PHYSICAL REVIEW B VOLUME 6, NUMBER 4 15 AUGUST 1972

Infrared Dispersion of Second-Order Electric Susceptibilities in Semiconducting Compounds*

C. Flytzanis†
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 10 January 1972)

A unified study is presented of the infrared behavior of the second-order electric susceptibilities $\chi^{(2)}$ in semiconducting compounds for both longitudinal and transverse fields. The molecular model used previously for the calculation of $\chi^{(2)}$ for frequencies above the lattice resonances is extended and applied to the calculation of $\chi^{(2)}$ for frequencies below the lattice resonances as well. An *ab initio* calculation of the different contributions is given and the local-field corrections are taken into account in a semiempirical way, consistent with the macroscopic infrared properties of these materials. In particular, the Raman, electro-optic, optical rectification, and far-infrared frequency mixing coefficients are explicitly considered for the seven semiconductors InSb, InAs, InP, GaSb, GaAs, GaP, and AlSb. The agreement with experiment is good. The relation between the ionic part of $\chi^{(2)}$ and the phonon-damping mechanisms in these compounds is also discussed and a generalization of the Lyddane-Sachs-Teller relation to the nonlinear regime is presented. Further, the relation of the different terms in $\chi^{(2)}$ to the covalent character of the bonds in these compounds is briefly discussed in terms of the exactly soluble unidimensional δ-function-bond model. This latter approach combined with the recent phenomenological descriptions of the bonding in tetrahedral covalent compounds can also be extended for the calculation of $\chi^{(2)}$ for the II–VI compounds.

I. INTRODUCTION

The formal quantum-mechanical expression of the second-order susceptibility $\chi^{(2)}(\omega_1, \omega_2)$, which relates the Fourier component $\vec{P}^{(2)}(\omega_1+\omega_2)$ of the second-order polarization to the Fourier components $\vec{E}(\omega_1)$ and $\vec{E}(\omega_2)$ of the applied electric field, has been derived by different authors.[1, 2] In applying these formulas to a particular crystal one must take into account the specific physical and geometrical characteristics of the medium as well as the frequencies of the incident and created fields with respect to the eigenstates of the crystal. These fall into two distinct regions, the low-frequency region due to lattice collective vibrations and the high-frequency region due to the onset of electronic transitions. For perfect crystalline dielectrics these regions are well separated and depending on the positions of the incident and created frequencies different mechanisms contribute to $\chi^{(2)}$. For these crystals, along with $\chi^{(2)}$ it is convenient to introduce also the macroscopic second-order polarizability per unit cell $\tilde{\beta}$, defined formally through the relation

$$\chi^{(2)}_{ijk}(\omega_1, \omega_2) = (1/v)\tilde{\beta}_{ijk}(\omega_1, \omega_2) , \tag{1.1}$$

where v is the volume of the unit cell.

The expression of $\tilde{\beta}$, containing explicitly the different contributions, has been derived[3] within the Born-Oppenheimer approximation[4] for a system of charges contained in a volume element of dimensions small compared to the wavelengths of the involved fields. Apart from some formal discussions[5, 6] or calculations[7] with simple models, however, no detailed study of the over-all infrared behavior of $\tilde{\beta}$ has been performed comparable to the one that exists for the region of optical transparency. Despite the good agreement obtained by some of these models, their *a priori* justification is not clear and a more systematic treatment of the infrared behavior of $\tilde{\beta}$ is required. The study of the infrared dispersion of $\tilde{\beta}$, furthermore, is closely related to some problems concerning electron–optic-phonon and optic-phonon–optic-phonon interaction in dielectrics and includes as special cases the linear electro-optic effect, the optical rectification effect, and the mixing of two frequencies in the near- and far-infrared frequency spectrum.

Here we present a unified study of the infrared behavior of $\chi^{(2)}$, for frequencies below the onset of electronic transitions but above the elastic resonances of the sample, for the simplest case of crystals possessing a nonzero $\chi^{(2)}$, namely, the family of the III–V compounds with $\bar{4}3m$ symmetry. These compounds are cubic with two atoms per unit cell and they consequently have a threefold-degenerate infrared-active long-wavelength optic mode which, due to long-range electric field effects is split into a doubly degenerate transverse mode and a longitudinal mode. In this wavelength region the linear susceptibility behaves as a scalar and $\chi^{(2)}$ has only one independent component $\chi^{(2)}_{xyz}$. When all the three frequencies, ω_1, ω_2, and $\omega_1+\omega_2$, are in the optical transparency region of the crystal above ω_T, $\chi^{(2)}$ was well accounted for by assuming[8, 9] that only the dipoles connected with the redistribution of the valence electron density by the electric fields give rise to polarizations; the movement of the nuclei and their tightly bound core electrons was disregarded in their calculation. When, however, one or more of the frequencies fall below ω_T, additional processes will come into play giving rise to contributions in $\tilde{\beta}$ which show a dispersion characteristic of the lattice.[10] These additional contributions in the nonlinear polarization arise from cross terms between the different lattice modes and between electric fields and lattice modes and can be understood only if allowance is made of electron-phonon and phonon-phonon interaction in the medium. In the frequency range considered only long-wavelength phonons come into play; hence the nuclear displacements are uniform throughout a volume of dimensions smaller than the wavelengths. This allows us to reduce effectively the study of the lattice vibration modes and their interaction with the electrons to those of a unit cell[11]; again only the redistribution of the electron density by the fields and the displacements will be involved. The use, then, of localized orbitals for the electrons as in Ref. 8 and the approaches of Huang[12] and Szigeti[13] to treat long-wavelength lattice waves are justified and one may consider a unit cell separated from the rest of the crystal and described by a Born-Oppenheimer wave function. This description is discussed in Sec. II. Microscopically, then, the total polarization in the crystal arises from the dipole moments induced in each unit cell by electric fields and short- and long-range lattice-deformation forces. These dipole moments can be expressed in terms of microscopic polarizabilities. However, the relation between these microscopic polarizabilities and the macroscopic ones is complicated by the fact that the electric fields acting on the electrons and ions of a unit cell are not the macroscopic ones. This problem will be treated in a semiempirical way consistent with the macroscopic optical properties of the crystal. The expressions of $\chi^{(1)}$ and $\chi^{(2)}$ in terms of microscopic polarizabilities and local field corrections will be given in Sec. III and their numerical calculation is presented in Sec. IV. In Sec. V we present a brief discussion of our results in terms of a simple and exactly soluble model for a unidimensional bond[14,3] which allows us to single out the important parameters which determine $\chi^{(2)}$. This, combined with the phenomenological description of the bonding in the tetrahedral compounds proposed recently by Phillips[15] and van Vechten,[15] can be used to compute $\chi^{(2)}$ in a simple way for a larger class of tetrahedrally bonded crystals.

II. INFRARED OPTICAL PROPERTIES AND MOLECULAR MODEL

The III–V compounds possessing the zinc-blende structure are of cubic symmetry (point group $\bar{4}3m$) with two different atoms per unit cell, each species forming face-centered cubic sublattices parallel to each other and the one displaced by a vector $\vec{R}=a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ along the diagonal of the other, where a is the lattice constant. Being diatomic these compounds possess three acoustic and three optic modes. In the frequency range considered the electromagnetic fields couple only with the optical modes of wavelength much larger than the cell dimensions; these modes correspond to a uniform displacement of one atom against the other within a unit cell while their center of gravity remains fixed. This leads to drastic simplifications in the description of the linear optical properties of cubic crystals in the frequency range below the onset of electronic transitions and Huang[11] has shown that these can be described simply in terms of macroscopic equations. Introducing an appropriate parameter $\vec{w}$, the relative displacement of the atoms multiplied by the root square of the effective mass of the unit cell, these macroscopic equations are[4]

$$\ddot{\vec{w}} = b_{11}\vec{w} + b_{12}\vec{E}\,, \tag{2. 1a}$$

$$\vec{P}^{(1)} = b_{21}\vec{w} + b_{22}\vec{E}\,, \tag{2. 1b}$$

where $\vec{P}^{(1)}$ and $\vec{E}$ are the linear polarization and the electric field such as they appear in the Maxwell equations $\vec{w}=(M/v)^{1/2}(\vec{u}_B-\vec{u}_A)$; $\vec{u}_i$ is the displacement of atom $i=A$, B from its equilibrium position $M^{-1}=M_A^{-1}+M_B^{-1}$; M_i is the mass of the atom $i=A$, B; and v is the unit-cell volume, or $v=N^{-1}$, where N is the number of cells per unit volume. Huang[11] shows that $b_{12}=b_{21}$. For monochromatic waves which are exclusively considered here $\vec{E}=\vec{E}_0 e^{-i\Omega t}$, $\vec{w}=\vec{w}_0 e^{-i\Omega t}$, and $\vec{P}^{(1)}=\vec{P}^{(1)} e^{-i\Omega t}$; substituting in (2. 1a) eliminating $\vec{w}$, solving for $\vec{P}^{(1)}$, and using the definition $\vec{D}^{(1)}=\vec{E}+4\pi\vec{P}^{(1)}=\epsilon\vec{E}$, one obtains

$$\epsilon = 1 + 4\pi b_{22} + \frac{4\pi b_{12} b_{21}}{-b_{11}-\Omega_2}$$

or

$$\epsilon = \epsilon_\infty + \frac{\epsilon_0-\epsilon_\infty}{1-(\Omega/\Omega_0)^2}\,, \tag{2. 2a}$$

since $\epsilon=\epsilon_0$ when $\Omega\to 0$ and $\epsilon=\epsilon_\infty$ when $\Omega\to\infty$, where ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants; by ∞ in the following we understand a frequency in the transparency region of the crystal. One obtains, then, $b_{11}=-\Omega_0^2$, $b_{21}=b_{12}=[(\epsilon_0-\epsilon_\infty)/4\pi]^{1/2}\Omega_0$ and $b_{22}=(\epsilon_\infty-1)/4\pi$. We also define formally the linear susceptibility $\chi^{(1)}$ by the relation

$$\epsilon = 1 + 4\pi\chi^{(1)}\,. \tag{2. 2b}$$

Using the charge neutrality condition $\vec{\nabla}\cdot\vec{D}=0$, one can show[4,16] that the eigenfrequencies of the optic modes which can exist in the crystal in the absence of any applied electric fields can be divided uniquely into transverse and longitudinal; they will be referred to by subscripts T and L, respectively.

One can show[4] that no electric field accompanies a transverse mode or $\vec{E}_T = 0$, and hence from (2.1b),

$$\vec{P}^{(1)} = b_{21}\vec{w}_T = Ne_T^*\vec{u}_T \; , \tag{2.3}$$

where $\vec{u}_T = (NM)^{-1}\vec{w}_T$; this relation also constitutes the definition of the macroscopic transverse effective charge e_T^*. The equation of motion (2.1a) becomes

$$\ddot{\vec{u}}_T + \Omega_T^2\vec{u}_T = 0 \; ,$$

where $\Omega_T = \Omega_0$ is the frequency of the transverse mode.

