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Pseudopotential Calculation of Transverse Effective Charges for III-V and II-VI Compounds of the Zinc-Blende Structure*

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A method is presented for the *ab initio* calculation of transverse effective charges for crystals possessing the zinc-blende structure. The method is implemented within the framework of the empirical pseudopotential method, and theoretical results are presented for the transverse effective charges of several III-V and II-VI compounds which yield both the magnitudes and signs of these quantities. The agreement between the theoretical and experimental values for the transverse effective charges is quite good for the III-V compounds, but is poor for the II-VI compounds. Reasons for this disagreement are discussed.

In Born's theory of lattice dynamics[1] the dipole moment of a crystal is expanded formally in powers of the displacements of the atoms from their equilibrium positions and in the components of the macroscopic electric field in the crystal as

$$M_\mu = \sum_{l\kappa\alpha} M_{\mu,\alpha}(l\kappa)u_\alpha(l\kappa) + \tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} M_{\mu,\alpha\beta}(l\kappa;l'\kappa') \times u_\alpha(l\kappa)u_\beta(l'\kappa') + \cdots + \sum_\nu \Big\{P^{(0)}_{\mu\nu} + \sum_{l\kappa\alpha} P_{\mu\nu,\alpha}(l\kappa) \times u_\alpha(l\kappa) + \cdots\Big\}E_\nu + \cdots . \quad (1)$$

In this expression $u_\alpha(l\kappa)$ is the α Cartesian component of the displacement of the κth ion in the lth primitive unit cell and E_ν is the ν component of the macroscopic field. The coefficient $M_{\mu,\alpha}(l\kappa)$, which is defined formally by

$$M_{\mu,\alpha}(l\kappa) = \left(\frac{\partial M_\mu}{\partial u_\alpha(l\kappa)}\right)_{\vec{u},\vec{E}} , \quad (2)$$

has the dimensions of a charge, and is an element of the transverse effective charge tensor. The subscripts $\vec{u}$, $\vec{E}$ on the derivative indicate that it is to be evaluated in the configuration in which the atomic displacements are all equal to zero and in which the macroscopic field vanishes. These coefficients govern the strength of the infrared absorption in crystals, and it is with their evaluation for III-V and II-VI compounds possessing the zinc-blende structure that this note is concerned.

The coefficients $\{M_{\mu,\alpha}(l\kappa)\}$ possess several properties which will be useful in what follows. As a consequence of the invariance of the dipole moment of a crystal against a rigid-body translation of the crystal as a whole, the following condition is obtained:

$$\sum_{l\kappa} M_{\mu,\alpha}(l\kappa) = 0 , \quad (3)$$

where the sum extends over all lattice sites of the crystal. The periodicity of the crystal requires that $M_{\mu,\alpha}(l\kappa)$ be independent of the cell index l. Therefore, in what follows we will denote this coefficient by $M_{\mu,\alpha}(\kappa)$. For atoms at sites of at least tetrahedral symmetry $M_{\mu,\alpha}(\kappa)$ is isotropic:

$$M_{\mu,\alpha}(\kappa) = \delta_{\mu\alpha}\epsilon(\kappa) . \quad (4)$$

We now specialize these results to crystals possessing the zinc-blende structure. For such crystals the primitive translation vectors are given by

$$\vec{a}_1 = \tfrac{1}{2}a_0(0,\ 1,\ 1), \quad \vec{a}_2 = \tfrac{1}{2}a_0(1,\ 0,\ 1), \quad \vec{a}_3 = \tfrac{1}{2}a_0(1,\ 1,\ 0) , \quad (5)$$

where a_0 is the lattice parameter. We choose the origin of coordinates midway between two nearest neighbors, so that the basis vectors are given by

$$\vec{x}(+) = \tfrac{1}{8}a_0(1,\ 1,\ 1) = -\vec{x}(-) = \vec{\tau} . \quad (6)$$

It follows from Eqs. (3) and (4) that for crystals of the zinc-blende structure

$$\epsilon(+) = e_T^* = -\epsilon(-) . \quad (7)$$

The coefficient e_T^* is called the transverse effective charge. Its magnitude can be obtained experimentally from the difference between the squares of the long-wavelength LO- and TO-mode frequencies,

$$\omega_L^2 = \omega_T^2 + \frac{4\pi(e_T^*)^2}{\epsilon_\infty \mu v_a} , \quad (8)$$

where ϵ_∞ is the optical-frequency dielectric constant, μ is the reduced mass of the two atoms in a primitive unit cell, and v_a is the volume of a primitive unit cell. The magnitude of e_T^* can also be obtained from measurements of the dielectric constant of such crystals, which (in the absence of lattice damping and spatial dispersion) is given by

$$\epsilon_{\mu\nu}(\omega) = \delta_{\mu\nu}\left(\epsilon_\infty + \frac{4\pi(e_T^*)^2}{\mu v_a}\,\frac{1}{\omega_T^2 - \omega^2}\right) . \quad (9)$$

Unfortunately, determinations of e_T^* based on either Eq. (8) or Eq. (9) cannot yield its sign but give only its magnitude.

