kohn-Sham Hamiltonian; such elements—contrary to diagonal ones—are indeed well defined even for the long-wavelength component of a macroscopic perturbation. Following Refs. 5, 9, and 10, the density response to such a long-wavelength component, $-\mathbf{E}\cdot\mathbf{x}$, is

$$\begin{aligned}\Delta n(\mathbf{r}) &= \sum_{c,v}\frac{\langle v|\hat{n}(\mathbf{r})|c\rangle\langle c|\mathbf{E}\cdot\mathbf{x}|v\rangle}{\epsilon_c-\epsilon_v}\\ &= \sum_{v}\langle v|\hat{n}(\mathbf{r})\hat{P}_c G_0(\epsilon_v)\hat{P}_c\mathbf{E}\cdot\mathbf{x}|v\rangle\,,\end{aligned} \tag{6}$$

where $\hat{n}(\mathbf{r})$ is the electron density operator, c and v indicate valence and conduction states, G_0 is the unperturbed Green's function, and $\hat{P}_c$ is the projector over the conduction-state manifold. The off-diagonal matrix elements of **x** are evaluated using the commutator with the unperturbed Kohn-Sham Hamiltonian, at the price of introducing an extra energy denominator[9,10] (i.e., an extra Green's function). The final result reads

$$\Delta n(\mathbf{r}) = \sum_{v}\langle v|\hat{n}(\mathbf{r})[P_cG_0(\epsilon_v)P_c]^2[H_0,\mathbf{E}\cdot\mathbf{x}]|v\rangle\,. \tag{7}$$

At variance with traditional linear-response methods based on dielectric matrices, the Green's-function approach of Ref. 5 yields not only the response density, but also the perturbed wave functions, up to first order. By using the Hellmann-Feynman and stress theorems[6] this opens the possibility of calculating the forces acting on individual ions, as well as the macroscopic stress induced by the perturbation. By definition, $\gamma_{14}^{(0)}$ and Z^* give the macroscopic stress and forces acting on ions per unit applied electric field, at vanishing macroscopic strain and ionic displacement; analogously, $\Phi\zeta$ and Φ give the macroscopic stress and forces acting on ions per unit ionic displacement, at vanishing electric field and macroscopic strain. These are all the ingredients necessary to obtain the piezoelectric constants.

Calculations have been performed for nine *AB* zinc-blende semiconductors (A = Al, Ga, In; B = P, As, Sb) using the local-density approximation (LDA),[11] norm-conserving pseudopotentials,[12] and plane-wave basis sets.

The equilibrium lattice constants of all the compounds have been determined very carefully from the pressure calculated with a large kinetic-energy cutoff for the plane-wave basis set (26 Ry) and 10 special points for the Brillouin-zone integrations. Such a high accuracy is necessary since the piezoelectric constant depends very sensitively on the lattice parameter at which it is calculated. Once this has been determined, subsequent calculations were performed with a lower cutoff (18 Ry), but a higher number special points (28), necessary to obtain converged results in the presence of macroscopic electric fields.[9] The resulting overall accuracy was checked to be better than ~5%.

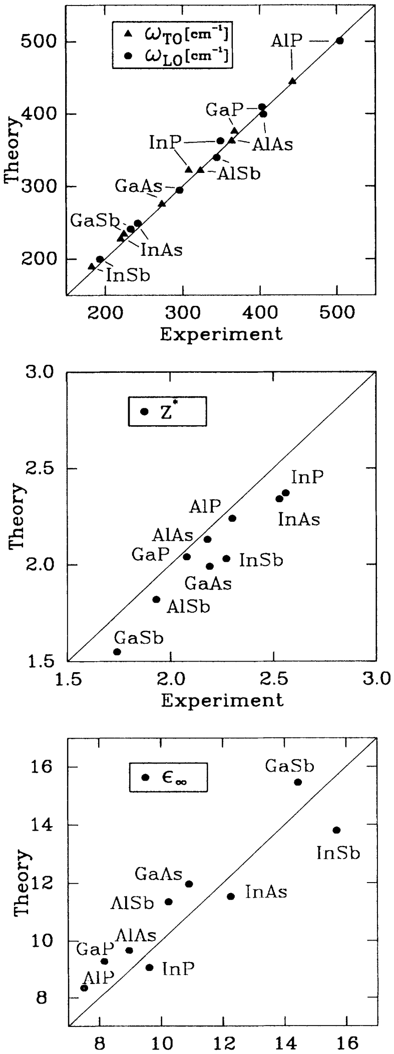

FIG. 1. Comparison between the calculated (y axis) and experimental (x axis) values for the zone-center phonon frequencies (upper panel), effective charges (middle panel), and dielectric constants (lower panel).

In order to illustrate the necessity to achieve a high accuracy in the determination of the lattice constant, we examine the case of GaAs. At equilibrium lattice constant ($a_0=10.39$ a.u.), the calculated value of the internal strain parameter is $\zeta=0.528\pm0.002$. Its dependence upon the lattice parameter is very strong: $\Delta\zeta/\zeta \sim 10\Delta a/a$. The ionic and electronic contributions to the piezoelectric constant have opposite sign and, for III-V's, almost the same magnitude. In the case of GaAs, for instance, our calculations give $(a^2/e)\gamma_{14}^{(0)}=-1.405$, $Z^*\zeta=1.053$, $\bar{\gamma}_{14}=-0.35$. We conclude that an error ~1% on a_0 would propagate up to ~30% on the final result $\bar{\gamma}_{14}$. We thus decided to calculate the theoretical equilibrium lattice constant with an accuracy of ~0.1%. This accuracy is certainly exaggerated for the lattice constant itself, but it is necessary for a consistent calculation of quantities which depend so sensitively on it. The sensitivity of the piezoelectric constant to the lattice parameter should be experimentally detectable. We are not aware of any measurements of piezoelectric constants under pressure; in the case of GaAs, our data indicate a pressure dependence of ζ and $\bar{\gamma}_{14}$: $\partial\zeta/\partial P\approx-2$, $\partial\bar{\gamma}_{14}/\partial P\approx-6$ (Mbar^{-1}).

