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Effective charges and piezoelectricity*

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The effective charge for piezoelectricity is calculated using the bond-orbital model and Martin's internal-displacement parameters. Direct and simple calculations made with no additional parameters lead to a semiquantitative description of this effect. The qualitatively different trend with polarity shown by this charge and by the macroscopic transverse effective charge is elucidated. It is noted that this approach is essentially equivalent to the approach used by Lannoo and Decarpigny in studying the transverse effective charge, but is very different from the approaches used in other current studies of effective charges.

The properties of partially ionic solids which conceptually are associated with effective ionic charges have long presented a puzzle. This is partly because in a crystal lattice there are many ways to divide up the electronic charge between anion and cation, each corresponding to a different effective charge. There are, however, experiments which lead to natural definitions, notably the piezoelectric effect and the splitting of longitudinal and transverse optical modes. Each can be interpreted in terms of a model in which point charges of $\pm e^*$ are associated with each ion and the magnitude of this charge is determined by experiment. As we will see, neither set of experiments leads to an effective charge that varies in the expected way with increasing polarity in an isoelectronic series such as Ge, GaAs, ZnSe, and CuBr, nor in fact do the two e^*'s agree with each other. The reason for this is known[1] and depends on the fact that when the metallic and nonmetallic sublattices are displaced with respect to each other, charges are transferred between them. These shifts contribute to the polarization in the piezoelectric effect and in an optical-vibrational mode and therefore contribute to the effective charges in the point-charge model. The transferred charges appear at the surface in the case of uniform distortions, or in the bulk in the case of slowly varying distortions, but are most conveniently computed in terms of bulk polarization.

Recently Lannoo and Decarpigny[2] and Harrison[3] have independently calculated the effective charge e_T^* to be associated with the optical-mode splitting using essentially equivalent tight-binding models of the electronic structure. In addition, Harrison's bond-orbital model provided the theoretical link with the parameters of the materials by also calculating the static dielectric constant in terms of the same model electronic structure. Attempts[4] to provide a theory of the piezoelectric charge have not been convincing. Thus it is most interesting to treat the piezoelectric effect with the same model which has been successful in treating the optical-mode splittings. We will use the notation of Ref. 3 and afterward make the relation to Ref. 2.

In the bond-orbital model the excess number α_p of electrons placed on the anion from each bond is called the *polarity*. Thus each anion in a tetrahedral structure contains a charge (in units of $-e$) of

$$Z^* = 4\alpha_p - \Delta Z \ , \qquad (1)$$

where ΔZ is the difference in valence from 4 ($\Delta Z = 1$ for nitrogen, $= 2$ for oxygen, etc.). Similarly, then, each bond provides an electronic dipole moment of

$$\vec{P} = \gamma\alpha_p(-e\vec{d}) \ , \qquad (2)$$

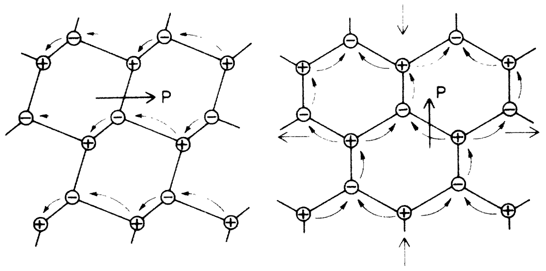
where $\vec{d}$ is vector distance from cation to anion and γ is a scale parameter to take into account local fields and charge asymmetries; a value of $\sqrt{2}$ gave a good fit to experiment.

The polarity was obtained[5] in terms of two of the parameters of the electronic structure

$$\alpha_p = V_3/(V_2^2 + V_3^2)^{1/2} \ . \qquad (3)$$

Here V_3 is half the energy change in transferring an electron from anion to cation; V_2 is half the splitting between bonding and antibonding states.

Effective charges are calculated in the context of the model by postulating appropriate atomic displacements and calculating the resulting movement of charge. If every cation were displaced by $\vec{\delta}$ with respect to every anion, and if α_p remained the same for every bond, a dipole moment per anion of $Z^*e\vec{\delta}$ would be induced. However, within each bond there is a change in α_p due to the change in bond length, as illustrated in Fig. 1(a). (Note that the figure shows a two-dimensional analog to the real crystal.) Such a motion cannot change the relative energy of cation and anion states to first order in δ, but it can change the bonding-antibonding splitting $2V_2$ in each bond. The dependence of V_2 on bond length was taken as[6] $s = -\partial \ln V_2/\partial \ln d = 3$. The corresponding changes in dipole moment of each bond



(a) (b)