From Eq. (1) we see that in the absence of a macroscopic electric field the crystal dipole moment is given to first order in the atomic displacements by

$$M_\mu = \sum_{l\kappa\alpha} M_{\mu,\alpha}(\kappa) u_\alpha(l\kappa) . \tag{10}$$

Let us assume for simplicity a displacement pattern such that $u_\alpha(l\kappa)$ is independent of the cell index l,

$$u_\alpha(l\kappa) = d_\alpha(\kappa) . \tag{11}$$

Such a displacement pattern is of the type found in a $\vec{q} = 0$ optical mode. It does not alter the translational periodicity of the crystal, but merely alters the structure of a primitive unit cell. Then for crystals of the zinc-blende structure we find that

$$M_\mu = N e_T^* [d_\mu(+) - d_\mu(-)] , \tag{12}$$

where N is the number of unit cells in the crystal. If we assume further that the displacements $\vec{d}(+)$ and $\vec{d}(-)$ are directed along the [111] direction, and are given by

$$\vec{d}(+) = \tfrac{1}{8} a_0(\delta, \delta, \delta) = -\vec{d}(-) , \tag{13}$$

we find that the x component of the crystal dipole moment is given by

$$M_x = \tfrac{1}{4} N a_0 e_T^* \delta . \tag{14}$$

Consequently, if we can calculate the x component of the dipole moment of the crystal when the two sublattices are displaced according to Eqs. (11) and (13), we can obtain e_T^* from the relation

$$e_T^* = \lim_{\delta \to 0} \frac{4}{N a_0} \frac{M_x}{\delta} . \tag{15}$$

If we denote by Z_κ ($\kappa = +, -$) the charge on the κth kind of ion core, the μ component of the crystal dipole moment with the sublattices displaced according to Eqs. (11) and (13) is given by

$$M_\mu = \sum_{l\kappa} Z_\kappa [x_\mu(l\kappa) + d_\mu(\kappa)] - e \int_\Omega x_\mu n(\vec{r}) d^3 r . \tag{16}$$

In this equation $\vec{x}(l\kappa)$ is the vector from the origin to the equilibrium position of the κth atom in the lth primitive unit cell, e is the magnitude of the electronic charge, and $n(\vec{r})$ is the electron number density calculated with the sublattices displaced. The integration in Eq. (16) is carried out over the volume of the crystal Ω.

In order that the expression given by Eq. (16) give the correct crystal dipole moment to be substituted into Eq. (15), from which the transverse effective charge is determined, we must ensure that the macroscopic field in the crystal is zero. This can be done by imposing periodic boundary conditions on the crystal. These, together with the fact that the displacements of the atoms are those in a $\vec{q} = 0$ optical mode, ensure that the macroscopic field in the crystal indeed vanishes.

The atomic displacements described by Eqs. (11) and (13) do not alter the translational periodicity of the crystal. Consequently, the electron number density $n(\vec{r})$ in the crystal in which the sublattices have been displaced according to Eqs. (11) and (13) still has the periodicity of the undeformed crystal. Instead of exploiting this fact it is more convenient to use the fact that $n(\vec{r})$ is also periodic with the periodicity of the unit cube for the zinc-blende lattice, which contains four primitive unit cells. The unit cube is shown in Fig. 1. It has the attractive feature that in the undistorted crystal it has zero net charge and a vanishing dipole moment.

We shall label the translation vectors of the superlattice whose unit cell is the unit cube by $\{\vec{x}(L)\}$ and the positions of the atoms in the unit cube by $\{\vec{x}(K)\}$. The vector $\vec{x}(L)$ can be expressed as

$$\vec{x}(L) = L_1 \vec{A}_1 + L_2 \vec{A}_2 + L_3 \vec{A}_3 , \tag{17}$$

where L_1, L_2, and L_3 are any three integers, and, from Fig. 1, the primitive translation vectors $\{\vec{A}_i\}$ are seen to be

$$\vec{A}_1 = a_0(1, 0, 0), \quad \vec{A}_2 = a_0(0, 1, 0), \quad \vec{A}_3 = a_0(0, 0, 1) . \tag{18}$$

The basis vectors $\{\vec{x}(K)\}$ are given by

$$\vec{x}(1) = \tfrac{1}{2} a_0(1, 0, 0), \quad \vec{x}(7) = \tfrac{1}{2} a_0(1, 1, 1),$$

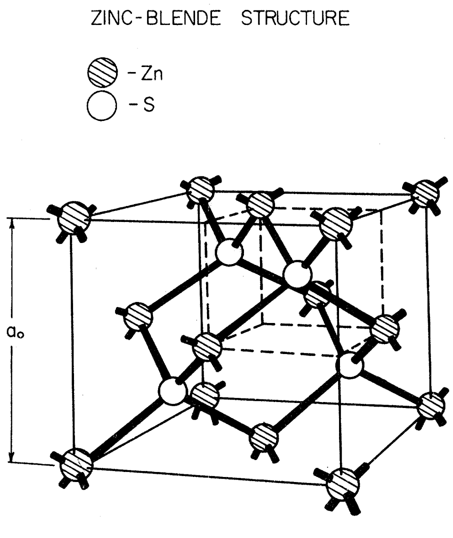

FIG. 1. Unit cube for crystals of the zinc-blende structure.

$$\begin{aligned}
&&& \vec{x}(13)=\tfrac{1}{2}a_0(-1,\,-1,\,1),\\
\vec{x}(2)&=\tfrac{1}{2}a_0(0,\,1,\,0), & \vec{x}(8)&=\tfrac{1}{2}a_0(1,\,1,\,-1),\\
&&& \vec{x}(14)=\tfrac{1}{2}a_0(-1,\,-1,\,-1),\\
\vec{x}(3)&=\tfrac{1}{2}a_0(0,\,0,\,1), & \vec{x}(9)&=\tfrac{1}{2}a_0(1,\,-1,\,1),\\
&&& \vec{x}(15)=\tfrac{1}{4}a_0(1,\,-1,\,1),\\
\vec{x}(4)&=\tfrac{1}{2}a_0(-1,\,0,\,0), & \vec{x}(10)&=\tfrac{1}{2}a_0(1,\,-1,\,-1),\\
&&& \vec{x}(16)=\tfrac{1}{4}a_0(-1,\,1,\,1),\\
\vec{x}(5)&=\tfrac{1}{2}a_0(0,\,-1,\,0), & \vec{x}(11)&=\tfrac{1}{2}a_0(-1,\,1,\,1),\\
&&& \vec{x}(17)=\tfrac{1}{4}a_0(-1,\,-1,-1),\\
\vec{x}(6)&=\tfrac{1}{2}a_0(0,\,0,\,-1), & \vec{x}(12)&=\tfrac{1}{2}a_0(-1,\,1,\,-1),\\
&&& \vec{x}(18)=\tfrac{1}{4}a_0(1,\,1,\,-1).
\end{aligned} \tag{19}$$

