

Piezoelectricity

Richard M. Martin

Xerox Palo Alto Research Center, Palo Alto, California 94304

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It is shown that piezoelectric effects can be easily derived from bulk properties and are expressible in terms of linear and *quadrupole* moments of variations in charge density induced by atomic displacements. The linear-moment contribution is determined by optic macroscopic effective charges and internal-strain parameters. The remaining terms measure directly the induced quadrupole moment, and hence provide insight into the nature of interatomic forces and chemical bonding. Special attention is focussed upon the zinc-blende structure. An important step in the derivation is the use of translation and rotation invariance to transform the basic equations to eliminate convergence difficulties and give expressions manifestly independent of surface configurations.

I. INTRODUCTION

The piezoelectric effect¹⁻³ is the production of electric polarization by application of stress to a crystal. According to convention,¹⁻³ the change in polarization \vec{P} produced to lowest order in the strain $\epsilon_{\alpha\beta}$ can be written

$$P_{\alpha} = \sum_{\beta\gamma} e_{\alpha\beta\gamma} \epsilon_{\beta\gamma} + \sum_{\beta} \chi_{\alpha\beta}^c E_{\beta}, \quad (1)$$

where α, β, γ , are Cartesian coordinates, and \vec{E} is the macroscopic electric field regarded as an independent variable. Thus the piezoelectric constant $e_{\alpha\beta\gamma}$ is the polarization per unit strain holding the macroscopic field \vec{E} constant, and $\chi_{\alpha\beta}^c$ is the "clamped" dielectric susceptibility.

The approach taken in the present work is to assume an arbitrary form for the change in charge density induced at each point \vec{r} in a crystal caused by the displacement of an atom. It is then shown that irrespective of the form of the induced charge density, the piezoelectric constants are uniquely specified by its *dipole* and *quadrupole* moments. In order to arrive at the final results, it is necessary to transform the expressions for the induced polarization into sums which are manifestly convergent independent of surface configuration. It follows that piezoelectricity is a bulk effect, contrary to suggestions⁴ that surface configurations can influence piezoelectric measurements.

The macroscopic theory of the piezoelectric effect^{1,2} has been thoroughly worked out to extract all independent components of the piezoelectric tensor $e_{\alpha\beta\gamma}$ for any crystallographic symmetry class. Of course, the group-theoretical analysis rests on the fact, proved here, that only bulk-symmetry invariances are imposed upon the piezoelectric constants. Here we illustrate the application to one crystal symmetry, cubic zinc blende, but are primarily concerned only with the microscopic derivation of piezoelectricity irrespective of symmetry requirements.

Microscopic theories of the origins of piezoelectricity have been described using a variety of specific models.³⁻⁸ Each model affords a particular description of charge displacement in a crystal as a result of ion motion. The present work, of course, does not modify the models, but rather (i) provides the basic connecting link among them and with more fundamental theories⁹ insofar as the piezoelectric effect is concerned and (ii) provides a simple correct procedure for evaluating the piezoelectric constants, eliminating the problems caused by the notoriously poor convergence of sums of Coulombic interactions.

On the other hand,⁴⁻⁶ previous general descriptions of piezoelectricity have relied upon pictures of charge flowing across imaginary boundaries at specific places in the unit cell, which are in turn chosen in accordance with particular assumptions about the surface configurations. Such descriptions are unwieldy and unpalatable for the description of a purely bulk effect and are eliminated in the present analysis.

The paper is organized to present in Sec. II a very simple derivation of the expressions for the longitudinal piezoelectric constants that can be measured in an experiment using wavelengths much smaller than any crystal dimensions. General expressions for any piezoelectric constant are derived in Sec. III for a uniform strain in a finite crystal. There it is necessary to utilize general invariance requirements to transform the sums into usable uniformly convergent expressions. In Sec. IV application to the zinc-blende-structure crystals is presented.

II. FINITE WAVELENGTH IN AN INFINITE CRYSTAL: LONGITUDINAL EFFECT

Consider a long-wavelength phonon mode of wave vector \vec{k} , $|\vec{k}| = 2\pi/\lambda$, in an effectively infinite crystal, i. e., $\lambda \ll$ crystal dimensions, but $\lambda \gg$ atomic dimensions. In this case only longitudinal

polarizations and charge-density waves are experimentally detectable. The longitudinal polarization is most easily discussed in terms of the induced charge-density variation $\delta\rho(\vec{r})$ defined in general at every point \vec{r} and related to $\vec{P}(\vec{r})$ by

$$\vec{\nabla} \cdot \vec{P}(\vec{r}) = -\delta\rho(\vec{r}). \quad (2)$$

It is well known¹⁰ that the spatially varying polarization $\vec{P}(\vec{r})$ on the left-hand side of Eq. (2) can be expanded to yield $\vec{\nabla} \cdot (\vec{P} + \vec{\nabla} \cdot \vec{Q} + \dots)$, where \vec{P} is a dipole density, \vec{Q} a quadrupole density, etc. We shall see that the piezoelectric constant involves both dipole and quadrupole, but not higher moments of the charge-density variation produced by displacement of an atom.