For a longitudinal mode one can show[4] that a macroscopic field $\vec{E}_L = -4\pi\vec{P}_L$ is set up, and hence from (2.1b),

$$\vec{P}_L^{(1)} = \frac{b_{21}}{1+4\pi b_{22}}\vec{w}_L = N\frac{e_T^*}{\epsilon_\infty}\vec{u}_L = Ne_L^*\vec{u}_L \; , \tag{2.4}$$

which constitutes the definition of the effective longitudinal macroscopic charge

$$e_L^* = e_T^*/\epsilon_\infty \; . \tag{2.5}$$

The equation of motion (2.1a) becomes

$$\vec{w}_L = -\Omega_0^2\vec{w}_L - 4\pi b_{22}\vec{P}_L^{(1)}$$

or

$$\ddot{\vec{u}}_L + \Omega_L^2\vec{u}_L = 0 \; , \tag{2.6}$$

where

$$\Omega_L^2 = (\epsilon_0/\epsilon_\infty)\Omega_T^2 \tag{2.7}$$

is the frequency of the longitudinal-optic mode; (2.7) is the Lyddane-Sachs-Teller relation.[17]

Taking into account (2.1b) and (2.3) the linear polarization induced by a transverse electromagnetic field can be written

$$\vec{P}^{(1)} = Ne_T^*\vec{u}_T + \frac{\epsilon_\infty - 1}{4\pi}\vec{E} \; . \tag{2.8}$$

The first term on the right-hand side arises from the displacements of the atoms and, since $\vec{u}_T$ obeys Eq. (2.4), this term displays a dispersion characteristic of the lattice; the second term in (2.8) arises from purely electronic contributions the lattice being held fixed. However, the electrons contribute substantially even in the first term through their deformation by the atomic displacements. This deformation follows the lattice displacements adiabatically and is uniquely determined by the lattice coordinates, hence the dipole moment connected with it is part of the lattice dipole moment; this accounts[13,16] for the actual values of the effective charges e_T^* which are different if only rigid motion of ions is assumed to take place. Besides the purely electronic contribution the second-order susceptibility also contains terms which in the infrared show dispersion characteristic of the lattice.[10] The origin of these additional terms is the same intercorrelation of electronic polarization and lattice displacements mentioned above. As a matter of fact, besides its direct coupling with the electrons, a low-frequency or static electric field also induces displacements of the ions along the polar transverse-optic mode of the crystal. The electronic distribution being determined by the relative nuclear positions is deformed in the course of these displacements. Accordingly, a change of the electric-field-induced electronic-dipole moments results from both short- and long-range deformation fields set up by the lattice. Furthermore, this same deformation of electron shells mediates interaction between phonons; together with the phonon interaction provided through the anharmonic term in the lattice potential, it modifies the lattice dipole moment and contributes nonlinear terms in the total polarization.

A possible approach is to start with the complete Hamiltonian of the crystal,

$$H = \sum_I \frac{\vec{P}_I^2}{2M_I} + \sum_i \frac{\vec{p}_i^2}{2m_i} + \sum_{i>j} \frac{e^2}{|\vec{r}_t - \vec{r}_j|} + \sum_{I,i} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|} + \sum_{I>J} \frac{Z_I Z_J e^2}{|R_I - R_J|} , \tag{2.9}$$

and then use a band description for the electronic density distribution, for an arbitrary nuclear configuration, to derive the different contributions in $\chi^{(2)}$; here (M, m), $(\vec{R}, \vec{r})$, and $(\vec{P}, \vec{p})$ are the masses, positions, and moment, respectively, of the nuclei and electrons. However, since in a dielectric we are only dealing with filled valence and core bands, it is immaterial whether we use a determinant of Bloch states or of localized orbitals to describe the valence electron density. Finally since we are concerned with matrix elements of one-particle operators, the determinant of the localized orbitals may be replaced by its diagonal. This amounts to regarding each electron as attached to a given cell of equilibrium position $\vec{R}_0$ in the lattice; we call H_0 the corresponding effective Hamiltonian of such a cell. It follows that the electronic distribution within a unit cell depends mainly on the relative positions of the ions in the cell and will be affected by changes of these relative positions. Here we assume that for each nuclear configuration $\vec{R} = \vec{R}_0 + \vec{u}$ the wave function of the unit cell is represented by a Born-Oppenheimer function

$$\Psi_{ev}(\vec{r}, \vec{R}) = \chi_{ev}(\vec{R})\phi_e(\vec{r}, \vec{R}) \; , \tag{2.10}$$

where $\vec{r}$ and $\vec{R}$ collectively denote the electronic and nuclear positions, respectively. $\phi_e(\vec{r}, \vec{R})$ is the wave function of the electrons in the field of the nuclei, which are held fixed in an arbitrary position $\vec{R}$, e being the corresponding quantum number with eigenvalue $\vec{E}_e(\vec{R})$, a function of $\vec{R}$; $\chi_{ev}(\vec{R})$ represents a wave function for the nuclei moving in the effective potential $E_e(\vec{R})$, the corresponding eigenvalues being ϵ_{ev}. We write the Hamiltonian of this restricted system as

$$H_0 = T_N + T_E + V(\vec{r}, \vec{R}) , \tag{2.11}$$

where T_N and T_E are the kinetic-energy operators for the nuclei and the electrons, respectively; $V(\vec{r}, \vec{R})$ is the potential-energy operator of the interactions between all the particles in the unit cell. In the adiabatic approximation, then, the eigenvalue problem is split into the following:

$$[T_E + V(\vec{r}, \vec{R})]\,\phi_e(\vec{r}, \vec{R}) = E_e(\vec{R})\phi_e(\vec{r}, \vec{R}) , \tag{2.12a}$$

$$[T_N + E_e(\vec{R})]\chi_{ev}(\vec{R}) = \epsilon_{ev}\chi_{ev}(\vec{R}) . \tag{2.12b}$$

We restrict ourselves to the ground state of the electronic system and we denote by $E_0(\vec{R})$ the energy, a function of the nuclear configuration. We assume that $E_0(\vec{R})$ can be developed in powers of $\vec{u} = \vec{R} - \vec{R}_0$ which, in the case of cubic crystals, is directly proportional to the normal coordinate of the long-wavelength optic mode.[18] Hence

$$E_0(\vec{R}) = E_0(\vec{R}_0) + \tfrac{1}{2}\, E^{(2)}_{0,\,ij} u_i u_j + \tfrac{1}{6} E^{(3)}_{0,\,ijk} u_i u_j u_k , \tag{2.13}$$

where we have limited the expansion up to third-order terms. $E_0(\vec{R})$ is actually the cohesive energy of the crystal in its ground state.

It is clear that the bonding electrons which reflect the structural characteristics of the crystal will be most deformed by the displacement $\vec{u}$, while the deep-lying core electrons will follow essentially undeformed the nuclear motion. We introduce the simplification that for each nuclear configuration $\phi_e(\vec{r}, \vec{R})$ describes only the system of the eight valence electrons per unit cell. These will be assumed to form a system of separated electron pairs accommodated in effectively localized bonds between adjacent atoms.[19] The core electrons, on the other hand, are assumed to be unaffected by the bonding and not coupled to the valence electrons; they are rigidly bound to the nuclei, canceling part of their positive charge and leaving positive charges $Z_A e$ and $Z_B e$ on each nuclear position. These will be taken pointlike and undeformed in the course of the nuclear displacements. Their values will be the valence charges 3 and 5, respectively, for the group-III and -V atom.

There are four equivalent tetrahedral bonds per unit cell which, in the equilibrium nuclear configuration $\vec{R}_0$ following Ref. 19, are described by orbitals of the form

$$\psi^{(0)}(r;\, R_0) = K(R_0)[\phi_A(r;\, R_0) + \lambda(R_0)\phi_B(r;\, R_0)] . \tag{2.14}$$

K is the normalization factor, ϕ_A and ϕ_B are nodeless Slater-type sp^3 orbitals whose coefficients ζ for the equilibrium configuration R_0 are determined by the Slater rules, and the parameter λ is determined by the usual linear-combination-of-atomic-orbitals (LCAO) method. Extending this picture we assume that the LCAO-MO (molecular-orbital) treatment can be used for each nuclear configuration $\vec{R}$ and we regard each bond AB as an independent unit represented in its ground state by two uncorrelated electrons with opposite spin directions; each electron will be described by an orbital of the form

$$\psi^{(0)}(\vec{r}, \vec{R}) = K(\vec{R})[\phi_A(r;\, \vec{R}) + \lambda(R)\phi_B(r;\, \vec{R})] , \tag{2.15}$$

where ϕ_A and ϕ_B have the same analytical form as in (2.14) but the parameters ζ_i and λ become continuous functions of the bond distance, $\zeta_i(R)$ and $\lambda(R)$, respectively. More specifically, it will be assumed that for small changes δR of the internuclear distance one can write

$$\zeta_A(R) = \zeta_A e^{\delta R/\rho} , \tag{2.16a}$$

$$\zeta_B(R) = \zeta_A e^{\delta R/\rho} , \tag{2.16b}$$

$$\lambda(R) = \lambda e^{\delta R/\rho} , \tag{2.17}$$

where ζ_i and λ are the values of the parameters in the undistorted lattice and ρ is the range over which the undistorted electronic distribution around each atom is expected to change appreciably; for each bond ρ^{-1} can be taken $\simeq \frac{1}{2}(\zeta_A + \zeta_B)$. These mean values for the different compounds are actually very nearly equal to an average value ζ_{av} and accordingly we will put $\rho^{-1} = \zeta_{av} \simeq 1.4$ a.u. We assume, furthermore, that the properties of a bond are affected only by the stretching of that bond and are unaffected by the stretching of other bonds or changes of bond orientations.

Finally we need the form of the lattice potential $\Phi(R) \equiv E_0(R)$; this also determines the cohesive energy of the crystal. Our knowledge of this quantity for covalent crystals is poor. To be consistent with the over-all electronic picture described above, one should use the Hartree product of the $\phi_e(\vec{r}, \vec{R})$ expressed in terms of (2.15) and compute $E_0(\vec{R})$ from (2.12a). This can be done along the lines of the work of Coulson and Dogget[20] or Korol and Tolpygo.[21] Such an approach which essentially amounts to adopting a valence force field would introduce short-range directional forces[22] and long- and intermediate-range electrostatic forces. Here we shall assume that the lattice energy per unit cell (pair of ions) can be written in the simple form

$$E_0(R) = -Ae^2/R + n_0 B e^{-R/\rho} , \tag{2.18}$$

which essentially implies a central force field and consists of a long-range attractive part $\Phi_L = -Ae^2/R$ and a short-range repulsive part $\Phi_S = n_0 B e^{-R/\rho}$. Intermediate-range electrostatic forces are not explicitly included but will be assumed absorbed[23] in the two terms of (2.18); $n_0 = 4$ is the number of nearest neighbors around an atom, B measures the strength, and ρ the range of the short-range repulsive potential. This arises from the extension of the electronic distribution around the atoms and is the same quantity as in (2.16a), (2.16b), and (2.17). For the case of the III-V compounds it is determined by the ζ coefficients in (2.14); as stated previously their values range around a value ζ_{av}. Taking $\rho \simeq \zeta_{\text{av}}^{-1}$ the same for all compounds, one finds $R_0/\rho \simeq 6.5$ while for ionic crystals one has[4] $R/\rho \simeq 10$. The first term in (2.18) is a Madelung-type energy; clearly both the nuclei and the electrons contribute, but since the charge distributions as described by (2.14) are rather extended and easily polarizable the calculation of A presents a formidable task. In the present work we assume that the long-range part in (2.18) is obtained by replacing the electronic charge distribution and the nuclear charges with point charges ze and $-ze$ located at the sites A and B, respectively, so that over-all charge neutrality is ensured; then $A = \alpha_M \times (ze)^2$, where $\alpha_M = 1.628$, the Madelung constant for the zinc-blende structure. The two parameters z and B will be determined[24, 25] then by use of the experimental values of the compressibility κ together with the lattice equilibrium condition.

In order to eliminate z and B we proceed as follows. Since the lattice potential must have a minimum at the equilibrium distance, the first derivative of (2.18) must vanish or, putting $\Phi_S = n_0 \phi_S$,

$$Ae^2/R_0^2 + n_0 \phi'_S(R_0) = 0 \ . \tag{2.19}$$

The compressibility κ of the crystal is defined by

$$\frac{1}{\kappa} = v \frac{d^2\Phi}{dv^2} \tag{2.20}$$

or, since $v \sim R^3$,

$$\frac{1}{\kappa} = \tfrac{1}{9} R_0^2 \frac{4}{v}\left(\phi''_S(R_0) - \frac{1}{2}\frac{Ae^2}{R_0^3}\right)$$

$$= \tfrac{1}{9} R_0^2 \frac{4}{v}\left(\phi''(R_0) + \frac{2}{R_0}\,\phi'_S(R_0)\right) , \tag{2.21a}$$

and using the explicit form for ϕ_S one obtains

$$\frac{1}{\kappa} = \tfrac{1}{9} 4 R_0^2 \frac{1}{v}\left(\frac{1}{\rho} - \frac{2}{R_0}\right)\frac{\phi_S}{\rho} . \tag{2.21b}$$

Then (2.21b) determines B and (2.19) determines z if κ is known; the latter can be determined experimentally from the elastic constants c_{11} and c_{12} of the crystal. As stated previously noncentral forces are not explicitly considered here. These forces are essentially three-body short-range forces and their contribution to the compressibility $\kappa = 3/(c_{11} + c_{12})$ will be small since this quantity determines uniform volume changes under hydrostatic pressure; hence only bond lengths are changed under this type of deformation while the angles remain unchanged. The same can be anticipated to be the case for the quantities related to the long-wavelength optic mode, to be introduced below; these arise mainly from distortions within the primitive unit cell and the nearest-neighbor interactions will be the dominant ones while noncentral forces involve next-nearest-neighbor interactions which are expected to be by an order of magnitude weaker. However, these forces are necessary in order to partially account for the breakdown of the Cauchy relations and for the stability of the lattice against shear stresses as determined by the elastic constant c_{44} and by $c_{11} - c_{12}$ in these crystals.