The charges on the ion cores are

$$\begin{aligned}
&Z_1 = Z_2 = \cdots = Z_6 = \tfrac{1}{2}Z_+\ ,\\
&Z_7 = Z_8 = \cdots = Z_{14} = \tfrac{1}{8}Z_+\ ,\\
&Z_{15} = Z_{16} = \cdots = Z_{18} = Z_-\ ,
\end{aligned} \tag{20}$$

and the displacements of the sublattices in the new notation are

$$\begin{aligned}
&\vec{d}(1) = \vec{d}(2) = \cdots = \vec{d}(14) = \tfrac{1}{8}a_0(\delta,\,\delta,\,\delta)\ ,\\
&\vec{d}(15) = \vec{d}(16) = \cdots = \vec{d}(18) = -\tfrac{1}{8}a_0(\delta,\,\delta,\,\delta)\ .
\end{aligned} \tag{21}$$

The assignment of fractional charges to atoms on the faces and corners of the unit cube is consistent with our assumption of periodic boundary conditions on the crystal.

The electronic contribution to the dipole moment of the crystal can now be rewritten

$$\begin{aligned}
M_\mu^{(e)} &= -e\int_\Omega x_\mu n(\vec{r})\,d^3r\\
&= -e\textstyle\sum_L\int_{\Omega_L} x_\mu n(\vec{r})\,d^3r\ ,
\end{aligned} \tag{22}$$

where the integration in the second expression is carried out over the volume of the Lth unit cube. We now make the change of integration variable

$$\begin{aligned}
&\vec{r} = \vec{\rho} + \vec{x}(L) - \vec{r}_0\ ,\\
&\vec{r}_0 = -\tfrac{3}{8}a_0(1,\,1,\,1)\ ,
\end{aligned} \tag{23}$$

where $\vec{r}_0$ is the vector from the point midway between the two atoms in a primitive unit cell to the center of the unit cube. The vector $\vec{\rho}$ is now restricted to range over the volume of the unit cube. With this change of variable, and the periodicity of $n(\vec{r})$, the expression (22) for $M_\mu^{(e)}$ becomes

$$\begin{aligned}
M_\mu^{(e)} = {}& Q^{(e)}\left[\textstyle\sum_L x_\mu(L) - N^* r_{0\mu}\right] - eN^*\\
&\times\int_{\Omega_0}\rho_\mu n(\vec{\rho}-\vec{r}_0)\,d^3\rho\ ,
\end{aligned} \tag{24}$$

where N^* is the number of unit cubes in the crystal, and

$$Q^{(e)} = -e\int_{\Omega_0} n(\vec{\rho}-\vec{r}_0)\,d^3\rho = -e\int_{\Omega_0} n(\vec{\rho})\,d^3\rho \tag{25}$$

is the total electronic charge in the unit cube.

The ionic contribution to the crystal dipole moment,

$$M_\mu^{(i)} = \sum_{l\kappa} Z_\kappa\left[x_\mu(l\kappa) + d_\mu(\kappa)\right]\ , \tag{26}$$

can also be rewritten as a sum of contributions from each unit cube:

$$\begin{aligned}
M_\mu^{(i)} &= \sum_{LK} Z_K\left[x_\mu(LK) - r_{0\mu} + d_\mu(K)\right]\\
&= \textstyle\sum_L x_\mu(L)\sum_K Z_K + \sum_L\sum_K x_\mu(K)Z_K\\
&\quad - r_{0\mu}\textstyle\sum_L\sum_K Z_K + \sum_L\sum_K Z_K d_\mu(K)\\
&= Q^{(i)}\left[\textstyle\sum_L x_\mu(L) - N^* r_{0\mu}\right] + N^*\textstyle\sum_K x_\mu(K)Z_K\\
&\quad + N^*\textstyle\sum_K Z_K d_\mu(K)\ ,
\end{aligned} \tag{27}$$

where

$$Q^{(i)} = \textstyle\sum_K Z_K \tag{28}$$

is the total ionic charge in the unit cube.

If, now, we write the electron number density $n(\vec{r})$ as the sum of the electron number density of the undistorted crystal, $n_0(\vec{r})$, and the change due to the relative displacement of the two sublattices, $\delta n(\vec{r})$, then on combining the ionic and electronic contributions, the total dipole moment of the crystal is obtained in the form

$$\begin{aligned}
M_\mu = {}& (Q^{(i)} + Q^{(e)})\left[\textstyle\sum_L x_\mu(L) - N^* r_{0\mu}\right]\\
&+ N^*\left[\textstyle\sum_K Z_K x_\mu(K) - e\int_{\Omega_0}\rho_\mu n_0(\vec{\rho}-\vec{r}_0)\,d^3\rho\right]\\
&+ N^*\left[\textstyle\sum_K Z_K d_\mu(K) - e\int_{\Omega_0}\rho_\mu\,\delta n(\vec{\rho}-\vec{r}_0)\,d^3\rho\right]\ .
\end{aligned} \tag{29}$$