The starting point of the present analysis is that for any phonon mode (optic or acoustic), the variation in charge density $\delta\rho(\vec{r})$ is the superposition of the variations produced by the displacements of each atom separately. Let l be the cell index, $K=1$, s the atom specie index, α, β Cartesian components, and $u_{lK\alpha}$ the displacement of the atom at \vec{R}_{lK} . To first order in the displacements, we have

$$\delta\rho(\vec{r}) = \sum_{lK\alpha} \frac{\partial\rho(\vec{r})}{\partial R_{lK\alpha}} \Big|_{\vec{r}, \vec{E}} u_{lK\alpha}, \quad (3)$$

where

$$\frac{\partial\rho(\vec{r})}{\partial R_{lK\alpha}} \Big|_{\vec{r}, \vec{E}} \equiv f_{K\alpha}(\vec{r} - \vec{R}_{lK}) \quad (4)$$

is the variation in charge density at point \vec{r} per unit displacement of atom lK holding all other atoms and the macroscopic electric field constant. The function $f_{K\alpha}(\vec{r})$ must, of course, be independent of cell index l . The electrical boundary condition $\vec{E} = \text{const}$ is the appropriate condition for the present work; in addition, the boundary condition eliminates the longest-range induced polarizations so that $f_{K\alpha}(\vec{r})$ is short range, i. e., the characteristic range $|\vec{r}|$ of $f_{K\alpha}(\vec{r})$ is \ll any wavelength, and the moments of f required later are well defined.

The atomic displacements associated with any phonon mode having wave vector \vec{k} can be written

$$\vec{u}_{lK} = (\vec{u}_0 + \vec{u}_K) e^{i\vec{k} \cdot \vec{R}_{lK}}, \quad (5)$$

where \vec{u}_0 , the displacement of the cell as a whole, is independent of K , and \vec{u}_K are relative displacements in each cell satisfying

$$\sum_K \vec{u}_K = 0. \quad (6)$$

The total polarization of wave vector \vec{k} produced by the displacements (5) is given by

$$-i\vec{k} \cdot \vec{P}_{\vec{k}} = V^{-1} \int d^3r e^{i\vec{k} \cdot \vec{r}} \sum_{lK\alpha} f_{K\alpha}(\vec{r} - \vec{R}_{lK}) u_{lK\alpha}. \quad (7)$$

In the limit at $\vec{k} \rightarrow 0$ we can expand the exponential

on the right-hand side of (7) in powers of \vec{k} to find

$$-i\vec{k} \cdot \vec{P}_{\vec{k}} = v_0^{-1} \int d^3r \left[-i\vec{k} \cdot \vec{r} - \frac{1}{2} (\vec{k} \cdot \vec{r})^2 + \dots \right] \times \sum_{K\alpha} f_{K\alpha}(\vec{r}) (\vec{u}_0 + \vec{u}_K)_\alpha, \quad (8)$$

where the constant term in the expansion of the exponential is eliminated by charge neutrality and v_0 is the unit-cell volume.

For an optic mode $\vec{u}_0 \rightarrow 0$ and Eq. (8) becomes

$$\begin{aligned} \hat{k} \cdot \vec{P}_{\vec{k}} &= v_0^{-1} \int d^3r \hat{k} \cdot \vec{r} \sum_{K\alpha} f_{K\alpha}(\vec{r}) u_{K\alpha} \\ &= v_0^{-1} \sum_{K\alpha\beta} \hat{k}_\alpha e_{K\alpha\beta}^* u_{K\beta}, \end{aligned} \quad (9)$$

where $e_{K\alpha\beta}^*$ is an effective charge tensor for atoms of type K ,

$$e_{K\alpha\beta}^* = \int d^3r r_\alpha f_{K\beta}(\vec{r}). \quad (10)$$

This is the "unscreened" effective charge^{9,11} directly related to the macroscopic transverse effective charge. In general, charge neutrality requires⁹

$$\sum_K e_{K\alpha\beta}^* = 0. \quad (11)$$

For example, in a diatomic cubic crystal, $e_{1\alpha\alpha}^* = -e_{2\alpha\alpha}^*$ and the transverse effective charge is $e_T^* = |e_{1\alpha\alpha}^*|$.