Having thus defined the Born-Oppenheimer wave functions and energy states of our system, we can apply the formulas of Appendix A to obtain the expressions of the polarizabilities of a unit cell. We begin by reproducing the Huang relations which refer to the linear polarization.

III. POLARIZABILITIES AND LOCAL-FIELD CORRECTIONS

The Huang equations (2.1a) and (2.1b) and the parameters ϵ_0, ϵ_∞, Ω_0 introduced in (2.2) are macroscopic and independent of any specific assumptions concerning the nature of the electronic charge distribution in the crystal. In this section we give an interpretation of these parameters in terms of the microscopic model described above and then proceed to derive the expression of the second-order susceptibility. First we derive expressions of the microscopic polarizabilities, as defined in Appendix B, relating the dipole moment induced in a unit cell to the effective field. Then we consider the relation between effective and applied macroscopic field. Throughout the discussion we shall assume that the fields are far from any resonances so that the frequencies can be assumed either zero or infinity depending on the cases. The frequency dependence will be introduced subsequently using a semiclassical approach.

A. Microscopic Polarizabilities

In Fig. 1, we show a group of four bonds centered around a group-III atom and the crystalline axes $KXYZ$ for the undistorted lattice. In this reference frame the bonds point along the principal diagonals [111], $[1\bar{1}\bar{1}]$, $[\bar{1}1\bar{1}]$, and $[\bar{1}\bar{1}1]$. Owing to the $\bar{4}3m$ symmetry, all bonds are equivalent to each other for the perfect lattice and can be obtained from one another by successive application of the group operations. In the same figure we show a coordinate system fixed to the bond. The z axis is oriented along the bond axis towards the group-V atom and 0 is the geometric midpoint of the bond. When the atoms are displaced according to an optic mode by small displacements $\vec{u} = \vec{R} - \vec{R}_0$, the lengths of the bonds change as do the angles between the bonds distorting the tetrahedral symmetry and rendering the bonds unequivalent. We single out such a bond in the presence of an arbi-

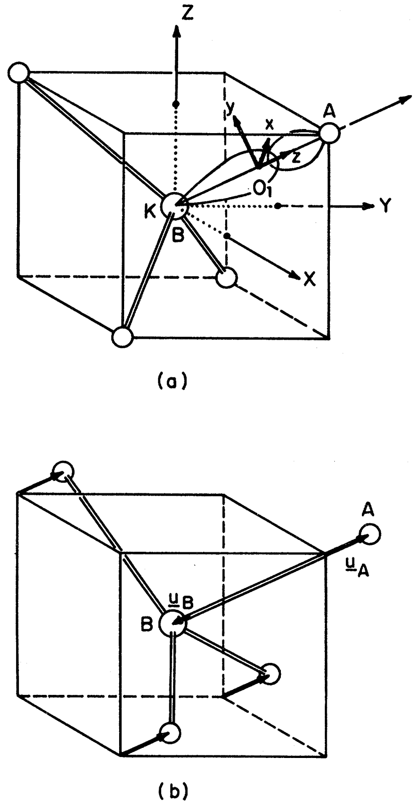

FIG. 1. (a) Four equivalent tetrahedral bonds in the unit cell; B is the III atom and A is the V atom. The crystalline axis [111] and the corresponding bond axis O_1z are pointing from the III atom to the V atom of the BA_1 bond and similarly for the other three bond directions. This convention is the one adopted by H. C. Gatos and N. C. Lavine, J. Electrochem. Soc. 107, 427 (1960) and is used throughout the text of the present work. (b) Unit cell distorted according to an optic mode of a particular polarization.

trary electric field $\vec{\mathcal{E}}$. The polarizabilities of different orders are then defined by the following expression:

$$W = W_0 - p_i \mathcal{E}_i - \tfrac{1}{2}\alpha_{ij}\mathcal{E}_i\mathcal{E}_j - \tfrac{1}{3}\beta_{ijk}\mathcal{E}_i\mathcal{E}_j\mathcal{E}_k , \qquad (3.1)$$

where W_0 is the bond ground energy; p is the permanent-bond dipole moment; α_{ij} and β_{ijk} are the first- and second-order bond-polarizability tensors. Their expressions are given by usual time-independent perturbation theory. They depend uniquely on the ground-electronic-state distribution which in the present model is represented by the wave function (2.15). Accordingly they are continuous functions of the bond distance and can be expanded in powers of the change of the internuclear distance δR which is linearly related to u.

For an arbitrary nuclear configuration $\vec{R} = \vec{R}_0 + \vec{u}$ the polarizabilities of a unit cell are given in terms of the polarizabilities of the four bonds by the expressions (B1) and (B2) of the Appendix B. In the present work, as in Ref. 8, we assume that the bonds possess axial symmetry which is preserved throughout the nuclear motion. Further, we assume that the polarizability of one bond is affected only by the stretching of that bond, and is unaffected by the stretching of other bonds or the changes of bond orientations. Expanding these quantities in powers of $\vec{u} = \vec{u}_B - \vec{u}_A$, inserting the values of the direction cosine for the undistorted lattice and writing $\alpha_{xx} = \alpha_\perp$, $\alpha_{zz} = \alpha_\parallel$, $\beta_{xyz} = \beta_\perp$, and $\beta_{zzz} = \beta_\parallel$ one obtains

$$\alpha_{ij}(\vec{R}) = \alpha^E_{ij} + \alpha^{(1)}_{ijk} u_k + \cdots ,$$

$$\beta_{ijk}(\vec{R}) = \beta^E_{ijk} + \cdots ,$$

where

$$\alpha^E_{ij} = \tfrac{4}{3}(\alpha_\parallel + 2\alpha_\perp)\delta_{ij} , \qquad (3.2)$$

$$\beta^E_{ijk} = \frac{4}{3\sqrt{3}}(\beta_\parallel - 3\beta_\perp)\epsilon_{ijk} , \qquad (3.3)$$

$$\alpha^{(1)}_{ijk} = \frac{4}{3\sqrt{3}}\left[\frac{\partial\alpha_\parallel}{\partial R} - \frac{\partial\alpha_\perp}{\partial R} - \frac{2}{R_0}(\alpha_\parallel - \alpha_\perp)\right]\epsilon_{ijk} , \qquad (3.4)$$

where δ_{ij} and ϵ_{ijk} are the Kronecker and Levi-Civita tensors, respectively.

The first two quantities are the conventional linear and second-order polarizabilities per unit cell for uniform electric fields and their expressions were derived in Ref. 8; $\alpha^{(1)}$ is the microscopic Raman polarizability tensor for a unit cell.

Following Appendix B, we define the lattice dipole moment for a unit cell by

$$\vec{\mu}(\vec{R}) = \int \phi_e(\vec{r}, \vec{R})\left(-e\textstyle\sum_i \vec{r}_i + eZ_A\vec{R}_A + eZ_B\vec{R}_B\right) \times \phi_e(\vec{r}, \vec{R})\, d\vec{r} ,$$

a function of the nuclear coordinates; i runs over the eight valence electrons per unit cell and eZ_i are positive point charges. This quantity can be written

$$\vec{\mu}(\vec{R}) = \vec{\pi}(\vec{R}) + e(Z_A - 4)\vec{R}_A + e(Z_B - 4)\vec{R}_B , \qquad (3.5)$$

where $\pi(\vec{R})$ is the permanent electronic dipole moment of a unit cell for an arbitrary internuclear configuration; its expression is given in Appendix B, Eq. (B6). The quantity (3.5) being a continuous function of $\vec{R}$ can be expanded in powers of $\vec{u} = \vec{R} - \vec{R}_0$ and one obtains

$$\vec{\mu}(\vec{R}) = \overleftrightarrow{\mu}^{(1)} \cdot \vec{u} + \tfrac{1}{2} u^{(2)} : \vec{u}\vec{u} ,$$

where the constant term is zero for the $\bar{4}3m$ point-group symmetry,

$$\overleftrightarrow{\mu}^{(1)} \cdot \vec{u} = \overleftrightarrow{\pi}^{(1)} \cdot \vec{u} + e(Z_A - 4)\vec{u}_A + e(Z_B - 4)\vec{u}_B \qquad (3.6)$$

and

$$\mu^{(2)}_{ijk} u_j u_k = \pi^{(2)}_{ijk} u_j u_k \,. \tag{3.7}$$

The expressions of $\pi^{(1)}$ and $\pi^{(2)}$ are given in Appendix B; we define the quantities Z_E and ζ_d by

$$-eZ_E/4 \equiv p_0/R_0 \tag{3.8}$$

and

$$-e\zeta_d \equiv \frac{\partial p}{\partial R} \,. \tag{3.9}$$

For an optic mode the center of gravity of the two atoms in a unit cell stays fixed, or $M_A\vec{u}_A + M_B\vec{u}_B = 0$. Then inserting the expression (B8) for $\pi^{(1)}$ in (3.5) one obtains after some rearrangement of the terms

$$\overleftrightarrow{\mu}^{(1)} \cdot \vec{u} = Q_d\vec{u} + M(Q_B/M_B - Q_A/M_A)\vec{u} \,, \tag{3.10}$$

where

$$Q_A = e(Z_A - 4 - \tfrac{2}{3} Z_E) \,, \tag{3.11}$$

$$Q_B = e(Z_B - 4 + \tfrac{2}{3} Z_E) \,, \tag{3.12}$$

$$Q_d = \tfrac{4}{3} e\zeta_d \,; \tag{3.13}$$

$\mu^{(1)}$ behaves as a scalar; we define the microscopic effective charge per unit cell e_f^* by the relation

$$\mu^{(1)} = e_f^* \tag{3.14}$$

or

$$e_f^* = Q_d + M(Q_B/M_B - Q_A/M_A) \,. \tag{3.15}$$

The quantities Q_A and Q_B refer to charges which are defined for the undistorted nuclear configuration while Q_d is a charge arising from the redistribution[26] of the electronic density by the change of the bond length.

The coefficient $\mu^{(2)}$ of the second-order dipole of a unit cell has a single independent component; inserting (B9) in (3.7) one has

$$\mu^{(2)}_{ijk} \equiv \mu^{(2)}\epsilon_{ijk} = \frac{4}{3\sqrt{3}}\left[\frac{\partial^2 p}{\partial R^2} + \frac{1}{R_0}\left(\frac{3p_0}{R_0} - \frac{\partial^2 p}{\partial R^2}\right)\right]\epsilon_{ijk} \,; \tag{3.16}$$

it is to be noted that $\mu^{(2)}$ arises only from the electronic part of the dipole moment (3.5).