The first line of this equation vanishes because the unit cube is electrically neutral, so that $Q^{(i)} + Q^{(e)} = 0$. The second line vanishes because the unit cube has a vanishing dipole moment. In fact, each of the two terms on the second line of this question vanishes separately, due to the cubic symmetry of the unit cube about its center. This fact allows us to combine the second term on the second line of this equation with the second term of the third line to obtain for the dipole moment

$$M_\mu = N^*\left[\textstyle\sum_K Z_K d_\mu(K) - e\int_{\Omega_0}\rho_\mu n(\vec{\rho}-\vec{r}_0)\,d^3\rho\right]\ . \tag{30}$$

Since the unit cube contains four primitive unit cells, we find that $N^* = \frac{1}{4}N$. With the aid of Eqs. (15) and (30), we obtain for the transverse effective charge

$$e_T^* = \tfrac{1}{2}(Z_+ - Z_-) - \lim_{\delta\to 0}\frac{e}{a_0\delta}\int_{\Omega_0} x n(\vec{r}-\vec{r}_0)\,d^3r\ . \tag{31}$$

We have remarked above that $n(\vec{r})$ is periodic with a period given by the primitive unit cell of the undeformed crystal. We can therefore expand it in a three-dimensional Fourier series:

$$n(\vec{r}) = \sum_{\vec{G}} \hat{n}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} , \tag{32}$$

where $\vec{G}$ is a translation vector of the reciprocal lattice. It follows that Eq. (31) can be rewritten

$$e_T^* = (Z_+ - Z_-) - \lim_{\delta\to 0} \frac{e}{a_0\delta} \sum_{\vec{G}} \hat{n}(\vec{G}) e^{-i\vec{G}\cdot\vec{r}_0} \times \int_{\Omega_0} x e^{i\vec{G}\cdot\vec{r}} d^3r . \tag{33}$$

The integral in this expression is given by

$$\int_{\Omega_0} x e^{i\vec{G}\cdot\vec{r}} d^3\vec{r} = \int_{-a_0/2}^{a_0/2} dy\, e^{iG_y y} \int_{-a_0/2}^{a_0/2} dz\, e^{iG_z z} \times \int_{-a_0/2}^{a_0/2} dx\, x e^{iG_x x} = -i\Omega_0 \frac{\Delta_x(\vec{G})}{G_x} , \tag{34}$$

where

$$\Delta_x(\vec{G}) = \delta_{G_y,0}\,\delta_{G_z,0}\,[(-1)^{G_x a_0/2\pi} - \delta_{G_x,0}] . \tag{35}$$

We obtain finally for the transverse effective charge

$$e_T^* = \tfrac{1}{2}(Z_+ - Z_-) + \lim_{\delta\to 0} \frac{ie\Omega_0}{a_0\delta} \sum_{\vec{G}} \hat{n}(\vec{G}) \frac{\Delta_x(\vec{G}) e^{-i\vec{G}\cdot\vec{r}_0}}{G_x} . \tag{36}$$

The result for e_T^* given by Eq. (36) is quite general. The only approximation made in its derivation is the assumption that the ion cores can be treated as point charges rather than as extended charge distribution. However, to the extent that the electronic core states centered on neighboring atoms do not overlap this is a good approximation, and one that is usually made in calculations of phonon dispersion curves in solids.

The only place in which significant approximations can be made in applying Eq. (36) to the evaluation of e_T^* is in the determination of the electron number density $n(\vec{r})$ or of its Fourier coefficients $\{\hat{n}(\vec{G})\}$. In this paper we use the empirical pseudopotential method[2] to obtain the electron number density. In this method the one-electron wave functions and energies of a crystal are given by the solutions of the Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r})\right)\psi_{n\vec{k}}(\vec{r}) = E_{n\vec{k}}\psi_{n\vec{k}}(\vec{r}) . \tag{37}$$

In writing this equation we have made use of the fact that, because the relative displacement of the sublattices described by Eq. (13) alters the structure of a primitive unit cell but does not change the translational periodicity of the crystal, the potential energy $V(\vec{r})$ has the periodicity of the undeformed crystal. The one-electron wave functions must therefore have the Bloch form, and we have used the index n to label the bands and $\vec{k}$ the wave vector in the first Brillouin zone which specify these functions. The potential energy $V(\vec{r})$ can be expanded in a three-dimensional Fourier series possessing the periodicity of the undeformed crystal,

$$V(\vec{r}) = \sum_{\vec{G}} \hat{V}(\vec{G}) e^{i\vec{G}\cdot\vec{r}} . \tag{38}$$

It is convenient to decompose the Fourier coefficients of the potential into symmetric and antisymmetric parts, each consisting of the product of a pseudopotential form factor and a structure factor:

$$\hat{V}(\vec{G}) = V_S(G)\cos\vec{G}\cdot(1+\delta)\vec{\tau} - iV_A(\vec{G})\sin\vec{G}\cdot(1+\delta)\vec{\tau} , \tag{39}$$

where the vector $\vec{\tau}$ and parameter δ have been defined in Eq. (6) and (13), respectively. In all the cases considered in this paper the form factors $V_S(G)$ and $V_A(G)$ are functions only of the magnitude of the reciprocal-lattice vector appearing in their arguments.