In an acoustic mode there are two contributions to \vec{P} which appear on equal footings in the long-wavelength limit. The unsymmetrized macroscopic strain is related to the average displacement of the unit cells through³

$$\epsilon_{\alpha\beta} = iu_{0\alpha} k_\beta. \quad (12)$$

In addition, the internal strains can always be expressed as a function of the macroscopic strains,^{3,12,13}

$$u_{K\alpha} = \sum_{\beta\gamma} \Gamma_{K\alpha\beta\gamma} \epsilon_{\beta\gamma}, \quad (13)$$

where the Γ 's are internal-strain parameters determined by interatomic force constants and the electrical boundary conditions. Evidently both linear and quadrupole moments of the induced charge densities $f_{K\alpha}(\vec{r})$ appear in the piezoelectric constant. Let us define the quadrupole moment per unit displacement of atom K by

$$Q_{K\alpha\beta\gamma} = \int d^3r r_\alpha f_{K\beta}(\vec{r}) r_\gamma. \quad (14)$$

Then Eq. (8) reduces to the simple form [using (11)]

$$\hat{k} \cdot \vec{P}_{\vec{k}} = \sum_{\beta\gamma} \epsilon_{\beta\gamma} \left[v_0^{-1} \sum_{K\alpha} \hat{k}_\alpha \left(\sum_{\delta} e_{K\alpha\delta}^* \Gamma_{K\delta\beta\gamma} - Q_{K\alpha\beta\gamma} \right) \right]. \quad (15)$$

Comparing with Eq. (1), we see that the term in square brackets is the longitudinal ($\vec{P}_{\vec{k}} \parallel \hat{k}$) piezoelectric constant for any crystal.

We must verify that the integral expressions for the dipole and quadrupole moments, Eqs. (10) and (14), are convergent and uniquely defined. The proof rests on the definition that $f_{K\alpha}(\vec{r})$ is the variation in charge density produced by moving an atom K in the absence of a macroscopic field. Strictly, the electrical condition cannot be formulated as a boundary condition independent of geometry. However, we can impose the physically realizable condition that all Coulomb fields are screened by free carriers and behave as $(\epsilon r)^{-1} e^{-r/\lambda_0}$. At large r ($\gtrsim \lambda_0$) the response $f_{K\alpha}(\vec{r})$ behaves as if it were a continuous medium with dielectric constant ϵ in the presence of the free carriers. It is straightforward to show that both e^* and Q are convergent and independent of the value of λ_0 which establishes the desired results. This is also sufficient proof that e^* and Q are well defined for a finite crystal discussed in Sec. III, since we can choose $\lambda_0 \ll$ crystal dimensions.

The simplicity of Eq. (15) requires several comments. First the transverse-optic effective charge is the exact coefficient of the internal strain term because the internal strain is an optic mode with the electrical boundary condition $E = 0$.^{9,11,14} Second, the macroscopic strain produces a piezoelectric effect *only* through the quadrupole moments Q because the dipole moments of the different atoms K cancel identically. Contributions of higher moments vanish in the long-wavelength limit. These results appear naturally and simply for a phonon in an infinite crystal; we shall see in Sec. III, that a more tedious analysis yields the same results for a uniform strain in a finite crystal.

III. UNIFORM STRAIN IN A FINITE CRYSTALS

Consider a uniform strain $\epsilon_{\alpha\beta}$, unsymmetrized so that rotations are included, in a finite, but macroscopic or bulk, crystal. No assumptions are made about the surface region except that it is a negligible fraction of the crystal volume. In the presence of a strain each atom is displaced $u_{IK\alpha} + \epsilon_{\alpha\beta} R_{IK\beta}$, where internal strains \vec{u}_{IK} are not required to be periodic in the surface region. Similarly, the change in charge density per unit displacement $f_{IK\alpha}(\vec{r} - \vec{R}_{IK})$ is allowed to be a function of l ; in fact, in some cases it is essential to allow $f_{IK\alpha}$ to vary near the surface to account for surface charges, for example on a [111] face of zinc blende where surface charges are required for the sample to have no net polarization in the absence of strain. The only requirement on $f_{IK\alpha}(\vec{r})$ is that it be short range compared to sample dimensions; this is always the case for bulk samples since we require $\vec{E} = 0$. Nevertheless, we shall see that although surface effects may be essential in a correct microscopic picture, the

final results can be cast in a form in which surface effects are manifestly negligible in a bulk sample.