Finally we need the expressions of the short-range oscillator strength $M\omega_s^2 \equiv \phi^{(2)}_{ij}$ and the coefficient $\phi^{(3)}_{ijk}$ of the third-order anharmonic potential appropriate to the oscillation of the two interpenetrating sublattices against each other. These quantities are defined by the expansion in Taylor series of the lattice potential (2.13), and their expressions are derived in Appendix B; $\phi^{(2)}$ behaves as a scalar and $\phi^{(2)}$ has a single independent component. The contribution to $\phi^{(2)}$ from the long-range part of ϕ reduces to zero by symmetry[4,25]; hence $\phi^{(2)}$ is determined solely by the short-range part of ϕ, or

$$\phi^{(2)}_{ij} = \frac{4}{3}\left(\frac{2}{R_0}\frac{\partial\phi_S}{\partial R} + \frac{\partial^2\phi_S}{\partial R^2}\right)\delta_{ij} \,; \tag{3.17}$$

only interactions with the four nearest neighbors were taken into account. Comparing (3.17) and (2.21a) one obtains

$$\omega_s^2 = \frac{3}{\kappa}\,\frac{v}{R_0^2}\,\frac{1}{M} \,. \tag{3.18}$$

The coefficient $\phi^{(3)}_{ijk}$ on the other hand contains contributions both from the long- and short-range part of (2.18). Further, atoms more distant than nearest neighbors contribute in the long-range part. The expression of $\phi^{(3)}$ is derived in Appendix B; one has

$$\phi^{(3)}_{ijk} = \frac{4}{3\sqrt{3}}\left[\frac{\partial^3\phi}{\partial R^3} + \frac{3}{R_0}\left(\frac{1}{R_0}\frac{\partial\phi}{\partial R} - \frac{\partial^2\phi}{\partial R^2}\right)\right]\epsilon_{ijk}$$
$$+ 15(ze)^2 {\sum_R}' n_R \frac{R_1R_2R_3}{R^7}\epsilon_{ijk} \,, \tag{3.19}$$

where in the term on the right-hand side the summation now is understood to extend over all atoms except the four nearest neighbors (see Appendix B). The first term contains the contribution from the four nearest neighbors while the second term contains the long-range interactions with the more distant atoms; in (3.19), $\phi = -(ze)^2/R + Be^{-R/\rho}$ and the derivatives are evaluated at $R = R_0$.

We have now derived in terms of known quantities the expressions of all the coefficients needed to determine the microscopic polarizabilities of a unit cell. Our next step is to derive the expressions of the corresponding macroscopic polarizabilities.

B. Macroscopic Transverse Polarizabilities and Local-Field Corrections

In using the localized model and trying to relate the microscopic polarizabilities to the macroscopic ones, one is faced with the problem of the field acting on the charges in a unit cell. These polarizable charges within a unit cell do not respond to the externally applied field E but rather to the effective field $\vec{\mathcal{E}}$. This is different from the macroscopic one and also contains the electric-field-induced interactions between the charges. These interactions between the more or less localized charge distributions are always present and modify mutually the wave functions and energies of the restricted Hamiltonians H_0. The origin of these interactions is in the terms neglected in attempting to reduce the complete Hamiltonian H to a sum of unit cell Hamiltonians H_0. These are long-range Coulomb and exchange forces. For well-localized and well-separated charge distributions the dipolar term in a multipole expansion of the Coulomb terms would be sufficient and the Lorentz field would apply. For uniform charge distribution on the other hand, all the higher multipoles are equally important and have to be included, reducing the field to the macroscopic one. For intermediate charge distributions these extreme cases do not apply; $\vec{\mathcal{E}}$

varies strongly over the unit cell and has a very complex functional dependency preventing any simple *a priori* calculations of this quantity. Following Ref. 8 we assume that for a cubic lattice we can write

$$\vec{\mathcal{E}}(\omega)=\vec{\mathrm{E}}(\omega)+L\vec{\mathrm{P}}(\omega)\ , \tag{3.20}$$

where L is a scalar and P is the total polarization. A second simplification is that $\vec{\mathcal{E}}$ is constant over the polarizable unit and equal to some appropriate average value. The second term on the right-hand side of (3.20) is the material component of the effective field which includes the interactions between the charges.[26] The total polarization P is the sum of all dipoles per unit volume induced by the effective field in each unit cell.

In deriving the expression of the macroscopic second-order polarizability one has to obtain the expression of the total polarization of frequency $\omega_1+\omega_2$. This is

$$\vec{\mathrm{P}}(\omega_1+\omega_2)=N\overleftrightarrow{\alpha}(\omega_1+\omega_2)\cdot[\vec{\mathrm{E}}(\omega_1+\omega_2)+L\vec{\mathrm{P}}(\omega_1+\omega_2)]$$
$$+N\underline{\beta}(\omega_1,\ \omega_2):[\vec{\mathrm{E}}(\omega_1)+L\vec{\mathrm{P}}(\omega_1)][\vec{\mathrm{E}}(\omega_2)+L\vec{\mathrm{P}}(\omega_2)]; \tag{3.21a}$$

α and β are given by the expressions (A13) and (A14), respectively. Further, we assume that the frequencies ω_1, ω_2, and $\omega_1+\omega_2$ are far from resonances.[27]

Rearranging the terms in (3.21a), taking into account that $\overleftrightarrow{\alpha}$ behaves as a scalar and keeping throughout terms up to the second order in the electric fields, one obtains

$$\vec{\mathrm{P}}(\omega_1+\omega_2)=Nf(\omega_1+\omega_2)\overleftrightarrow{\alpha}(\omega_1+\omega_2)\cdot\vec{\mathrm{E}}(\omega_1+\omega_2)$$
$$+Nf(\omega_1+\omega_2)\underline{\beta}(\omega_1,\ \omega_2)f(\omega_1)f(\omega_2):\vec{\mathrm{E}}(\omega_1)\vec{\mathrm{E}}(\omega_2)\ , \tag{3.21b}$$

where

$$f(\omega)=\frac{1}{1-LN\alpha(\omega)}\ . \tag{3.22}$$

Formally, one has

$$\vec{\mathrm{P}}(\omega_1+\omega_2)=\vec{\mathrm{P}}^{(1)}(\omega_1+\omega_2)+\vec{\mathrm{P}}^{(2)}(\omega_1+\omega_2)\ , \tag{3.23}$$

with

$$P_i^{(1)}(\omega)=\chi_{ij}^{(1)}(\omega)E_j(\omega)\equiv N\tilde{\alpha}_{ij}(\omega)E_j(\omega)$$

and[28]

$$P_i^{(2)}(\omega_1+\omega_2)=\chi_{ijk}^{(2)}(\omega_1,\ \omega_2)E_j(\omega_1)E_k(\omega_2)$$
$$\equiv N\tilde{\beta}_{ijk}(\omega_1,\ \omega_2)E_j(\omega_1)E_k(\omega_2)\ ,$$

where $\overleftrightarrow{\tilde{\alpha}}$ and $\tilde{\beta}$ are the macroscopic linear and second-order polarizabilities per unit cell. Comparing (3.23) with (3.21b) one obtains

$$\tilde{\alpha}_{ij}(\omega)=f(\omega)\,\alpha_{ij}(\omega)\ , \tag{3.24}$$

$$\underline{\tilde{\beta}}(\omega_1,\ \omega_2)=f(\omega_1+\omega_2)\,\underline{\beta}(\omega_1,\ \omega_2)f(\omega_1)f(\omega_2)\ . \tag{3.25}$$

The macroscopic quantities of interest for us are the second-order polarizabilities for transverse fields. But before deriving their expressions we shall give an interpretation of the Huang equations for the linear polarization in terms of the present model and, in particular, obtain the expressions of ϵ_∞, ϵ_0, ϵ_T^*, and Ω_T. As it was mentioned in the beginning of this section in using expressions (A13) and (A14) the frequencies will be assumed zero or infinity depending on whether they are larger or smaller than the lattice frequency ω_T, respectively.

The expression of the linear microscopic polarizability per unit cell is given in Appendix A. For a field $E(\omega)$ where ω is much higher than the lattice resonance only the first term α^E, due to the valence electrons, contributes, and the linear macroscopic polarizability $\tilde{\alpha}^E$ is

$$\tilde{\alpha}_E=f\alpha^E\ ,$$

and the linear polarization

$$\vec{\mathrm{P}}^{(1)}(\omega)=Nf\alpha^E\vec{\mathrm{E}}(\omega)\ , \tag{3.26}$$

where

$$f=\frac{1}{[1-(L/f)(\epsilon_\infty-1)/4\pi]} \tag{3.27}$$

and

$$(\epsilon_\infty-1)/4\pi=Nf\alpha^E\ . \tag{3.28}$$

For a field $E(\Omega)$ where $\Omega<\omega_T$, then both terms in (A13) contribute and the corresponding total linear macroscopic polarizability is

$$\tilde{\alpha}=f_0(e_f^*/M\omega_s^2+\alpha^E)$$

or

$$\vec{\mathrm{P}}^{(1)}(\Omega)=Nf_0(e_f^{*2}/M\omega_s^2+\alpha^E)\vec{\mathrm{E}}(\Omega)\ , \tag{3.29}$$

where

$$f_0=\frac{1}{1-NL(e_f^{*2}/M\omega_s^2+\alpha^E)}=f+NL\frac{ff_0e_f^{*2}}{M\omega_s^2}\ . \tag{3.30}$$

After some rearrangement of the terms in (3.29) one obtains

$$\vec{\mathrm{P}}^{(1)}(\Omega)=N\left(\frac{f_0fe_f^{*2}}{M\omega_s^2}+f\alpha^E\right)\vec{\mathrm{E}}(\Omega)=\frac{\epsilon_0-1}{4\pi}\vec{\mathrm{E}}(\Omega) \tag{3.31}$$

or, taking into account (3.28),

$$\frac{\epsilon_0-\epsilon_\infty}{4\pi}=N\frac{ff_0e_s^{*2}}{M\omega_s^2}=N\frac{e_T^{*2}}{M\omega_T^2}\ , \tag{3.32}$$

where

$$e_T^*=fe_f^*\ , \tag{3.33a}$$

$$\omega_T^2=(f/f_0)\omega_s^2\ . \tag{3.33b}$$

The last assignments are actually consistent with the equation of movement of the ionic displacement $\vec{u}_T$ which is written

$$M\ddot{\vec{u}}_T + M\omega_s^2\vec{u}_T = e_f^*[\vec{E}(\Omega) + L\vec{P}^{(1)}(\Omega)] \, ;$$

since

$$\vec{P}^{(1)}(\omega) = Ne_T^*\vec{u}_T + \frac{\epsilon_\infty - 1}{4\pi}\vec{E}(\omega) \, ,$$

one gets

$$M\ddot{\vec{u}}_T + M(\omega_s^2 - NL\, e_T^* e_f^*/M)\vec{u}_T = fe_f^*\vec{E}(\omega) \tag{3.34}$$

or

$$M\ddot{\vec{u}}_T + M\omega_T^2\vec{u}_T = e_T^*\vec{E}(\Omega) \, ,$$

which is identical with (2.1a) if the relations (3.33a) and (3.33b) hold. This concludes also the interpretation of the Huang relations in terms of the parameters of our microscopic picture of a III–V compound. As it can be seen from (3.34), ω_T^2 is determined by the competition of the short- and long-range polarization forces. The latter are expressed in terms of the effective field factor f. Lacking any other evidence about the actual value of this quantity in the III–V compounds we determine f as in Ref. 8 by requiring that the value of ϵ_∞ as calculated from (3.28) be equal to its experimental value.

We proceed now to derive the expression of β for the different frequency regions with respect to ω_T.

(a) When ω_1, ω_2, and $\omega_1 + \omega_2$ are in the transparency region above ω_T then $f(\omega_i) = f$ and from (B14), $\beta = \beta^E$; the second-order macroscopic polarizability $\tilde{\beta}_E$ is

$$\tilde{\beta}_E = f^3\beta_E$$

and the corresponding susceptibility

$$\chi_E^{(2)} = Nf^2\beta^E \, , \tag{3.35}$$

which is the expression obtained in Ref. 8. This quantity describes the second-harmonic generation and the frequency mixing in the transparency region of the crystal.

(b) When ω_1, $\omega_1 + \omega_2 > \omega_T > \omega_2$ then from (A14), $\beta = \beta^E + e_f^*\alpha^{(1)}/2M\omega_s^2$, and denoting by β_{EO} the corresponding macroscopic polarizability one has from (3.25)

$$\tilde{\beta}_{EO} = f\left(\beta^E + \frac{1}{2}\frac{e_f^*}{M\omega_s^2}\alpha^{(1)}\right)ff_0$$

or, after some rearrangement of the terms in the last expression and use of (3.30), one gets

$$\tilde{\beta}_{EO} = \tilde{\beta}_E + \tfrac{1}{2}\tilde{\alpha}^{(1)} e_T^*/M\omega_T^2 \, , \tag{3.36}$$

where

$$\tilde{\alpha}^{(1)} = f^2(\alpha^{(1)} + 2NL\, e_T^*\beta^E) \tag{3.37}$$

is the macroscopic Raman polarizability tensor[29] of a unit cell for transverse phonons. The question arises whether this tensor is actually the same as the one conventionally defined[30] through the third-order susceptibility $\chi^{(3)}$. This is indeed the case and it is shown in Appendix C.