The one-electron wave function is now expanded in plane waves,

$$\psi_{n\vec{k}}(\vec{r}) = \frac{1}{\Omega^{1/2}} \sum_{\vec{G}} C_{n\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} . \tag{40}$$

The coefficients $\{C_{n\vec{k}}(\vec{G})\}$ are then determined from the eigenvalue equation

$$\sum_{\vec{G}'} H_{\vec{k}}(\vec{G}, \vec{G}')\, C_{n\vec{k}}(\vec{G}) = E_{n\vec{k}} C_{n\vec{k}}(\vec{G}) , \tag{41a}$$

where the Hamiltonian matrix is given by

$$H_{\vec{k}}(\vec{G}, \vec{G}') = (\hbar^2/2m)(\vec{k}+\vec{G})^2 \delta_{\vec{G},\vec{G}'} + V(\vec{G}' - \vec{G}) = H_{\vec{k}}^*(\vec{G}', \vec{G}) . \tag{41b}$$

In addition, they satisfy the orthonormality and closure conditions

$$\sum_{\vec{G}} C_{n\vec{k}}^*(\vec{G})\, C_{n'\vec{k}}(\vec{G}) = \delta_{nn'} , \tag{42a}$$

$$\sum_n C_{n\vec{k}}^*(\vec{G})\, C_{n\vec{k}}(\vec{G}') = \delta_{\vec{G},\vec{G}'} , \tag{42b}$$

which follow from the orthonormality of the Bloch functions.

The electron number density $n(\vec{r})$ is given by

$$n(\vec{r}) = \sum_{n\vec{k}} \theta_{n\vec{k}} |\psi_{n\vec{k}}(\vec{r})|^2 , \tag{43}$$

where $\theta_{n\vec{k}} = 2$ if n is one of the valence bands, and $\theta_{n\vec{k}} = 0$ if n is one of the conduction bands. When we substitute the expansion (40) into Eq. (43) we find that $n(\vec{r})$ can be expanded in the form given by Eq. (32), where the Fourier coefficient $\hat{n}(\vec{G})$ is given by

$$\hat{n}(\vec{G}) = \frac{1}{\Omega} \sum_{\vec{G}'} \sum_{n\vec{k}} \theta_{n\vec{k}} C_{n\vec{k}}^*(\vec{G}')\, C_{n\vec{k}}(\vec{G}' + \vec{G}) . \tag{44}$$

Equation (44), together with Eqs. (36), (39), (41), and (42), formally solves the problem of calculating the transverse effective charge.

As the two sublattices are displaced according to Eq. (13), the point group of a crystal of the zinc-blende structure is reduced from T_d to C_{3v}. The point group C_{3v} has six operations under which the Hamiltonian matrix is invariant. It follows, therefore, that in carrying out the sum over $\vec{k}$ in Eq. (44) we need to consider $\vec{k}$ vectors within only one-sixth of the first Brillouin zone. In this irreducible one-sixth of the zone we chose wave vectors of the form

$$\vec{k} = \frac{2\pi}{na_0} [(P_x, P_y, P_z), (-P_x, -P_y, -P_z), (-P_x, P_y, P_z), (P_x, -P_y, -P_z)] \quad (P_x, P_y, P_z = \text{integers}), \tag{45a}$$

where

$$n \geq P_x \geq P_y \geq P_z \geq 0, \quad 0 < P_x + P_y + P_z \leq \tfrac{3}{2} n . \tag{45b}$$

From the above set of vectors, we used only those for which P_x, P_y, and P_z were odd integers. All of the computations were done for $n = 4$, giving 10 vectors in the reduced zone and hence an equivalent 32 points in the entire zone.

In calculating the coefficients $\{C_{n\vec{k}}(\vec{G})\}$, and from them the Fourier coefficients of the electron number density $\{\hat{n}(\vec{G})\}$, the pseudopotential form factors obtained by Cohen and Bergstresser[2] were used for the III-V and II-VI compounds, and those of van Haeringen and Junginger[3] were used for the IV-IV compound SiC. Two comments have to be made about these form factors in the context of the present calculations.

Not all of the form factors required in the present calculations are to be found in Refs. 2 and 3 This is due to the fact that in the undistorted zinc-blende structure ($\delta = 0$) the structure factor $\cos\vec{G}\cdot\vec{\tau}$ vanishes for $G^2 = 4$, while the structure factor $\sin\vec{G}\cdot\vec{\tau}$ vanishes for $G^2 = 8$ (G is measured in units of $2\pi/a_0$). Consequently, the pseudopotential form factors $V_S(4)$ and $V_A(8)$ are not tabulated in Refs. 2 and 3. For nonzero values of δ, however, these form factors are required. In the present calculations they were determined by making a three-parameter fit to the tabulated form factors according to

$$V_S(G) = \alpha_S + \beta_S G^2 + \gamma_S G^4 , \qquad V_A(G) = \alpha_A + \beta_A G^2 + \gamma_A G^4 . \tag{46}$$

The complete set of pseudopotential form factors for the crystals considered in this paper is presented in Table I.

The second comment which must be made concerning the pseudopotential form factors used in these calculations is that the sign of the antisymmetric form factors $\{V_A(G)\}$ is determined by specifying which of the two kinds of atoms comprising the crystal occupies the "+" sublattice, and which occupies the "−" sublattice; interchanging the atoms on the two sublattices changes the signs of the $\{V_A(G)\}$, but leaves the $\{V_S(G)\}$ unaltered. Thus when the pseudopotential form factors are obtained semiempirically, by fitting theoretical expressions for one-electron energies at symmetry points in the first Brillouin zone to experimental values for these energies, and particular signs are assigned the antisymmetric form factors obtained in this way, this is equivalent to making a definite choice of which atom is situated on which sublattice. However, this choice cannot be determined without making an independent calculation of the individual-atom pseudopotential form factors and combining them into the antisymmetric form factors for both possible assignments of the two kinds of atoms to the two sublattices. For only one of the two assignments will the signs of the calculated antisymmetric form factors agree with those of the empirically determined form factors, thus fixing the atomic configuration.