The polarization produced by the strain is

$$P_\alpha = V^{-1} \sum_{IK\beta} \int d^3r r_\alpha f_{IK\beta}(\vec{r} - \vec{R}_{IK}) (u_{IK\beta} + \sum_\gamma \epsilon_{\beta\gamma} R_{IK\gamma}) - P_\alpha^0 \sum_\beta \epsilon_{\beta\beta}, \quad (16)$$

where $V = Nv_0$ is the volume of the crystal and the final term which results from dilation and is present only in a ferroelectric where a static polarization \vec{P}^0 exists. The contribution resulting from internal strains \vec{u}_K can be straightforwardly summed just as in the optic-mode case,¹¹ the sum is uniformly convergent and is readily shown to be

$$P_\alpha^{\text{int}} = V_0^{-1} \sum_{K\beta\gamma\delta} e_{K\alpha\beta}^* \Gamma_{K\beta\gamma\delta} \epsilon_{\gamma\delta}. \quad (17)$$

Here e^* is the transverse effective charge and Γ is the internal-strain parameter defined in (10) and (13).

In the remaining terms involving macroscopic strain, however, the sum over IK is weighted by the distance \vec{R}_{IK} and is not uniformly convergent. It appears that the value of the sum depends upon the starting and stopping points. Here we adopt the procedure of using invariance relations to convert the sum (16) into one which is manifestly convergent. The invariance requirements which the f 's must satisfy are the following: charge neutrality,

$$\int d^3r f_{IK\alpha}(\vec{r}) = 0, \quad (18a)$$

which is satisfied for each atom IK and direction α ; translation invariance,

$$\sum_{IK} f_{IK\alpha}(\vec{r} - \vec{R}_{IK}) = -\frac{\partial}{\partial r_\alpha} \rho(\vec{r}), \quad (18b)$$

which states that uniform translation of each atom in the crystal must yield the same variation in charge density at every point \vec{r} as if the static charge density $\rho(\vec{r})$ were rigidly shifted; and rotation invariance,

$$\sum_{IK} \left[f_{IK\alpha}(\vec{r} - \vec{R}_{IK}) R_{IK\beta} - f_{IK\beta}(\vec{r} - \vec{R}_{IK}) R_{IK\alpha} \right] = \left(-r_\beta \frac{\partial}{\partial r_\alpha} \rho(\vec{r}) + r_\alpha \frac{\partial}{\partial r_\beta} \rho(\vec{r}) \right), \quad (18c)$$

which similarly states that the charge density rigidly rotates with a rotation of the atoms. These invariances are exact within the adiabatic approximation,⁹ in which case the electrons follow atom motion instantaneously. Of course, this is valid for the case at hand, the acoustical properties of insulators.

From Eq. (18) we can derive a relation sufficient

to transform (16) into a uniformly convergent sum. Define

$$\begin{aligned} S_{\alpha\beta\gamma} &= V^{-1} \sum_{IK} \int d^3r r_\alpha f_{IK\beta} (\vec{r} - \vec{R}_{IK}) R_{LK\gamma} \\ &= V^{-1} \sum_{IK} \int d^3r (\vec{r} - \vec{R}_{IK})_\alpha f_{IK\beta} (\vec{r} - \vec{R}_{IK}) R_{LK\gamma} \quad (19) \end{aligned}$$

using (18a), which is the sum needed in Eq. (16). The rotational-invariance condition (18c) can now be rewritten

$$\begin{aligned} S_{\gamma\beta\alpha} &= S_{\gamma\alpha\beta} + V^{-1} \int d^3r r_\gamma \left(r_\beta \frac{\partial}{\partial r_\alpha} \rho(\vec{r}) - r_\alpha \frac{\partial}{\partial r_\beta} \rho(\vec{r}) \right) \\ &= S_{\gamma\alpha\beta} - \delta_{\alpha\gamma} P_\beta^0 + \delta_{\beta\gamma} P_\alpha^0, \quad (20) \end{aligned}$$

where the final form was derived by partial integration, and \vec{P}^0 is the static polarization in the absence of strain

$$P_\alpha^0 = V^{-1} \int d^3r r_\alpha \rho(\vec{r}). \quad (21)$$

A second equality is derived from the observation that using the translation condition (18b), one finds

$$\begin{aligned} V^{-1} \sum_{IK} \int d^3r r_\alpha f_{IK\beta} (\vec{r} - \vec{R}_{IK}) r_\gamma \\ = -V^{-1} \int d^3r r_\alpha \frac{\partial}{\partial r_\beta} \rho(\vec{r}) r_\gamma = \delta_{\alpha\beta} P_\gamma^0 = \delta_{\beta\gamma} P_\alpha^0. \quad (22) \end{aligned}$$