FIG. 1. (a) Each cation is displaced to the right in this schematic diagram giving an electric polarization per pair of $Z^*e\delta$. In addition, each elongated bond becomes more polar, transferring electrons to the left, and each compressed bond becomes more covalent, also transferring electrons to the left. These transfers add to the electric polarization and therefore to the macroscopic transverse charge. (b) When the anion lattice is sheared as shown, the cations are pulled upward, giving a vertical piezoelectric polarization per pair of $Z^*e\delta$. The electron transfers due to changes in bond length are seen in this case to oppose the direct polarization and reduce the piezoelectric charge.

$$\delta\vec{P} = -\gamma s \alpha_p (1 - \alpha_p^2)(-e\vec{d})\delta/d \tag{4}$$

add to the dipole $Z^*e\vec{\delta}$ to give a *macoscopic transverse charge* describing the splitting of longitudinal- and transverse-optical-mode frequencies;

$$e_T^* = Z^* + \tfrac{4}{3}\gamma s \alpha_p (1 - \alpha_p^2) \ . \tag{5}$$

We may similarly calculate the piezoelectric effect. This is illustrated in Fig. 1(b), though a very much different geometry is appropriate in the zinc-blende structure. We introduce a pure shear strain

$$S_4 = \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \tag{6}$$

by introducing displacements $u_y = \frac{1}{2}S_4 z$ and $u_z = \frac{1}{2}S_4 y$. This will give rise to internal displacements of the anion sublattice with respect to the cation sublattice of

$$\Delta u_x = \tfrac{1}{4}\zeta a S_4 \ , \tag{7}$$

where ζ is Kleinman's[7] internal-displacement pa-

TABLE I. Polarity, effective ionic charge from Eq. (1), internal displacement, piezoelectric charge from Eq. (9) and from experiment, and transverse effective charge from Eq. (5) and from experiment.

	α_p[a]	Z^*[a]	ζ	e_p^*	e_p^* (expt)[b]	e_T^*[a]	e_T^* (expt)[a]
Zinc-blende structure							
CuCl	0.78	0.11	0.87[b]	−0.15	0.35	1.85	1.12
CuBr	0.77	0.08	0.89[c]	−0.15		1.85	1.49
CuI	0.74	−0.06	0.87[c]	−0.35		1.85	2.40
AgI	0.79	0.16	0.90[c]	−0.03		1.84	1.40
ZnS	0.69	0.76	0.82[b]	0.31	0.33	2.80	2.15
ZnSe	0.70	0.78	0.79[b]	0.24	0.13	2.81	2.03
ZnTe	0.68	0.73	0.79[b]	0.18	0.08	2.79	2.00
CdTe	0.76	1.02	0.87[b]	0.75	0.09	2.86	2.35
HgTe	0.78	1.11	0.89[c]	0.90		2.85	2.96
BN	0.43	0.71	0.68[c]	−0.24		2.68	2.47
AlP	0.47	0.87	0.70[c]	−0.03		2.94	2.28
AlAs	0.44	0.74	0.68[c]	−0.20		2.74	2.30
AlSb	0.56	1.24	0.73[b]	0.44	−0.22	3.41	1.93
GaP	0.48	0.94	0.67[b]	−0.09	−0.28	3.03	2.04
GaAs	0.47	0.87	0.68[b]	−0.10	−0.47	2.94	2.16
GaSb	0.43	0.71	0.69[b]	−0.18	−0.42	2.68	2.15
InP	0.55	1.21	0.74[c]	0.46		3.38	2.55
InAs	0.51	1.03	0.76[b]	0.36	−0.13	3.16	2.53
InSb	0.48	0.90	0.78[b]	0.31	−0.24	2.99	2.42
SiC	0.35	1.41	0.64[c]	0.43		3.15	2.57
Wurtzite structure							
BeO	0.68	0.70	0.8[b]	0.18	0.06	2.78	1.83
ZnO	0.69	0.76	0.8[b]	0.25	1.04	2.80	2.09
CdS	0.74	0.95	0.9[b]	0.74	0.60	2.85	2.27
CdSe	0.74	0.97	0.9[b]	0.76	0.52	2.85	2.25
GaN	0.61	1.43	0.78[c]	0.82		3.60	3.20
AlN	0.57	1.29	0.76[c]	0.59		3.47	2.75

[a] Reference 3.
[b] Reference 1.
[c] Interpolated from Ref. 1 values using Eq. (11).

rameter, which has been tabulated by Martin.[1] It was defined so that it would equal 1 if all bond lengths remain the same under a pure shear. We may directly compute the change in bond length for each bond surrounding an anion;

$$\delta/d = \pm \tfrac{1}{3} S_4(1-\zeta) \ . \qquad (8)$$

The dipoles from the four bonds given by Eq. (4) are all equal and subtract from the contribution of the direct anion displacement. This leads to an effective charge for piezoelectricity given by

$$e_p^* = Z^* - 4\gamma s\, \alpha_p(1-\alpha_p^2)\,(1-\zeta)/3\zeta \ . \qquad (9)$$

This charge is related to the piezoelectric constant by $e_{14} = e_p^* \zeta e/a^2$.