The susceptibility corresponding to (3.36) is actually the coefficient which describes[31] the linear electro-optic effect (EO) and will be denoted by $\chi_{EO}^{(2)}$,

$$\chi_{EO}^{(2)} = N(\tilde{\beta}_E + \tfrac{1}{2}\tilde{\alpha}^{(1)} e_T^*/M\omega_T^2) \, . \tag{3.38}$$

It is convenient to write $\chi_{EO}^{(2)}$ in the form

$$\chi_{EO}^{(2)} = \chi_E^{(2)}(1 + C_1) \, , \tag{3.39}$$

where

$$C_1 = \tilde{\alpha}^{(1)} e_T^*/2\tilde{\beta}_E M\omega_T^2 \tag{3.40}$$

measures the ratio of the lattice-induced contribution over the purely electronic contribution in $\chi_{EO}^{(2)}$.

The relation between this coefficient and the conventional electro-optic coefficient r_{ijk} which measures[31] the change of the dielectric constant ϵ_∞ caused by a static electric field is

$$r = -(4\pi/\epsilon_\infty^2)\chi_{EO}^{(2)} \, .$$

Similarly, one can treat the case where ω_1, $-\omega_2 > \omega_T$, but $\omega_1 + \omega_2 < \omega_T$; denoting by $\tilde{\beta}_{OR}$ the corresponding polarizability one has from (B14) and (3.25)

$$\tilde{\beta}_{OR} = f_0\left(\beta^E + \frac{1}{2}\frac{e_f^*}{M\omega_s^2}\alpha^{(1)}\right)ff = \tilde{\beta}_E + \tfrac{1}{2}\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} \, , \tag{3.41}$$

which is identical to (3.36). This coefficient is closely related to the optical rectification (OR) coefficient $\chi^{(2)}$ which indeed is equal to $\chi_{EO}^{(2)}$ as can be expected by the generalized symmetry relations[1] of $\chi_{ijk}^{(2)}(\omega_1, \omega_2)$.

(c) Consider now the case ω_1, $\omega_2 < \omega_T < \omega_1 + \omega_2$; then from (B14) and (3.25)

$$\tilde{\beta}_M = f\left(\beta^E + \frac{1}{2}\frac{e_f^*}{M\omega_s^2}\alpha^{(1)} + \frac{1}{2}\frac{e_f^*}{M\omega_s^2}\alpha^{(1)} + \tfrac{1}{2}\mu^{(2)}\frac{e_f^*}{M\omega_s^2}\frac{e_f^*}{M\omega_s^2}\right)f_0 f_0 \tag{3.42a}$$

or

$$\tilde{\beta}_{M'} = \tilde{\beta}_E + \tfrac{1}{2}\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\tilde{\mu}^{(2)}\frac{e_T^*}{M\omega_T^2}\frac{e_T^*}{M\omega_T^2} \, ,$$

where

$$\tilde{\mu}^{(2)} = [\mu^{(2)} + NLe_T^*\alpha^{(1)} + NLe_T^*(2\beta^E NLe_T^* + \alpha^{(1)})]f \tag{3.43}$$

is the macroscopic coefficient of the lattice second-order dipole moment.

(d) Finally, we consider the case of ω_1, ω_2, $\omega_1 + \omega_2 < \omega_T$. One obtains from (3.25) and (B13) after some reshuffling of the terms

$$\tilde{\beta}_{M''} = \tilde{\beta}_E + \tfrac{1}{2}\,\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\,\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\,\tilde{\alpha}^{(1)}\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\,\tilde{\mu}^{(2)}\frac{e_T^*}{M\omega_T^2}\,\frac{e_T^*}{M\omega_T^2}$$
$$+\tfrac{1}{2}\,\tilde{\mu}^{(2)}\frac{e_T^*}{M\omega_T^2}\,\frac{e_T^*}{M\omega_T^2} + \tfrac{1}{2}\,\tilde{\mu}^{(2)}\frac{e_T^*}{M\omega_T^2}\,\frac{e_T^*}{M\omega_T^2} - \tfrac{1}{2}\,\tilde{\phi}^{(3)}\frac{e_T^*}{M\omega_T^2}\,\frac{e_T^*}{M\omega_T^2}\,\frac{e_T^*}{M\omega_T^2}, \quad (3.42\text{b})$$

where

$$\tilde{\phi}^{(3)} = \{\phi^{(3)} - NLe_T^*\,\mu^{(2)} - NLe_T^*(\mu^{(2)} + NLe_T^*\alpha^{(1)}) - NLe_T^*[\mu^{(2)} + NLe_T^*\alpha^{(1)} + NLe_T^*(\alpha^{(1)} + 2NLe_T^*\beta^E)]\}\,. \quad (3.44)$$

In analogy with (3.40) it is convenient to introduce also the quantities

$$C_2 = \frac{1}{2}\,\frac{\tilde{\mu}^{(2)}}{\tilde{\beta}_E}\left(\frac{e_T^*}{M\omega_T^2}\right)^2, \quad (3.45\text{a})$$

$$C_3 = -\frac{1}{2}\,\frac{\tilde{\phi}^{(3)}}{\tilde{\beta}_E}\left(\frac{e_T^*}{M\omega_T^2}\right)^3. \quad (3.45\text{b})$$

The susceptibilities corresponding to (3.42a) and (3.42b) can then be written

$$\chi_{M'}^{(2)} = \chi_E^{(2)}(1 + 2C_1 + C_2)\,, \quad (3.46\text{a})$$

$$\chi_{M''}^{(2)} = \chi_E^{(2)}(1 + 3C_1 + 3C_2 + C_3)\,, \quad (3.46\text{b})$$

respectively. These two coefficients describe two different cases of frequency mixing in the infrared. However, due to the finite linewidth of the phonons it is experimentally difficult to measure the first one.

This concludes the derivation of the expression of the macroscopic second-order polarizability in the different regions of the infrared spectrum of the crystal.

The expressions for $\chi^{(2)}$ derived above are only valid for frequencies ω_1, ω_2, and $\omega_1 + \omega_2$ not in the neighborhood of ω_T. The actual frequency-dependent expression of $\chi^{(2)}(\omega_1, \omega_2)$ can be obtained most conveniently using the semiclassical approach outlined in Appendix D. Introducing also phonon damping one obtains

$$\chi^{(2)}(\omega_1, \omega_2) = \chi_E^{(2)} + \chi_{H'}^{(2)}(\omega_1, \omega_2) + \chi_{H''}^{(2)}(\omega_1, \omega_2) + \chi_N^{(2)}(\omega_1, \omega_2)\,, \quad (3.47)$$

where the different terms are

$$\chi_{H'}^{(2)}(\omega_1, \omega_2) = C_1\left(\frac{1}{D(\omega_1)} + \frac{1}{D(\omega_2)} + \frac{1}{D(\omega_1 + \omega_2)}\right)\chi_E^{(2)}\,, \quad (3.48\text{a})$$

$$\chi_{H''}^{(2)}(\omega_1, \omega_2) = C_2\left(\frac{1}{D(\omega_1)D(\omega_2)} + \frac{1}{D(\omega_1 + \omega_2)D(\omega_1)} + \frac{1}{D(\omega_1 + \omega_2)D(\omega_2)}\right)\chi_E^{(2)}\,, \quad (3.48\text{b})$$

$$\chi_N^{(2)}(\omega_1, \omega_2) = C_3\,\frac{1}{D(\omega_1)D(\omega_2)D(\omega_1 + \omega_2)}\,\chi_E^{(2)}\,, \quad (3.48\text{c})$$

with

$$D(\omega_i) = 1 - (\omega_i/\omega_T)^2 - i\omega_i\Gamma/\omega_T^2\,,$$

and Γ is a phenomenological phonon relaxation time. For frequencies far from ω_T it is easily verified that this expression of $\chi^{(2)}$ reduces to the different frequency-independent expressions derived previously.

The two mechanisms that are responsible for the contributions (3.48b) and (3.48c) in $\chi^{(2)}$, namely, the phonon interaction through the second-order lattice dipole moment and through the anharmonic potential, respectively, also determine the phonon relaxation time $\tau = \Gamma^{-1}$ and the energy loss per unity time $\omega\epsilon''(\omega)$ in the infrared in these crystals. The infrared spectra of these crystals besides the broad main absorption peak at the fundamental frequency ω_T also show somewhat weaker two-phonon absorption peaks corresponding to the different combination frequencies at the critical points of the optic and acoustic modes. The broadening of the main peak, as measured by Γ, is caused[32] by the $\phi^{(3)}$ mechanism but the origin of the two-phonon sidebands, below and above ω_T, is due to both the $\mu^{(2)}$ and the $\phi^{(3)}$ mechanism and the total energy loss is most conveniently expressed[33] in terms of $\omega\epsilon''(\omega)$, where $\epsilon''(\omega)$ is the imaginary part of the linear dielectric constant. The two pertinent quantities Γ and $\omega\epsilon''(\omega)$ are actually frequency and temperature dependent and formal expressions for the case of cubic crystals have been derived by different authors[32-35] with different assumptions. The most detailed analysis is the one presented by Szigeti.[33] This author uses perturbation theory to derive the expression for $\omega\epsilon''(\omega)$. The final expression contains thermal averages and summations over the whole Brillouin zone and over all phonon branches. His treatment is in principle only valid for frequencies not in the immediate neighborhood of ω_T. Further, the theory has to be reconsidered[36] for the covalent crystals like the III–V compounds studied here. However, for a qualitative discussion we reproduce here the expression of $\omega\epsilon''(\omega)$ derived in Ref. 33. In the high-temperature limit, above the Debye temperature, one has[33]

$$\omega\epsilon''(\omega)\,d\omega = \frac{\pi^2 kT}{36v}\sum_{\tau,\tau'}\left\{3\tilde{\mu}^{(2)} - \frac{e_T^*\tilde{\phi}^{(3)}}{M(\omega_T^2 - \omega^2)}\right\}^2 \times\left(\frac{\omega}{M\omega_\tau\omega_{\tau'}}\right)^2, \quad (3.49)$$

where the summation goes over all the pairs of the phonon branches, τ and τ' in the $\vec{k}$ space such that $\omega_\tau + \omega_{\tau'}$ or $\omega_\tau - \omega_{\tau'}$ lie in the interval $(\omega, \omega + d\omega)$; T stands for the transverse-optic mode at $k \simeq 0$ while $\tilde{\mu}^{(2)}$ and $\tilde{\phi}^{(3)}$ are the appropriate second-order dipole moment and anharmonic potential coefficients, respectively.

Taking into account (3.45a) and (3.45b) the quantity inside the curly brackets in (3.49) is essentially $\sim 3C_2 + C_3$ which as it can be seen from (3.48a) and (3.48b) also determines $\chi_H^{(2)\prime\prime} + \chi_N^{(2)}$. Hence the knowledge of the latter quantity will allow one to determine which mechanism is the dominant one in (3.49). In particular, it is easy to see from (3.48a), (3.48b), and (3.49) that both $\chi_H^{(2)\prime\prime} + \chi_N^{(2)}$ and $\omega\epsilon''(\omega)$ will vanish for a frequency either above or below ω_T depending upon whether $\phi^{(3)} e_T^* / M\omega_T^2 \mu^{(2)} < 0$ or > 0, respectively. However, there is a fundamental difference between the two quantities in that while in (3.48a) and (3.48b) strictly long-wavelength infrared-active modes come into play this is not the case for the quantity $\omega\epsilon''(\omega)$ where phonons in different branches (optic and acoustic) and points of the Brillouin zone contribute the only restrictions being the wave-vector and energy-conservation and the crystal-symmetry requirements. In fact the occurrence of the critical points is crucial in the case of $\omega\epsilon''(\omega)$ and accounts for the familiar substructure of the infrared-absorption profile while these critical points are irrelevant in $\chi^{(2)}$. From (3.49) one can also obtain the integrated infrared absorption coefficient

$$\alpha_{\mathrm{ir}} = \frac{2}{\pi} \int \frac{\epsilon''(\omega)}{\omega}\, d\omega \;, \qquad (3.50)$$

a dimensionless quantity.