From this it follows that

$$\begin{aligned} V^{-1} \sum_{IK} \int d^3r (\vec{r} - \vec{R}_{IK})_\alpha f_{IK\beta} (\vec{r} - \vec{R}_{IK}) (\vec{r} - \vec{R}_{IK})_\gamma \\ = (N/V) \sum_K Q_{K\alpha\beta\gamma} \\ = \delta_{\alpha\beta} P_\gamma^0 + \delta_{\beta\gamma} P_\alpha^0 - S_{\gamma\beta\alpha} - S_{\alpha\beta\gamma}. \quad (23) \end{aligned}$$

The first equality in (23) follows from the bulk nature of the crystal, and the second from expanding the product $(\vec{r} - \vec{R}_{IK})_\alpha (\vec{r} - \vec{R}_{IK})_\gamma$ and using (18a). Finally, substituting (20) into (23) leads to the desired relation

$$S_{\alpha\beta\gamma} = -S_{\gamma\alpha\beta} - v_0^{-1} \sum_K Q_{K\alpha\beta\gamma} + \delta_{\alpha\beta} P_\gamma^0 + \delta_{\alpha\gamma} P_\beta^0. \quad (24)$$

The identity relates the ill-defined sum $S_{\alpha\beta\gamma}$ to a sum of the same form with a minus sign and cyclicly permuted indices, plus terms which are well defined, the quadrupole moments $Q_{K\alpha\beta\gamma}$ and the static moments \vec{P}^0 . Using the relation three times in succession, each time cyclicly permuting the indices, and changing the sign of the S term on the right-hand side of the relation clearly returns S to the original order of the indices. This

results in an equation involving only $S_{\alpha\beta\gamma}$ and well-defined quantities, which can be solved for $S_{\alpha\beta\gamma}$. The resulting expression is easily shown to be

$$S_{\alpha\beta\gamma} = -\frac{1}{2} v_0^{-1} \sum_K (Q_{K\alpha\beta\gamma} - Q_{K\gamma\alpha\beta} + Q_{K\beta\gamma\alpha}) + \delta_{\alpha\beta} P_\gamma^0, \quad (25)$$

which depends on surface configuration only in a ferroelectric where depolarizing factors influence the static polarization \vec{P}^0 .

Inserting expressions (17) and (25) into (16) we find the final form for the polarization

$$\begin{aligned} P_\alpha = \sum_\beta (\epsilon_{\alpha\beta} P_\beta^0 - \epsilon_{\beta\alpha} P_\alpha^0) + v_0^{-1} \sum_{K\beta\gamma} \left[\sum_6 e_{K\alpha\beta}^* \Gamma_{K\beta\beta\gamma} \right. \\ \left. - \frac{1}{2} (Q_{K\alpha\beta\gamma} - Q_{K\gamma\alpha\beta} + Q_{K\beta\gamma\alpha}) \right]. \quad (26) \end{aligned}$$

This is the general expression for the piezoelectric polarization in any crystal. The first term results from the rotation and dilation of the existing moment in a ferroelectric. It is quite analogous to rotation-induced Brillouin scattering described by Nelson and Lax.¹⁵ The second term might be termed the "proper" piezoelectric effect for which the piezoelectric coefficient is

$$\begin{aligned} e_{\alpha\beta\gamma}^P = v_0^{-1} \sum_K \left[\sum_6 e_{K\alpha\beta}^* \Gamma_{K\beta\beta\gamma} \right. \\ \left. - \frac{1}{2} (Q_{K\alpha\beta\gamma} - Q_{K\gamma\alpha\beta} + Q_{K\beta\gamma\alpha}) \right]. \quad (27) \end{aligned}$$

The "proper" piezoelectric constant $e_{\alpha\beta\gamma}^P$ is purely a bulk property expressed in terms of well-defined microscopic quantities. It is easy to show that since $Q_{\alpha\beta\gamma} = Q_{\gamma\beta\alpha}$ [see Eq. (14)], $e_{\alpha\beta\gamma}^P$ is symmetric in $\beta\gamma$,

$$e_{\alpha\beta\gamma}^P = e_{\alpha\gamma\beta}^P, \quad (28)$$

so that only proper strains and not rotations produce the proper piezoelectric effect. Furthermore, for the longitudinal effect $\alpha = \gamma$, Eq. (27) reduces to exactly the same expression as derived for the infinite crystal, Eq. (15).

The comments on the form of the piezoelectric constants made at the end of Sec. II apply here also. The definition of e^* and Q in (10) and (14) are unique and independent of sample geometry or size since the long-range effects of the macroscopic fields are eliminated by definition. The purely macroscopic strain generates a piezoelectric polarization only through the quadrupole moments, which appear in the microscopic theory because of restrictions on the charge-density variations which must be satisfied for translation and rotation invariance. Similarly, the internal-strain contribution is uniquely determined—apart from sign—by optic effective charges and internal-strain parameters.