Values of polarity have been given in Ref. 3 along with the effective transverse charges from Eq. (5) and from experiment. We add to this the piezoelectric charges of Eq. (9) based upon the internal displacement parameters of Ref. 1 and also the experimental values from Ref. 1. These are all given in Table I. The absolute agreement is considerably closer for the piezoelectric charges, however, because of the cancellation apparent in Eq. (9). The values are near zero. This very simple model does describe the very different behavior of the effective charges in these two phenomena and this is accomplished without the introduction of any additional parameters or corrections.

The physical difference in the two phenomena may be stated as follows: In the vibrational problem a displaced anion feels a restoring force due to its neighboring bonds. The bond with a cation in front of it is shortened and the tendency to equilibrate charge between the two results in a forward electron flow adding to the dipole produced. This is reflected in the positive sign in the second term of Eq. (5). In the piezoelectric effect the anion is pulled into its displaced position by a stretched bond in front of it, and a reversed electron flow occurs. This is reflected by the negative sign in Eq. (9). The same conclusion is of course drawn if we focus on a bond behind the anion.

Essentially the same results would have been obtained following the point of view of Lannoo and Decarpigny.[2] Their energy difference $\alpha_B - \alpha_A$ is to be identified with twice our V_3. Their β is to be identified with our V_2 and their ion charge q_A is to be identified with our Z^*. Finally, their f, which they call the ionicity parameter, is related to our polarity by $1 - f^2 = (1-\alpha_p^2)^{3/2}$. The principal difference is that they choose to identify their f with the square root of the Phillips ionicity, whereas we evaluated ours directly from the static dielectric constant computed within the context of the model.

Though the differences in the two approaches might be regarded as details, they are of some importance. Phillips's ionicity approach,[8] based conceptually on pseudopotentials and isotropic bands, failed to predict properties such as this—it could only interpret them—until a tight-binding approach was used as intermediary. Once that was done, the tight-binding approach itself provides the most meaningful conceptual basis. The principal difference between Refs. 2 and 3 is in the difference in approximations to dielectric constants and in the range of properties that are encompassed in the treatments.

It is interesting to note in passing that Martin's internal-displacement parameter can be very well fit by the formula

$$1 - \zeta \cong 0.40(1-\alpha_p^2) \ . \qquad (10)$$

Perhaps an even better fit can be obtained using the ionicity parameter of Lannoo and Decarpigny:

$$1 - \zeta \cong 0.44(1-f^2) = 0.44(1-\alpha_p^2)^{3/2} \ , \qquad (11)$$

although the difference is not an important one and they are empirical fits to scattered data in any case. Combining Eqs. (1), (9), and (10) or (11) gives a universal formula for the piezoelectric charge depending only upon the polarity of the material, just as Eq. (5) gives a universal formula for the effective transverse charge depending only upon polarity. Equation (11) has been used to predict ζ values for materials where they were not available, and to predict piezoelectric charges for the corresponding materials in Table I.

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[1] R. M. Martin, Phys. Rev. B 5, 1607 (1972) gives a very complete description. It has been discussed also by J. C. Phillips and J. A. Van Vechten, Phys. Rev. Lett. 23, 1115 (1969).

[2] M. Lannoo and J. N. Decarpigny, Phys. Rev. B 8, 5704 (1973).

[3] W. A. Harrison, Phys. Rev. B 8, 4487 (1973).

[4] Difficulties in the analysis of T. Hidaka [Phys. Rev. B 5, 4030 (1972)] have been discussed by K. Hübner, Phys. Status Solidi B 56, 117 (1973). Hübner, in turn, neglected the strong variation of the internal displacements with ionicity, and at some points (but not others) neglected the variation of the dielectric constant with ionicity. He then introduced charge parameters for each material from an unpublished source leading finally to agreement with experiment.

[5] Actually, Eq. (3) was taken as the definition of α_p and Eqs. (1) and (2) were derived in Ref. (3), but this is equivalent.

[6] Recent studies by Harrison and Ciraci, to be published, suggest slightly different values of s and γ and the other parameters of the model, but do not significantly modify the conclusions reached here.

[7] L. Kleinman, Phys. Rev. 128, 2614 (1962).

[8] For the most complete description see J. C. Phillips *Bonds and Bands in Semiconductors* (Academic, New York, 1973).