Because of the presence of the resonant term $(\omega_T^2 - \omega^2)^{-1}$ in (3.49), the anharmonic potential is the dominant mechanism near ω_T and determines the broadening of the main peak at ω_T. Here we shall only give a rough estimate of the broadening parameter Γ using Mitskevich's expression.[35] There it is shown that the complex dielectric constant of a cubic crystal has the following form:

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = \epsilon_\infty(T) + \frac{\epsilon_0(T) - \epsilon_\infty(T)}{\Omega_\omega^2 - \Omega_0^2 + i\omega\Gamma(\omega)}\, \Omega_0^2 \;,$$

where $\Omega_0 \simeq \omega_T$, $\Omega_\omega = \omega_T + \Delta(\omega)$, and $\Delta(\omega)$ is a frequency-independent shift, and

$$\omega_T \Gamma = \frac{\pi k T}{M} \left(\frac{\tilde{\phi}^{(3)}}{M\omega_T^2} \right)^2 \theta_3(\omega) \;,$$

where $\theta_3(\omega)$ is a dimensionless frequency-dependent form factor which contains summations over the k space and over the phonon branches. Replacing the different quantities in $\theta_3(\omega)$ by averages over the Brillouin zone, for the case of the zinc-blende structure one obtains the following expression for ω_T:

$$\omega_T \Gamma = \frac{\pi k T}{M} \left(\frac{\tilde{\phi}^{(3)}}{M\omega_T^2} \right)^2 \theta \;, \qquad (3.51)$$

where θ is a quantity of the order of unity.

In view of the uncertainties concerning the actual temperature and frequency dependence of the different quantities the numerical use of (3.51) is bound to be only an order-of-magnitude estimation of Γ. A detailed study of phonon relaxation in covalent crystals will be given elsewhere.[36]

C. Macroscopic Longitudinal Polarizabilities

The previously derived expressions for $\tilde{\beta}$ actually refer to transverse polarization. One can analogously define the corresponding quantities referring to the longitudinal polarization. We shall discuss explicitly only two cases, but before doing so for the nonlinear polarization we consider the linear longitudinal polarization and derive the expressions of the corresponding linear macroscopic polarizabilities. The microscopic polarizabilities previously defined are actually independent on whether the fields are longitudinal or transverse; the macroscopic polarizabilities, on the other hand, have different expressions for the two polarizations.[13,16,30] This is due to the macroscopic field $-4\pi P_L$ that is present when the polarization is longitudinal, while it is absent when the polarization is transverse. The derivation of the expression of the longitudinal polarization will proceed as in the case of the transverse polarization with the additional inclusion of the macroscopic field $-4\pi P_L$. We shall consider only the case where all fields are longitudinal and the corresponding quantities will be distinguished with the subscript L.

Following the pattern of Sec. III B, the total longitudinal polarization at the frequency $\omega_1 + \omega_2$ is the sum of all unit-cell dipoles induced in a unit volume or

$$\begin{aligned} \vec{\mathrm{P}}_L(\omega_1+\omega_2) = N \overleftrightarrow{\alpha}(\omega_1+\omega_2)\cdot[\vec{\mathrm{E}}(\omega_1+\omega_2) + L\vec{\mathrm{P}}_L(\omega_1+\omega_2) \\ - 4\pi\vec{\mathrm{P}}_L(\omega_1+\omega_2)] + N\underline{\beta}(\omega_1, \omega_2) : [\vec{\mathrm{E}}(\omega_1) + L\vec{\mathrm{P}}_L(\omega_1) \\ - 4\pi\vec{\mathrm{P}}_L(\omega_1)][\vec{\mathrm{E}}(\omega_2) + L\vec{\mathrm{P}}_L(\omega_2) - 4\pi\vec{\mathrm{P}}_L(\omega_2)] \,. \end{aligned}$$

After rearranging the terms one obtains

$$\begin{aligned} \vec{\mathrm{P}}_L(\omega_1+\omega_2) = N \frac{f(\omega_1+\omega_2)}{\epsilon(\omega_1+\omega_2)} \overleftrightarrow{\alpha}(\omega_1+\omega_2)\cdot\vec{\mathrm{E}}(\omega_1+\omega_2) \\ + N \frac{f(\omega_1+\omega_2)}{\epsilon(\omega_1+\omega_2)} \underline{\beta}(\omega_1, \omega_2) \frac{f(\omega_1)}{\epsilon(\omega_2)} : \vec{\mathrm{E}}(\omega_1)\vec{\mathrm{E}}(\omega_2), \end{aligned} \qquad (3.52)$$

where $f(\omega_i)/\epsilon(\omega_i)$ is either f/ϵ_∞ or f_0/ϵ_0 depending on whether $\omega_i > \omega_T$ or $\omega_i < \omega_T$, respectively. Formally one has

$$\vec{\mathrm{P}}_L(\omega_1+\omega_2) = \vec{\mathrm{P}}_L^{(1)}(\omega_1+\omega_2) + \vec{\mathrm{P}}_L^{(2)}(\omega_1+\omega_2) \;, \qquad (3.53)$$

where

$$P^{(1)}_{i,L}(\omega)=N\tilde{\alpha}_{ij,L}(\omega)E_j(\omega)\ , \tag{3.54}$$

$$\vec{\mathrm{P}}^{(2)}_L(\omega_1+\omega_2)=N\underline{\tilde{\beta}}_L(\omega_1+\omega_2):\vec{\mathrm{E}}(\omega_1)\vec{\mathrm{E}}(\omega_2), \tag{3.55}$$

where $\tilde{\alpha}_L$ and $\tilde{\beta}_L$ are the linear and second-order macroscopic longitudinal polarizabilities, respectively. Comparing (3.53) with (3.52), one has

$$\tilde{\alpha}_{ij,L}(\omega)=[f(\omega)/\epsilon(\omega)]\alpha_{ij}(\omega)\ , \tag{3.56}$$

$$\underline{\tilde{\beta}}_L(\omega_1,\ \omega_2)=\frac{f(\omega_1+\omega_2)}{\epsilon(\omega_1+\omega_2)}\underline{\beta}(\omega_1,\ \omega_2)\frac{f(\omega_1)}{\epsilon(\omega_1)}\frac{f(\omega_2)}{\epsilon(\omega_2)}\ . \tag{3.57}$$

We consider first the linear polarizability. For ω well above ω_L, $\alpha(\omega)=\alpha^E$ and consequently

$$\tilde{\alpha}_L=(f/\epsilon_\infty)\alpha^E\equiv\tilde{\alpha}_{E,L}. \tag{3.58}$$

For $\omega_i<\omega_L$, $\alpha(\omega)=\alpha^E+\alpha^N$ and

$$\tilde{\alpha}_L=e^{*2}_L/M\omega^2_L+\tilde{\alpha}_{E,L}, \tag{3.59}$$

where $e^*_L=e^*_T/\epsilon_\infty$ and $\omega^2_L=(\epsilon_0/\epsilon_\infty)\omega^2_T$; the last relation is the Lyddane-Sachs-Teller relation[17] for the linear case.

The expressions (3.58) and (3.59) are the longitudinal counterpart to (3.21) and (3.26), respectively. In a similar way one derives the second-order longitudinal polarizabilities corresponding to the different cases of transverse polarization (3.32), (3.34), etc. Here we consider explicitly only the two cases that correspond to (3.32) and (3.34), respectively; for the other two we only give the results.

(a) In the first case where only the electrons contribute one has

$$\tilde{\beta}_L\equiv\tilde{\beta}_{E,L}=(1/\epsilon_\infty)^3\beta^E\ , \tag{3.60}$$

which defines formally the second-order longitudinal electronic polarizability $\tilde{\beta}_{E,L}$.

(b) Similarly for the second case where $\beta=\beta^E+\frac{1}{2}(e^*_f/M\omega^2_s)\alpha^{(1)}$ one has from (3.57)

$$\tilde{\beta}_L\equiv\tilde{\beta}_{\mathrm{EO},L}=\frac{f}{\epsilon_\infty}\left(\frac{f_0}{\epsilon_0}\frac{f}{\epsilon_\infty}\beta^E+\frac{1}{2}\frac{e^*_L}{M\omega^2_L}\alpha^{(1)}\frac{f}{\epsilon_\infty}\right)\ ,$$

or since

$$\frac{f_0}{\epsilon_0}=\frac{f}{\epsilon_\infty}+4\pi N\left(\frac{L}{4\pi}-1\right)\frac{e^{*2}_L}{M\omega^2_L}\ ,$$

$$\tilde{\beta}_{\mathrm{EO},L}=\left[\left(\frac{1}{\epsilon_\infty}\right)^3\tilde{\beta}_E+4\pi N\left(\frac{f}{\epsilon_\infty}\right)^2\left(\frac{L}{4\pi}-1\right)\frac{e^{*2}_L}{M\omega^2_L}\beta^E+\frac{1}{2}\left(\frac{f}{\epsilon_\infty}\right)^2\frac{e^*_L}{M\omega^2_L}\alpha^{(1)}\right]\ ,$$

and using (3.27) one obtains finally

$$\tilde{\beta}_{\mathrm{EO},L}=\left(\frac{1}{\epsilon_\infty}\tilde{\beta}_E+\frac{1}{2}\frac{e^*_L}{M\omega^2_L}\tilde{\alpha}^{(1)}_L\right)\left(\frac{1}{\epsilon_\infty}\right)^2, \tag{3.61}$$

which, in analogy to (3.36), defines the macroscopic Raman tensor coefficient for longitudinal phonons

$$\tilde{\alpha}^{(1)}_L=\tilde{\alpha}^{(1)}\left(1-\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\frac{1}{C_1}\right), \tag{3.62}$$

and C_1 is the quantity defined by (3.38). Expression (3.61) simplifies further and can be written

$$\tilde{\beta}_{\mathrm{EO},L}=(1/\epsilon_0\,\epsilon^2_\infty)\,\tilde{\beta}_E(1+C_1)=(1/\epsilon_0\epsilon^2_\infty)\,\tilde{\beta}_{\mathrm{EO}}\ . \tag{3.63}$$

(c) For the third case, the one corresponding to (3.42a), one obtains

$$\tilde{\beta}_{M',L}=\frac{1}{\epsilon_\infty}\left(\frac{1}{\epsilon^2_\infty}\tilde{\beta}_E+\frac{1}{2}\frac{\tilde{\alpha}^{(1)}_L}{\epsilon_\infty}\frac{e^*_L}{M\omega^2_L}+\frac{1}{2}\frac{\tilde{\alpha}^{(1)}_L}{\epsilon_\infty}\frac{e^*_L}{M\omega^2_L}+\frac{1}{2}\tilde{\mu}^{(2)}_L\frac{e^*_L}{M\omega^2_L}\frac{e^*_L}{M\omega^2_L}\right)\ , \tag{3.64a}$$

where

$$\tilde{\mu}^{(2)}_L=\tilde{\mu}^{(2)}\left[1-2\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\frac{C_1}{C_2}+\left(\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\right)^2\frac{1}{C_2}\right]\ . \tag{3.65}$$

Expression (3.64a) also simplifies to

$$\tilde{\beta}_{M',L}=(1/\epsilon_\infty\epsilon^2_0)\,\tilde{\beta}_E(1+2C_1+C_2)\equiv(1/\epsilon_\infty\epsilon^2_0)\beta_{M'}\ . \tag{3.66}$$