IV. ZINC-BLENDE STRUCTURE

The zinc-blende structure is particularly interesting. A purely longitudinal piezoelectric effect appears for uniaxial strain ϵ along the [111] direction,⁵ $P = (2/\sqrt{3})e_{14}\epsilon$, $e_{14} = e_{xyz}$. The piezoelectric constant is defined with the atom at position 1 in Fig. 1 (minus end of 111 bond) arbitrarily chosen to be the metal atom.⁵ It is this choice and not the coincident fact that the + (111) face is terminated on metal ions that determines the sign of the piezoelectric effect. It is convenient here to introduce the conventional dimensionless internal-strain parameters ζ .^{12, 13, 16} In this case, it is easy to show that $u_1 - u_2 = (2/\sqrt{3})\zeta a/4$, where $0 < \zeta < 1$ for reasonable interatomic forces and a is the cube edge. Letting z' be the coordinate projected along the [111] direction, Eq. (27) or (15) becomes

$$e_{14} = \frac{1}{8}\zeta a v_0^{-1} \int d^3r z' [f_{1z'}(\vec{r}) - f_{2z'}(\vec{r})] - \frac{1}{4}\sqrt{3} v_0^{-1} \int d^3r (z')^2 [f_{1z'}(\vec{r}) + f_{2z'}(\vec{r})]. \quad (29)$$

A more perspicuous form of (29) is derived by defining $f_{\alpha}^+(\vec{r}) = f_{1\alpha}(\vec{r})$ and $f_{\alpha}^-(\vec{r}) = f_{2\alpha}(-\vec{r})$, where + refers to the metal and - to the nonmetal. The inversion operation in f^- transforms the symmetry of the nonmetal atom to that of site 1. Thus, $\Delta f_{\alpha}(\vec{r}) \equiv f_{\alpha}^+(\vec{r}) - f_{\alpha}^-(\vec{r})$ is the *chemical*, not site symmetry, difference between the displacement charge densities of the metal and nonmetal. Transforming (29) to the usual Cartesian coordinate system and using the tetrahedral site symmetry, (29) becomes

$$e_{14} = v_0^{-1} \int d^3r \left(\frac{1}{8}\zeta a z - \frac{1}{2}xy \right) \Delta f_z(\vec{r}). \quad (30)$$

Defining a dimensionless coefficient for the xy quadrupole moment per unit displacement along z

$$\Delta Q_{xyz} = (2/ae) \int d^3r xy \Delta f_z(\vec{r}), \quad (31)$$

the expression for e_{14} can be written in the simple dimensionless form

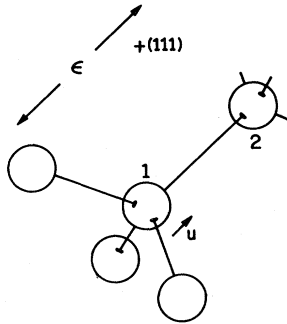


FIG. 1. Unic cell in zinc blende. Macroscopic strain ϵ and internal strain u of atom 1 relative to its neighbors are indicated.

TABLE I. Piezoelectric constants of zinc-blende and Wurtzite-structure (for which we assign an effective $e_{14} \equiv e_{33}/\sqrt{3}$, following Ref. 5) crystals. The contributions to the dimensionless constant $(a^2/e)e_{14}$ are dipole = $\zeta (e_T^*/e)$ and quadrupole = $-\Delta Q_{xyz}$ [see Eq. (32)].

Mat.	e_{14}	$\frac{a^2}{e} e_{14}$	ζ^a	$\frac{e_T^*{}^b}{e}$	$\frac{\zeta e_T^*}{e}$	ΔQ_{xyz}
AlSb	-0.07 ^c	-0.16	0.73	1.93	1.41	1.57
GaP	-0.10 ^d	-0.19	0.67	2.04	1.37	1.56
GaAs	-0.16 ^c	-0.32	0.68	2.16	1.47	1.79
GaSb	-0.13 ^c	-0.29	0.69	2.15	1.48	1.77
InAs	-0.05 ^c	-0.10	0.76	2.53	1.92	2.02
InSb	-0.07 ^c	-0.19	0.78	2.42	1.89	2.08
ZnS	0.15 ^e	0.27	0.82	2.15	1.76	1.49
ZnSe	0.05 ^e	0.10	0.79	2.03	1.60	1.50
ZnTe	0.03 ^e	0.06	0.79	2.00	1.58	1.52
CdTe	0.03 ^e	0.08	0.87	2.35	2.04	1.96
CuCl	0.16 ^f	0.31	0.87	1.12	0.97	0.66
BeO	0.05 ^g	0.05	≈ 0.80	≈ 1.85	≈ 1.5	≈ 1.5
ZnO	0.64 ^h	0.83	≈ 0.80	≈ 2.10	≈ 1.7	≈ 0.9
CdS	0.25 ^e	0.54	≈ 0.90	≈ 2.3	≈ 2.1	≈ 1.6
CdSe	0.20 ^e	0.47	≈ 0.90	≈ 2.3	≈ 2.1	≈ 1.6

^aReference 16.