TABLE I. Pseudopotential form factors.[a]

	$V_S(3)$	$V_S(4)$	$V_S(8)$	$V_S(11)$	$V_A(3)$	$V_A(4)$	$V_A(8)$	$V_A(11)$
GaAs	−0.23	−0.17	0.01	0.06	0.07	0.05	0.01	0.01
GaP	−0.22	−0.15	0.03	0.07	0.12	0.07	−0.02	0.02
GaSb	−0.22	−0.16	0.00	0.05	0.06	0.05	0.02	0.01
InP	−0.23	−0.17	0.01	0.06	0.07	0.05	0.01	0.01
InAs	−0.22	−0.16	0.00	0.05	0.08	0.05	0.00	0.03
InSb	−0.20	−0.15	0.00	0.04	0.06	0.05	0.02	0.01
AlSb	−0.21	−0.15	0.02	0.06	0.06	0.04	0.00	0.02
ZnS	−0.22	−0.15	0.03	0.07	0.24	0.14	−0.05	0.04
ZnSe	−0.23	−0.17	0.01	0.06	0.18	0.12	0.00	0.03
ZnTe	−0.22	−0.16	0.00	0.05	0.13	0.10	0.02	0.01
CdTe	−0.20	−0.15	0.00	0.04	0.15	0.09	−0.02	0.04
SiC[b]	−0.31	−0.22	0.01	0.06	0.14	0.20	0.12	−0.06

[a] These data have units of Rydbergs.

[b] These data were obtained from W. van Haeringen and H. G. Junginger, Solid State Commun. 7, 1135 (1969). The remainder were obtained from M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966).

If the pseudopotential form factors are to be used only for band-structure calculations, only the relative signs of the antisymmetric form factors among themselves are relevant, and not their true signs. This is because a change in the sign of each antisymmetric form factor, according to Eqs. (39) and (41), corresponds merely to taking the transpose of the Hamiltonian matrix, which does not alter its eigenvalues, the one-electron energies. Thus the band structure of a crystal containing two atoms in a primitive unit cell is independent of the assignment of the two atoms to the two sublattices. For this reason, most authors in presenting empirical pseudopotential form factors for diatomic crystals do not attempt to specify to which atomic configuration their results apply. While this information is not essential to have in studying the band structure of a crystal, it is essential for determining the ionic contribution to the transverse effective charge, as given by Eq. (36).

In the present calculations, the assignment of an atom in a III-V or II-VI compound to a particular sublattice was based on a comparison of the signs of the antisymmetric form factors given by Cohen and Bergstresser[2] with those computed on the basis of the bare ion model potentials of Animula and Heine[4] for the crystals considered. The results were that for the III-V and II-VI compounds it is the "+" sublattice that is occupied by the atoms from columns III and II of the periodic table, respectively. In the case of the IV-IV compound SiC, van Haeringen and Junginger[3] constructed the pseudopotential form factors on the assumption that the Si atoms occupy the sites of the "+" sublattice, and the C atoms the sites of the "−" sublattice.

Thus, in calculating e_T^* we are in each case calculating the transverse effective charge of the atom A in the compound AB.

For the III-V compounds of the zinc-blende structure the ion core charges were taken to be $Z_+ = 3e$ and $Z_- = 5e$ in the present calculations. In the case of the II-VI compounds the values assumed for these charges were $Z_+ = 2e$ and $Z_- = 6e$. For SiC the values $Z_+ = Z_- = 4e$ were used. By making these choices we have neglected the renormalization of the ion core charges due to the "orthogonalization hole" at the ion sites, familiar from pseudopotential theory.[5] For those cases where this renormalization has been calculated,[6] it is found to represent less than a 10% correction to the bare ion charge. However, the neglect of the orthogonalization hole in the present calculations is an approximation which could well be removed in more accurate calculations of effective charges.

The Hamiltonian matrix was constructed by truncating the expansion of the eigenfunctions (40) through the restriction that $(\vec{k}+\vec{G})^2 \leq 9(2\pi/a_0)^2$. This restriction was dictated by the limitations of the computer on which the present calculations were carried out. It produced Hermitian matrices of order 27 on the average for the values of $\vec{k}$ used.

The Hermitian matrix can be made into a real symmetric matrix by separating it into its real and imaginary parts,

$$\vec{\mathrm{H}} = \vec{\mathrm{H}}_R + i\vec{\mathrm{H}}_I \ , \tag{47}$$

where $\vec{\mathrm{H}}_R$ is a real symmetric matrix, while $\vec{\mathrm{H}}_I$ is a real antisymmetric matrix. Then, if we write the column vector of the coefficients $\{C_{n\vec{k}}(\vec{\mathrm{G}})\}$ in a similar fashion as

$$\vec{\mathrm{C}} = \vec{\mathrm{C}}_R + i\vec{\mathrm{C}}_I \ , \tag{48}$$

the eigenvalue equation (41a) can be written in the partitioned form

$$\begin{pmatrix} \vec{\mathrm{H}}_R & -\vec{\mathrm{H}}_I \\ \vec{\mathrm{H}}_I & \vec{\mathrm{H}}_R \end{pmatrix} \begin{pmatrix} \vec{\mathrm{C}}_R \\ \vec{\mathrm{C}}_I \end{pmatrix} = E \begin{pmatrix} \vec{\mathrm{C}}_R \\ \vec{\mathrm{C}}_I \end{pmatrix} \quad . \tag{49}$$