(d) Finally for the fourth case, one has

$$\begin{aligned}\tilde{\beta}_{M'',L}&\\=\Bigg(&\frac{1}{\epsilon^3_\infty}\tilde{\beta}_E+\frac{1}{2}\frac{\alpha^{(1)}_L}{\epsilon^2_\infty}\frac{e^*_L}{M\omega^2_L}+\frac{1}{2}\frac{\alpha^{(1)}_L}{\epsilon^2_\infty}\frac{e^*_L}{M\omega^2_L}+\frac{1}{2}\frac{\alpha^{(1)}_L}{\epsilon^2_\infty}\frac{e^*_L}{M\omega^2_L}\\&+\frac{1}{2}\frac{\tilde{\mu}^{(2)}_L}{\epsilon_\infty}\frac{e^*_L}{M\omega^2_L}\frac{e_L{}^*}{M\omega^2_L}+\frac{1}{2}\frac{\tilde{\mu}^{(2)}_L}{\epsilon_\infty}\frac{e^*_L}{M\omega^2_L}\frac{e^*_L}{M\omega^2_L}\\&+\frac{1}{2}\frac{\tilde{\mu}^{(2)}_L}{\epsilon_\infty}\frac{e^*_L}{M\omega^2_L}\frac{e^*_L}{M\omega^2_L}-\frac{1}{2}\tilde{\phi}^{(3)}_L\frac{e^*_L}{M\omega^2_L}\frac{e^*_L}{M\omega^2_L}\frac{e^*_L}{M\omega^2_L}\Bigg),\end{aligned} \tag{3.64b}$$

where

$$\tilde{\phi}^{(3)}_L=\tilde{\phi}^{(3)}\left[1-3\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\frac{C_2}{C_3}+3\left(\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\right)^2\frac{C_1}{C_3}-\left(\frac{\epsilon_0-\epsilon_\infty}{\epsilon_\infty}\right)^3\frac{1}{C_3}\right]\ . \tag{3.67}$$

Expression (3.64b) can also be written

$$\tilde{\beta}_{M'',L}=(1/\epsilon^3_0)\,\tilde{\beta}_E(1+3C_1+3C_2+C_3)\equiv(1/\epsilon^3_0)\tilde{\beta}_{M''}\ . \tag{3.68}$$

In general as it can be inferred from the previous derivations of (3.60), (3.63), (3.66), and (3.68) the relations between the longitudinal and transverse polarizabilities can be simply expressed in terms of purely macroscopic coefficients.

Expressions (3.62), (3.65), (3.67), and similar ones are the generalizations of (2.05) and (2.07) and can be considered as the Lyddane-Sachs-Teller relations for the nonlinear case. Here they are derived for the long-wavelength region ($\vec{k}\simeq0$); their generalization for $\vec{k}\neq0$ is given in Ref. 36. These relations determine the relative intensities of the different two-phonon sidebands in the infrared absorption spectra in these crystals as described by (3.49).

In the case of the nonlinear polarization one can also have mixed transverse-longitudinal second-order polarizabilities. Their expressions which will not be given here can be easily derived along the lines of the procedure already followed to derive the expressions or the purely longitudinal polarizabilities. Their relationship to the latter quantities and the transverse ones can be expressed in terms of purely macroscopic quantities.

One can also derive the frequency behavior of these longitudinal and longitudinal-transverse second-order susceptibilities. The equation-of-motion approach (see Appendix D) used previously to derive the frequency behavior of the transverse susceptibilities [expressions (3.47) and (3.48a)–(3.48c)] can be extended to apply for longitudinal fields as well. One only needs to introduce the additional electric field $-4\pi\vec{P}_L$ and replace $\vec{E}$ by $\vec{E}-4\pi\vec{P}_L$ whenever necessary; otherwise the method is the same as for the case of transverse fields. The expressions will not be reproduced. In analogy to (3.47) all these susceptibilities can be written in the form

$$\chi^{(2)}_{pp'p''}(\omega_1,\omega_2)=\chi^{(2)}_{pp'p'',E}+\chi^{(2)}_{pp'p'',H'}(\omega_1,\omega_2)+\chi^{(2)}_{pp'p'',H''}(\omega_1,\omega_2)+\chi^{(2)}_{pp'p'',N}(\omega_1,\omega_2)\,,$$

where p, p', and p'' stand for T or L and the different $\chi^{(2)}_{pp'p'',i}$ are given by expressions of the form (3.48a)–(3.48c) with the transverse quantities replaced by the appropriate ones whenever necessary. In particular the purely transverse and longitudinal susceptibilities previously considered are recovered simply by taking $p=p'=p''=T$ and $p=p'=p''=L$, respectively. Here we stress only the fact that the purely longitudinal susceptibilities thus obtained will disperse with the frequency ω_L instead of ω_T [compare (D4) with (D5)]; the mixed transverse-longitudinal ones, on the other hand, will show both types of frequency behavior.

The complete class of the purely transverse, purely longitudinal, and mixed transverse-longitudinal second-order susceptibilities considered here are the limiting values on the different branches of the polariton curve of a generalized second-order susceptibility where time retardation is explicitly taken into account. In the present work these limiting expressions were obtained by the explicit introduction of the additional field $-4\pi P_L$ for the longitudinal fields which is a consequence of Maxwell's equations.[4] Clearly an alternative and more complete approach is to simultaneously consider the Maxwell equations and the equation of motion of the phonon mode with nonlinear terms explicitly included.

For very low frequencies a further complication occurs, namely, the different macroscopic polarizabilities are shape dependent. Although this also can be treated straightforwardly, as in the linear case, we do not give further attention to this problem. A very careful discussion of this question for the linear case can be found in Szigeti's paper.[13]

IV. CALCULATION AND RESULTS

In this section we present the numerical calculation of the susceptibilities in terms of the primary quantities of the system, namely, the coefficients α^E, β^E, $\alpha^{(1)}$, $\mu^{(1)}$, $\mu^{(2)}$, ω_s, and $\phi^{(3)}$. The calculation of α^E and β^E in terms of the corresponding bond polarizabilities $\alpha_{\parallel}$, $\beta_{\perp}$, and $\beta_{\parallel}$, $\beta_{\perp}$, respectively, was extensively discussed in Ref. 8. There, using the variational perturbation technique as proposed by Dalgarno and Lewis[37] and by Schwartz,[37] it was shown that the linear and second-order bond polarizabilities are given by

$$\alpha_{\parallel}=4e\frac{\partial}{\partial\mathcal{E}_{\parallel}}\langle\psi^{(0)}|\bar{z}F|\psi^{(0)}\rangle\,,\tag{4.1a}$$

$$\alpha_{\perp}=4e\frac{\partial}{\partial\mathcal{E}_{\perp}}\langle\psi^{(0)}|xF|\psi^{(0)}\rangle\,,\tag{4.1b}$$

$$\beta_{\parallel}=3e\frac{\partial^2}{\partial\mathcal{E}^2_{\parallel}}\langle\psi^{(0)}|F\bar{z}F|\psi^{(0)}\rangle\,,\tag{4.2a}$$

$$\beta_{\perp}=2e\frac{\partial^2}{\partial\mathcal{E}_{\parallel}\,\partial\mathcal{E}_{\perp}}\langle\psi^{(0)}|FxF|\psi^{(0)}\rangle+e\frac{\partial^2}{\partial\mathcal{E}^2_{\perp}}\langle\psi^{(0)}|F\bar{z}F|\psi^{(0)}\rangle\,.\tag{4.2b}$$

Here account was taken of the fact that there are two electrons per bond; $\bar{z}=z-\langle\psi^{(0)}|z|\psi^{(0)}\rangle$ and F satisfies the differential equation

$$\nabla[\rho(\vec{r})\nabla F]=(2m/\hbar^2)(H'-\langle\psi^{(0)}|H'|\psi^{(0)}\rangle)\rho(r)\,,\tag{4.3}$$

or, equivalently, it minimizes the functional

$$J(\bar{F})=\langle\psi^{(0)}|2\bar{F}(H'-\langle\psi^{(0)}|H|\psi^{(0)}\rangle-(\hbar^2/2m)\nabla F\nabla F|\psi^{(0)}\rangle\,,\tag{4.4}$$

where $H'=-ex\mathcal{E}_{\perp}-ez\mathcal{E}_{\parallel}$ and $(\mathcal{E}_{\perp},0,\mathcal{E}_{\parallel})$ is the uniform electric field $\mathcal{E}$ expressed in the bond coordinate system; $\rho(r)=\psi^{(0)}(\vec{r})\psi^{(0)}(\vec{r})$ is the ground-state electronic density.

The crucial point of this technique is that it shows that the bond polarizabilities are uniquely determined by the electronic ground-state density distribution. In Ref. 8, the values of the bond polarizabilities were obtained only for the equilibrium internuclear distance R_0. This same technique, however, can be used to calculate the polarizabilities for different internuclear distances R and obtain $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ as functions of R. For small changes δR of R around the equilibrium value R_0 one can then develop $\alpha(R)$ in powers of $\delta R = R - R_0$, and obtain

$$\alpha_{\parallel}(R) = \alpha_{\perp} + \frac{\partial \alpha_{\parallel}}{\partial R}\, \delta R + \cdots ,$$

$$\alpha_{\perp}(R) = \alpha_{\perp} + \frac{\partial \alpha_{\perp}}{\partial R}\, \delta R + \cdots ,$$

or using the explicit expression of $\alpha(R)$,

$$\frac{\partial \alpha_{\parallel}}{\partial R} = 4e \frac{\partial}{\partial R} \frac{\partial}{\partial \mathcal{E}_{\parallel}} \langle \psi^{(0)}(R) | \bar{z} F | \psi^{(0)}(R) \rangle , \qquad (4.5a)$$

$$\frac{\partial \alpha_{\perp}}{\partial R} = 4e \frac{\partial}{\partial R} \frac{\partial}{\partial \mathcal{E}_{\perp}} \langle \psi^{(0)}(R) | x F | \psi^{(0)}(R) \rangle , \qquad (4.5b)$$

where $\psi^{(0)}(R)$ is the bond wave function for an internuclear distance R. The microscopic Raman tensor $\alpha^{(1)}$ is then calculated from (3.4).

Similarly, the electronic bond dipole moment for an internuclear distance R, defined by

$$p(R) = 2e \langle \psi^{(0)}(R) | z | \psi^{(0)}(R) \rangle , \qquad (4.6)$$

can be calculated for different R and then its derivatives can be obtained from a Taylor expansion

$$p(R) = p_0 + \frac{\partial p}{\partial R}\, \delta R + \frac{1}{2} \frac{\partial^2 p}{\partial R^2} (\delta R)^2 + \cdots .$$

From the values of these derivatives of p the unit-cell dipole moments $\mu^{(1)} \equiv e_f^*$ and $\mu^{(2)}$ can be calculated from (3.15) and (3.16), respectively.

The quantities $\alpha_{\parallel}(R)$, $\alpha_{\perp}(R)$, and $p(R)$ were calculated for nine different values of R around the equilibrium distance R_0 and subsequently their derivatives were obtained by polynomial fitting procedure. For the calculation of $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ the variational procedure as described in Ref. 8 was performed for every value of R; only trial functions of F with $\{4, 4\}$ parameters were used which were determined by requiring that the functional (4.4) be a minimum. The values of α^E and β^E were obtained from the values of $\alpha_{\parallel}$, $\alpha_{\perp}$, $\beta_{\parallel}$, and $\beta_{\perp}$ as calculated in Ref. 8 with the same trial functions.

The wave functions of the form (2.15) were used where the R dependence was introduced into the coefficients ξ and λ as specified in expressions (2.16a), (2.16b), and (2.17). No attempt was made to obtain the R dependence of the coefficients by repeating the LCAO-MO calculations of Coulson, Rédei, and Stocker[19] for every distance R. For the equilibrium configuration the same values for ξ_i were used as in the calculation of Ref. 8.

Once the values of the derivatives of $\alpha_{\parallel}(R)$ and $\alpha_{\perp}(R)$ were obtained the corresponding unit-cell coefficient $\alpha^{(1)}$ was calculated from (3.4).