^bReference 11.

^cReference 5.

^dD. R. Nelson and E. H. Turner, J. Appl. Phys. **39**, 3337 (1968).

^eReference 6.

^fT. Inoguchi, T. Okamoto, and M. Koba, Sharp Tech. J. **12**, 59 (1969).

^gS. B. Austerman, D. A. Berlincourt, and H. H. A. Krueger, J. Appl. Phys. **34**, 339 (1963).

^hA. R. Hutson, Phys. Rev. Letters **4**, 505 (1960).

$$(a^2/e) e_{14} = \zeta (e_T^*/e)_{\text{metal}} - \Delta Q_{xyz}. \quad (32)$$

The quadrupole-moment contribution is large only if the charge-density response $\Delta f_z(\vec{r})$ is delocalized. For example, in the rigid-point-ion approximation only the first term in (30) remains. The quadrupole term, however, is found experimentally to be as important as the dipole term. This may be seen from Table I where measured values of e_{14} and e_T^*/e are listed. The internal-strain contribution is an order of magnitude larger than the measured e_{14} and *must* be cancelled by a quadrupole term of the same order of magnitude to explain the measured e_{14} . In Table I, Wurtzite crystals have been included with equivalent⁵ cubic parameters.

Elementary considerations of the bonding in these crystals is sufficient to estimate the magnitude of the two contributions to e_{14} and to show why they should tend to cancel. All that is needed is the ansatz that $f_z^{\pm}(\vec{r})$ is roughly monotonic in $|\vec{r}|$ and is large for \vec{r} along bond directions and small along antibonding directions. Referring to bond directions around site 1 in Fig. 1 one sees that z and xy always have the same sign. Therefore, the two contributions to e_{14} always have opposite signs. For a more quantitative discussion, assume $\Delta f_z(\vec{r})$ is restricted to one-dimensional

bond lines. Then if the weighted mean value of xy , (\overline{xy}) is greater (less) than $\frac{1}{4}\zeta a\bar{z}$, the second contribution is larger (smaller) than the first. Roughly the two terms cancel identically if the dominant charge response in $\Delta f_z(\vec{r})$ is centered at the fraction ζ of the distance along the bond. Since¹⁶ $\zeta \approx 0.5$, it is quite reasonable that such calculation occurs.

The most important result is that if ζ and the sign of the effective charge can be established independently, the piezoelectric constant provides a direct measure of the difference between metal and nonmetal of the induced quadrupole moments. This is a measure of charge-response delocalization and is important in understanding the nature of bonding and interatomic forces in crystals. Let us make the most reasonable choice¹⁷ that $e^* > 0$ on the metal; then from e_T^* , ζ , and e_{14} we find the dimensionless quadrupole moments listed in the final column of Table I. It should be emphasized that ζ was calculated from a phenomenological model. The expected accuracy is 20% for the III-V crystals, less accurate for the II-VI crystals, and for the Wurtzite crystals only an estimate is presented. The accuracy in ΔQ_{xyz} is essentially the same, since e_T^* is accurately known.

Lax¹⁸ has emphasized that a very important feature of interatomic forces in diamond-structure crystals are quadrupole-quadrupole forces. Of course, piezoelectric constants vanish for the diamond structure, but the importance of the quadrupole moments in the closely related III-V crystals clearly implies large quadrupole moments in the IV crystals also. Lax estimated that a displacement u_{1z} leads to radial moments on each neighboring site of magnitude $e'u_{1z}$, $e' \approx e$. This gives $Q_{xyz} \approx 4/\sqrt{3}$, which is consistent with the measured values of $\Delta Q_{xyz} \approx 1-2$ listed in Table I.

The measured signs of the piezoelectric constants show that [if $e_T^*(\text{metal}) > 0$] the quadrupole term dominates for III-V crystals but the dipole for II-V and I-VIII crystals. The primary conclusion is that although variations in either $\zeta(e_T^*/e)$ or ΔQ_{xyz} with chemical trends such as the ionicity¹⁹ are quite smooth (excepting ZnO and CuCl), no trends are well enough established to predict quantitatively the piezoelectric constants. In particular, analysis of the most interesting cases, Wurtzite-structure crystals with first-row atoms, for which ζ is not established,^{18,20} must await further refinements. We can, however, note one expected trend: for more ionic crystals for which

atoms are presumably more rigid, ΔQ_{xyz} decreases more rapidly than does $\zeta(e_T^*/e)$ in agreement with the interpretation of ΔQ_{xyz} as an induced quadrupole moment.