This procedure produces a real symmetric matrix which is twice as large as the original. If we begin with a general Hermitian matrix of order N, we obtain N eigenvalues and eigenvectors. However, since the real symmetric matrix obtained from it by the above procedure is twice as large, we obtain from it $2N$ eigenvalues and eigenvectors. Not all of these eigenvectors are linearly independent, however. In fact, by enlarging an $N\times N$ Hermitian matrix into a $2N\times 2N$ real symmetric matrix, we have induced an apparent twofold degeneracy into the system. For it is readily seen that if E is an eigenvalue of Eq. (49) whose $2N$-dimensional, real eigenvector is $(\vec{\mathrm{C}}_R \vec{\mathrm{C}}_I)$, corresponding to a complex, N-dimensional eigenvector of $\vec{\mathrm{H}}$ given by Eq. (48), then E is also an eigenvalue of Eq. (49) with a $2N$-dimensional real eigenvector given by $(-\vec{\mathrm{C}}_I \vec{\mathrm{C}}_R)$, corresponding to a complex N-dimensional eigenvector of $\vec{\mathrm{H}}$ given by $-\vec{\mathrm{C}}_I + i\vec{\mathrm{C}}_R$. These two N-dimensional complex eigenvectors of $\vec{\mathrm{H}}$ differ only by a factor of i, and therefore are linearly dependent. If the Hamiltonian has an eigenvalue with true degeneracy g, we will obtain $2g$ degenerate eigenvectors from the solution of Eq. (49), which will be linear combinations of g pairs of eigenvectors, in which the members of each pair differ by a factor of i. To obtain a set of N orthonormal and complete eigenvectors of the original Hermitian matrix, a Gram-Schmidt orthogonalization procedure[7] was applied to the $2N$ eigenvectors of the real symmetric matrix. The N complex eigenvectors obtained in this way, and the corresponding eigenvalues, were used in the calculation of the effective charges.

The effective charges were calculated for several zinc-blende-type crystals. These results are presented in Table II, along with experimental data for comparison.

Several calculations were performed as checks on various approximations and assumptions made in this work. As one such check we also calculated the electronic contributions to the dielectric constant of each crystal, in the limit as the frequency of the incident electromagnetic field tends to zero, from the expression

$$\epsilon_\infty = \lim_{\omega\to 0}\left(1 - 4\pi\frac{N}{\Omega}\frac{e^2}{m\omega^2} - \frac{4\pi e^2}{m^2\omega^2\Omega}\right.$$

$$\times \sum_{\vec{k}}\sum_{nn'}\frac{\theta_{n\vec{k}} - \theta_{n'\vec{k}}}{E_{n\vec{k}} - E_{n'\vec{k}} - \hbar\omega}$$

$$\left.\times \langle n\vec{k}|p_x|n'\vec{k}\rangle\langle n'\vec{k}|p_x|n\vec{k}\rangle\right)$$

$$= 1 - \frac{8\pi e^2\hbar^2}{m^2\Omega}\sum_{\vec{k}}\sum_{nn'}\theta_{n\vec{k}}\frac{\langle n\vec{k}|p_x|n'\vec{k}\rangle\langle n'\vec{k}|p_x|n\vec{k}\rangle}{(E_{n\vec{k}} - E_{n'\vec{k}})^3}$$

$$= 1 - \frac{8\pi e^2\hbar^4}{m^2\Omega}\sum_{\vec{k}}\sum_{nn'}\theta_{n\vec{k}}\frac{F_x^{nn'}(\vec{k})F_x^{n'n}(\vec{k})}{(E_{n\vec{k}} - E_{n'\vec{k}})^3}, \tag{50a}$$

with

$$F_\alpha^{nn'}(\vec{k}) = \sum_{\vec{G}} C^*_{n\vec{k}}(\vec{G})\,C_{n'\vec{k}}(\vec{G})\,G_\alpha$$

$$= [F_\alpha^{n'n}(\vec{k})]^*. \tag{50b}$$

Here N is the number of valence electrons in the crystal, m is the electronic mass, and $\langle n\vec{k}|p_\mu|n'\vec{k}\rangle$ is the matrix element of the μth component of the electron momentum operator between the Bloch states $\psi_{n\vec{k}}(\vec{r})$ and $\psi_{n'\vec{k}}(\vec{r})$. The coefficients $\{C_{n\vec{k}}(\vec{G})\}$ and the corresponding energies $\{E_{n\vec{k}}\}$ entering Eq. (50) were obtained from Eqs. (38)–(42) with $\delta = 0$. The results are presented in Table II, together with the corresponding experimental values. (The notation ϵ_∞ serves to emphasize that the dielectric constant being calculated is the dielectric constant at frequencies large compared with the transverse optical-mode frequency of the crystal, so that the ionic motion is frozen out, but small compared with the frequency of the lowest electronic transition.)

In order to examine the sensitivity of our results to the number of $\vec{k}$ values in the first Brillouin zone used in our calculations, we computed the quantities of interest for GaAs using the even integers for the P's omitted from the definition of $\vec{k}$ given by Eqs. (45). The results showed less than a 2% change in the values of the effective charges and optical-frequency dielectric constants.

The crystal distortion was chosen as a relative displacement of the sublattices in the [111] direction. The distortion used for all calculations corresponds to a value of $\delta = +0.0015$ in Eq. (13). In order to examine the sensitivity of the results to the magnitude of δ, several different trials were made for GaAs. Values of δ equal to ± 0.015, ± 0.005, and ± 0.0015 were tried. The effective charges and optical-frequency dielectric constants were virtually insensitive to the variation of the distortion parameter.

The first results of our calculations that we wish to stress is that for the II-VI, III-V, and IV-IV compounds of the zinc-blende structure considered here, the transverse effective charge of the atom A in the chemical formula AB for the compound is found to be positive in each case, so that the charge on the atom B is negative.