As byproducts of this work, we provide the first systematic calculation of dielectric constants, effective charges, LO and TO phonon frequencies, and internal strain parameters of all the III-V semiconductors. In Fig. 1 we compare the dielectric constants, effective charges, and LO-TO phonon frequencies of III-V semiconductors. As a general rule, we observe that quantities which do not depend on the response to macroscopic fields (ω_{TO}) or do not depend sensitively on it (ω_{TO}) are predicted with very high accuracy ($\lesssim 3\%$), while those involving macroscopic electric fields (ϵ, Z^*) are predicted with an accuracy of ~10%, consistent with previous investigations.[5,9] As a general rule, the dielectric constant is overestimated by LDA. Inspection of Fig. 1 would suggest that this is not indeed the case for In compounds. We believe that this is an artifact of our pseudopotential approach which neglects the relaxation of

TABLE I. Theoretical internal strain parameters of nine III-V semiconductors. In parentheses we report the lattice constant (a.u.) at which the calculation has been done.

ζ (a_0)	P	As	Sb
Al	0.618 (10.18)	0.617 (10.55)	0.635 (11.42)
Ga	0.533 (10.00)	0.528 (10.39)	0.571 (11.20)
In	0.652 (10.68)	0.642 (11.04)	0.656 (11.84)

TABLE II. Calculated values of the piezoelectric constants for nine III-V semiconductors. The experimental values are reported in parentheses.

$\bar{\gamma}_{14}$	P	As	Sb
Al	0.11 (· · ·)	−0.03 (· · ·)	−0.13 (−0.16)
Ga	−0.18 (−0.18)	−0.35 (−0.32)	−0.40 (−0.39)
In	0.12 (|0.09|)	−0.08 (−0.10)	−0.20 (−0.18)

In-4*d* electrons. This leads to an overestimate of the LDA gap with respect to all-electron results;[13] we argue therefore that a proper treatment of relaxation effect would make In compounds follow the general trend.

In Table I we report our calculated values for the internal strain parameters and the lattice constants at which they are calculated. Experimental values are either lacking or affected by systematic errors;[14] the only case where a comparison is possible is GaAs where recent accurate measurements[15] give a value of the internal strain parameter ($\zeta_{\mathrm{GaAs}} = 0.55 \pm 0.02$) in excellent agreement with the theoretical predictions. Our calculations also agree with previous theoretical work[6] ($\zeta_{\mathrm{GaAs}} = 0.48$), the small difference being due to the more accurate lattice parameter used here.

In Table II we report our calculated values of the piezoelectric constants of III-V semiconductors together with available experimental data: The agreement with experiment is of the order of that found for other quantities involving macroscopic electric fields (∼10%). All of the chemical trends are correctly predicted. We find that, contrary to common belief, two III-V semiconductors and (AlP and InP) have a positive piezoelectric constant. For these two compounds, we have no experimental data to which to compare our results. We note, however, that this positive sign is compatible with the chemical trends emerging from Table II. On the other hand, the piezoelectric constant being the sum of two almost canceling contributions, it is not surprising that its sign may change for chemically similar compounds.

In this Letter we have demonstrated that physical properties of crystals involving *macroscopic* electric fields can be calculated from first principles using essentially no other approximation than LDA. The accuracy of such predictions (∼10%), though satisfactory and sufficient for reproducing chemical trends, is not as high as that achieved in the study of properties involving *microscopic* perturbations, i.e., wavelengths of the order of the crystal lattice constant.

We are grateful to Alfonso Baldereschi and Paolo Giannozzi for many illuminating discussions and useful suggestions. This work has been partially supported by the Italian Ministry of Education through the Centro Interuniversitario di Struttura della Materia and is part of the collaborative project between SISSA and the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA) computing center.

---

[a] Present address: IRRMA, Lausanne, Switzerland.

[b] Permanent address: SISSA, Trieste, Italy.

[1] See, for instance, W. G. Cady, *Piezoelectricity* (McGraw-Hill, New York, 1946).

[2] R. M. Martin, Phys. Rev. B **5**, 1607 (1972).

[3] J. B. McKitterick, Phys. Rev. B **28**, 7384 (1983).

[4] M. R. Press and D. E. Ellis, Phys. Rev. B **38**, 3102 (1988).

[5] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[6] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3780 (1985).

[7] L. Kleinman, Phys. Rev. **128**, 2914 (1962).

[8] R. Resta and K. Kunc, Phys. Rev. B **34**, 7146 (1986).

[9] S. Baroni and R. Resta, Phys. Rev. B **33**, 7017 (1986).

[10] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **35**, 5585 (1987); **35**, 5602 (1987).

[11] Exchange-correlation data are taken from J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[12] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[13] G. B. Bachelet and N. E. Christensen, Phys. Rev. B **31**, 879 (1985).

[14] C. S. G. Counsins, L. Gerwald, J. Staun Olsen, B. Selsmark, and B. J. Sheldon, J. Phys. C **20**, 29 (1987).

[15] C. S. G. Cousins, L. Gerward, J. Staun Olsen, B. Selsmark, B. J. Sheldon, and G. E. Webster, J. Semicond. Science Technol. (to be published).