V. SUMMARY AND CONCLUSIONS

Explicit expressions for piezoelectric constants in terms of microscopic variations in charge density induced by atom displacement have been derived and shown to depend only on the internal-strain parameters $\Gamma_{K\alpha\beta\gamma}$ ^{3,12} and the first and second moments of the charge-density variation produced by motion of an atom, $e_{K\alpha\beta}^*$ and $Q_{K\alpha\beta\gamma}$, respectively. All quantities are evaluated for atom motion in the absence of a macroscopic field, i. e., in the absence of long-range forces between the atoms. In principle, the internal-strain parameters can be determined if the force constants of the solid are known (see Ref. 3). In addition it was shown that the $e_{K\alpha\beta}^*$ are exactly the transverse effective charge tensors which can be measured (apart from sign) in optic experiments. Therefore, piezoelectric constants can provide direct measurements of the quadrupole moments of the induced-charge-density variation. Since in a rigid-ion model, the quadrupole terms are zero, the piezoelectric constants provide possibly the most sensitive test available for the applicability of a rigid-ion model.

In order to derive explicit expressions for the piezoelectric constants, it was necessary to convert the basic formulas into uniformly convergent sums. This was accomplished by using translation- and rotation-invariance requirements on the microscopic quantities and led to the appearance of the quadrupole moments in the piezoelectric constants. The present proofs demonstrate conclusively that, contrary to the suggestion of Ref. 4, piezoelectricity is a purely bulk effect.

Note added in proof. The results of this paper pertaining to the bulk nature of the piezoelectric effect are illustrated for a simple model of zinc blende by the present author.²¹ There it is shown that, contrary to Ref. 4, surface effects vanish within the model (which is the same as that used by Woo in Ref. 4).

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Temperature Dependence of the Damping of Nonlinear Lattice Resonance in Ionic Crystals*

Charlie Harper[†]

Lawrence Radiation Laboratory, University of California, Berkeley, California 94720

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A general expression for the n th-order nonlinear complex-susceptibility tensor is derived by use of many-time temperature-dependent Green's functions. The damping constant for non-linear absorption is obtained from the susceptibility tensor. It is shown that the n th-order non-linear susceptibility tensor is generated from lower-order Green's functions and that the explicit temperature dependence of the damping constant is not affected by increasing the strength of the applied field. It is found, by observing the frequency dependence of the susceptibility, that the frequency ω of the applied field is converted into n th-harmonic waves of frequency $n\omega$.

I. INTRODUCTION

The phenomenon of infrared absorption in ionic crystals is connected with the dynamics of lattice vibrations. The traditional theory of lattice dynamics was developed mainly by Born and von Karman¹⁻³ more than fifty years ago. In this theory, one may think of a crystalline solid as consisting of a set of coupled springs (forces) and masses (ions). The fundamental assumption is that atomic (ionic) displacements in the lattice from their equilibrium positions are small in comparison with interatomic spacings. Hence, truncation of expansion terms of interatomic potentials in powers of the displacements at the first few anharmonic terms (usually, third or fourth) is valid. This approximation is generally valid for a large class of crystalline solids, but it has recently been discovered that it is not valid for the so-called quantum crystals (for example, solid helium).⁴ We will not consider quantum crystals in this paper.

The process of optical absorption involves the interaction of an electric field with the electric moment of a crystal when one optically active phonon branch is considered. The electric moment may be expanded in powers of the thermal dis-

placements of the ions from their equilibrium positions; the linear term in this expansion is the usual dipole moment. Higher-order terms give rise to continuous absorption.¹ The Hamiltonian of the crystal consists of the sum of harmonic and anharmonic parts; the anharmonic part is obtained by expanding the potential energy of the crystal in powers of the ionic displacements from the equilibrium positions.

An interesting problem in the infrared absorption process is that of explaining the observed temperature dependence of the damping constant of the fundamental lattice vibration absorption peak at high temperature. Measurements carried out by Heilmann⁵ on LiF and by Hass⁶ on NaCl show that the damping constant varies approximately as T^2 at high temperature.

In the Born¹ and more recent Maradudin-Wallis⁷ classical treatments of this problem, it is found that this damping constant is linearly related to temperature. Jepsen and Wallis⁸ derived results which showed that the damping constant was proportional to T^2 in the classical limit. Their calculation, unlike previous classical treatments, included quartic anharmonic terms in the Hamiltonian. De-