From the results of Table II we see that the closest agreement between the theoretical and experimental results for the transverse effective charges occurs for the III-V compounds. With the exception of GaSb, for which the discrepancy is 25%, the differences between the theoretical and experimental values of e_T^* are all less than 20% of the experimental values. With the exception of GaAs, where the discrepancy is large, the same is true of the calculated and experimental results for the electronic contribution to the dielectric constant. The comparatively large discrepancy

TABLE II. Effective charges and optical-frequency dielectric constants.

	ϵ_∞		e_T^*/e		
Crystal	Theory	Experimental	Theory	Experimental	Ref.
SiC	11.19	10.0	1.42	2.7	10
AlSb	12.45	12.0	2.28	2.2	11
GaP	11.42	10.2	2.37	2.0	12
GaAs	17.77	12.9	2.39	2.2	13
GaSb	16.74	15.7	2.51	2.0	13
InP	13.30	12.6	2.44	2.7	13
InAs	17.84	15.1	2.52	2.7	13
InSb	17.61	17.9	2.58	2.5	13
ZnS	4.69	5.14	3.68	2.0	14
ZnSe	5.40	5.90	3.75	1.8	15
ZnTe	5.84	7.28	3.84	2.0	15
CdTe	5.88	7.3	3.92	2.35	16

between the theoretical and experimental results for e_T^* for GaSb may be due in part to the fact that the band structure of GaSb computed by Cohen and Bergstresser[2] shows some disagreement with experiment, leading Cohen and Bergstresser to suggest that the pseudopotential form factors used in their work, and in ours, may need to be adjusted.

The discrepancies between the theoretical and experimental results for the transverse effective charges, and dielectric constants, of the II-VI compounds are disappointingly large, and suggest that in its present form the method for calculating effective charges developed in this paper is not well suited for application to these compounds. Some reasons for these discrepancies will be discussed below.

The theoretical results for e_T^* show certain trends. If in a compound AB we fix the atom A we find that e_T^* is larger in magnitude the lower atom B is in its column in the periodic table. Similarly, if we fix atom B, the magnitude of e_T^* is larger the lower atom A is in its column of the periodic table. These trends are only partially reflected in the experimental results. However, the experimental values for the effective charges are not known with great accuracy, and it may be that more accurate experimental determinations of e_T^* would confirm the predicted trends.

Several approximations have been made in the present calculations which it would be well to remove in a more refined calculation. First, it was assumed that the self-consistent pseudopotential moves rigidly with the ion cores as they are displaced according to Eq. (13). This is probably not a bad approximation considering the small displacements used in the present calculations. In a more refined calculation only the bare-ion pseudopotential would be assumed to move rigidly with the nuclei, and the self-consistent pseudopotential, obtained from the bare-ion pseudopotential by screening it with an appropriate dielectric function, would be recalculated at the displaced lattice sites. This appears to be a feasible calculation in the Hartree approximation, for example.

The electron number density was calculated using the pseudopotential wave functions. This corresponds to using the smooth part of the orthogonalized plane-wave function. As we have remarked earlier, if one corrects for this approximation by including the contribution to the number density arising from the orthogonalization of the plane-wave part of the wave function to the atomic core states, the result is to renormalize the charges on the bare ions. Estimates of the magnitude of this renormalization have not been made for semiconductors to our knowledge, but it seems to be less than a 10% effect in metals.[6] The error in the ionic contribution to the transverse effective charge could be larger than this, however, if the fractional changes in Z_+ and Z_- are rather different, due to the fact that it is their difference that enters the expression for e_T^*.

We have not included a spin-orbit interaction term in our pseudo-Hamiltonian (37). Procedures for doing so within the framework of pseudopotential theory now exist.[8] However, it was felt that the effects of the spin-orbit interaction on an integral property of the wave functions, such as the electron number density, are small, and could be neglected in an exploratory calculation such as presented here. This assumption warrants further investigation, particularly in the case of compounds containing heavy elements.

The final approximation made was the restriction of the number of plane waves retained in the expansion of the wave function $\psi_{n\vec{k}}(\vec{r})$ to approximately 27. This restriction may well be the most serious approximation made in this work. In their calculations of electron charge densities in III-V compounds on the basis of the empirical pseudopotential method, Walter and Cohen[9] used up to 90 plane waves to obtain physically reasonable results for the charge density associated with each of the four valence bands. If such a large number of plane waves is indeed required for the accurate calculation of electron charge densities, then the reasonably good agreement between the transverse effective charges of the III-V compounds calculated in this work and their experimental values may be largely fortuitous. The use of a comparatively few plane waves in the calculation of the electron number density and the transverse effective charge is likely to be a more drastic approximation for the II-VI compounds than it is for the III-V compounds, and may be responsible for the disagreement between the theoretical and experimental results for these compounds presented in Table II. The II-VI compounds are more ionic than the III-V compounds, and it is not unreasonable that a larger number of plane waves is required in the expansion of their wave functions to reproduce the greater localization of the electrons about their nuclei. It may well be that calculations of effective charges for the II-VI compounds based on the use of the tight binding approximation for the determination of the wave functions of the valence electrons will prove to be simpler and more accurate than calculations based on the pseudopotential method as described here. It is our opinion that in subsequent calculations of transverse effective charges by the method used in the present work the first improvement that should be incorporated into these calculations is the use of a larger number of plane waves in the expansion of the pseudo-wave-functions.

In conclusion, we feel that the results of this paper show that, despite its simplicity, the present approach to the calculation of transverse effective charges is a practical one from the computational standpoint, and one which is capable of yielding quantitatively accurate results.

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