Finally, the coefficients $\phi^{(2)}$ and $\phi^{(3)}$ of the lattice potential were estimated. $\phi^{(2)}$ or equivalently ω_s was actually calculated from the experimental values of the compressibility κ using the relation (3.18); $\phi^{(3)}$ was calculated from (3.19) where $R/\rho = 6.5$ for all the compounds considered. The main contribution comes from the short-range potential. To the long-range contribution, only interactions of one atom with its four nearest neighbors are important; in fact the contributions of successive layers of more distant atoms have alternate signs and cancel each other to some extent. Neglecting then in (3.19) the contributions from interactions of an atom with more distant atoms than nearest neighbors and making use of (2.19) and (2.18) one obtains

$$\phi^{(3)} = \frac{4}{3\sqrt{3}} \frac{\partial^3 \phi}{\partial R^3} + \frac{3}{R_0} \left(\frac{1}{R_0} \frac{\partial \phi}{\partial R} - \frac{\partial^2 \phi}{\partial R_0} \right)$$

$$= -\frac{4}{3\sqrt{3}} \left\{ \frac{1}{\rho^2} + \frac{3}{R_0} \left[\frac{1}{\rho} + \frac{1}{R_0} \left(1 - 5 \frac{n_0}{\alpha_M} \right) \right] \right\} \frac{\phi_S}{\rho} , \qquad (4.7a)$$

or using (2.21b) one obtains

$$\phi^{(3)} = -\frac{16}{3} \frac{\{1/\rho^2 + (3/R_0)[1/\rho + (1/R_0)(1 - 5 n_0/\alpha_M)]\}}{(1/R_0)(1/\rho - 1/R_0)} \frac{1}{\kappa} . \qquad (4.7b)$$

The sign of $\phi^{(2)}$ was found positive while that of $\phi^{(3)}$ was found negative. This is due to the fact that both quantities are determined by the short-range repulsive part of the potential (2.18). As it was mentioned previously in adopting this form for the potential we have not taken into account explicitly intermediate-range electrostatic forces. If such forces were included the simple relations (3.18) and (4.7b) would no longer hold. Due to the complex form of these forces it is difficult to ascertain their influence on the behavior of $\phi^{(2)}$ and $\phi^{(3)}$. However, even if such forces were explicitly included one may assume that to a good approximation the potential can again be separated into two monotonic functions of R, one increasing (attractive) and the other decreasing (repulsive) with R. Since $\phi^{(3)}$ arises from energy changes it will be dominated by the most rapidly changing part of the potential and this is more likely to be the shorter-range repulsive part of the potential. As a matter of fact although the attractive part will give by far the largest contribution to the cohesive energy (2.13) the first derivatives of the two parts must cancel each other, as it is required by the equilibrium condition, and $\phi^{(2)} = M\omega_s^2$ must be positive reflecting the fact that the repulsive part changes more rapidly with distance than the attractive part; one may expect that the same trend will be followed by the third-order derivative. Hence $\phi^{(3)}$ will be negative. It is to be noted that this is *a fortiori* true if the repulsive short-range forces were represented by a R^{-n} law.

Once the microscopic unit-cell quantities were calculated the corresponding macroscopic fre-

TABLE I. Infrared and lattice data of III–V cubic compounds.

Compound	a[a] (Å)	ω_T[b] (cm^{-1})	e_T^*[c] (esu)	ϵ_∞[c]	ϵ_0[c]	$10^{12}\kappa$[b] (barye^{-1})
InSb	6.48	185	2.5	15.68	17.88	2.132
InAs	6.09	219	2.6	11.80	14.55	1.727
InP	5.87	304	2.5	9.61	12.61	1.45[d]
GaSb	6.09	231	1.8	14.44	15.69	1.855
GaAs	5.63	269	2.2	11.10	13.13	1.337
GaP	5.45	367	2.0	8.46	10.18	1.12[e]
AlSb	6.14	319	1.9	9.88	11.21	1.694

[a] G. Gieseche, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 2, p. 63.

[b] S. Mitra, in *Optical Properties of Solids*, edited by L. Nudelman and S. Mitra (Plenum, New York, 1969), p. 333.

[c] M. Haas, in Ref. a.

[d] F. S. Hickernell and W. R. Gayton, J. Appl. Phys. 37, 462 (1966); the compressibility value was calculated from the measured values of the elastic constants given in this reference.

[e] R. Weil and W. O. Groves, J. Appl. Phys. 39, 4049 (1968).

quency ω_T, effective charge e_T^* and susceptibilities were calculated from (3.33a), (3.33b), (3.39), (3.46a), and (3.46b) where the value of the local-field factor f was obtained as in Ref. 8, namely, by requiring that ϵ_∞ calculated from (3.28) will be equal to its experimental value; the same values of f obtained in Ref. 8 with the $\{4, 4\}$ parameter trial functions were used here too.

The values of the partial susceptibilities $\chi_{H'}^{(2)}$, $\chi_{H''}^{(2)}$, and $\chi_N^{(2)}$ or rather the ratios C_1, C_2, and C_3 are displayed in Table II along with the existing experimental values. Although the signs of $\chi^{(2)}$ require to specify the axes conventions, the signs of the ratios C_i on the other hand, as it can be seen from their definitions, are meaningful irrespective of the conventions. The values of $\chi_E^{(2)}$ as calculated in Ref. 8 with the $\{4.4\}$ parameter trial functions and the axes conventions of Fig. 1, the same as in Ref. 8, were used throughout the calculation.

In Table III, we display for reference the calculated values of the effective charge e_T^*, and the lattice infrared frequency ω_T which were used for the calculation of the macroscopic susceptibilities $\chi^{(2)}$ and the ratios C_i. In the same table we include for comparison the values of $\epsilon_0 - \epsilon_\infty$, the lattice contribution to the linear dielectric constant ϵ_0. The sign of e_f^*, the microscopic effective charge, and consequently that of e_T^*, was found negative with the adopted conventions of Fig. 1; this amounts to saying that during the displacements of the ions according to the electric-field-induced optic mode the static field sees a negative charge on ion III and a positive charge on ion V or equivalently a III–V bond is elongated when a static field is directed from atom III to atom V of the bond.

In Table IV, we give the calculated values of the macroscopic Raman tensor $\tilde{\alpha}^{(1)}$ for all the compounds considered along with the existing experimental values. For all the crystals this quantity was found positive. A calculation of $\tilde{\alpha}^{(1)}$ was also performed using the Unsöld approximation as described in Ref. 8. These values of $\tilde{\alpha}^{(1)}$ were roughly equal to the values obtained with the $\{4, 4\}$

TABLE II. Lattice-induced contributions to the second-order susceptibilities of III–V cubic compounds.

	Calc.				Expt.	
Compound	C_1	C_2	C_3	$3C_2+C_3$	C_1	$3C_2+C_3$[a]
InSb	−0.66	0.06	−0.03	0.15		
InAs	−0.28	0.08	−0.03	0.22		
InP	−0.14	0.09	−0.03	0.23		
GaSb[b]	−2.00 (−0.28)	0.19 (0.03)	−0.09 (−0.01)	0.48 (0.08)		
GaAs	−0.83	0.14	−0.07	0.35	−0.59,[c] −0.51,[d] −0.68[e]	1.15 0.39
GaP	−0.37	0.11	−0.05	0.27	−0.53,[f] −0.75[e]	0.92 0.28
AlSb[b]	−1.97	0.35	−0.11	0.93		

[a] See Ref. 43. The values of $3C_2+C_3$ were extracted from the measured values of $\chi_M^{(2)}$ given in this reference by using the values of C_1 given in Ref. 42 (GaAs) and Ref. 10 (GaP) and the measured values of $\chi_E^{(2)}$ given in Ref. 43. Since the sign of $\chi_M^{(2)}$ is not known two values of $3C_2+C_3$ are obtained; the upper value corresponds to assuming $\chi_M^{(2)} > 0$ and the lower value to $\chi_M^{(2)} < 0$.

[b] See Text. The values of the C_i for GaSb inside the parentheses were obtained by using the experimental values of e_T^* (Tables I and III) and $\chi_E^{(2)}$ (Ref. 45, $\chi_E^{(2)} = 30 \times 10^{-7}$ esu for GaSb).

[c] See Ref. 42.

[d] See Ref. 41.

[e] See Ref. 43; this value of C_1 was obtained from the measured values of $\chi_E^{(2)}$ and $\chi_{EO}^{(2)}$ and the relation $C_1 = (\chi_{EO}^{(2)} - \chi_E^{(2)})/\chi_E^{(2)}$.

[f] See Ref. 10.

TABLE III. Calculated effective charges and infrared lattice frequencies of III-V cubic compounds.

	Calc.			Expt.[a]		
Compound	e_T^*[b] (esu)	ω_T (cm^{-1})	$\epsilon_0 - \epsilon_\infty$	e_T^*[c] (esu)	ω_T (cm^{-1})	$\epsilon_0 - \epsilon_\infty$
InSb	−3.1	175	3.83	2.5	185	2.20
InAs	−2.7	217	3.01	2.6	219	2.75
InP	−2.2	325	1.89	2.5	304	3.00
GaSb	−2.6	213	3.00	1.8	231	1.25
GaP	−2.0	382	1.55	2.0	367	1.74
AlSb	−1.6	328	0.92	1.9	319	1.33

[a] See Table I.

[b] For the sign of e_T^* see text.

[c] Only the absolute value of e_T^* is measured experimentally.

parameter variational functions, but since the Unsöld approximation underestimates β^E by almost an order of magnitude,[8] the resulting value of C_1 was less than −1; hence a negative value for the total electro-optic coefficient $\chi_{EO}^{(2)} = \chi_E^{(2)}(1 + C_1)$.

In Table V, we give the values of $\tilde{\mu}^{(2)}$ and $\tilde{\phi}^{(3)}$. With the axis conventions of Fig. 1 the sign of $\tilde{\mu}^{(2)}$ was found positive for all compounds considered, the same sign as its microscopic counterpart $\mu^{(2)}$. The sign of $\tilde{\phi}^{(3)}$ was found negative, the same sign as its microscopic counterpart $\phi^{(3)}$. As it can be seen from (3.43) and (3.45) besides $\mu^{(2)}$ and $\phi^{(3)}$, both $\tilde{\mu}^{(2)}$ and $\tilde{\phi}^{(3)}$, respectively, contain contributions which have their origin to polarization effects.

It is clear from (3.47) that $\chi^{(2)}$ and $\chi_{H''}^{(2)} + \chi_N^{(2)}$ will vanish for some frequencies whose values with respect to ω_T will be determined by the signs of C_i; as one can see from Table II the C_i's alternate in sign. These frequencies where $\chi^{(2)}$ vanishes are simply obtained by solving algebraic equations of order not higher than third whose coefficients are simple expressions of the C_i's. Accordingly, their roots will be expressed in terms of the C_i's. The relations (3.62), (3.65), (3.67), and similar ones, then, can be reexpressed in terms of these roots. This is analogous to the alternative way of deriving the Lyddane-Sachs-Teller relation in the linear case, namely, by finding the frequency for which ϵ given by (2.2a) vanishes.

In Table V, we give for comparison an estimation of Γ using the approximate expression (3.51) and assuming $T = 300\,^\circ\mathrm{K}$. The order-of-magnitude agreement with the existing experimental estimations seems satisfactory although this does not lead one to any conclusions concerning the adequacy of this simple model; in fact Γ is frequency and temperature dependent. Further, since $e_T^* \tilde{\phi}^{(3)} / M\omega_T^2 \tilde{\mu}^{(2)} > 0$ expression (3.52) vanishes for a value of $\omega > \omega_T$.

Taking into account the relationship that exists between $\chi_{H''}^{(2)} + \chi_N^{(2)}$ and $\omega\epsilon''(\omega)$, we conclude from the calculated values of C_2 and C_3 that the two-phonon sidebands in the infrared spectra of the III–V compounds arise mainly through the second-order dipole moment. In the past quantitative arguments were given[34] supporting the assumption that the third-order potential is the dominant mechanism in the III–V compounds and in particular in GaP. This was based on the fact that in Si the integrated absorption coefficient in the infrared, which, as it can be seen from (3.50) with $e_T^* = 0$, is due to the second-order dipole moment only, is by at least an order of magnitude smaller than in GaP, where both $\tilde{\mu}^{(2)}$ and $\tilde{\phi}^{(3)}$ contribute, and on the assumption that the same $\tilde{\mu}^{(2)}$ processes con-

TABLE IV. Calculated Raman tensors for III-V cubic compounds.

Compound	Calc. $10^{16}\, \tilde{\alpha}^{(1)}$ (cm^2)	Expt. $10^{16}\, \tilde{\alpha}^{(1)}$ (cm^2)
InSb	206	
InAs	84	
InP	41	
GaSb	169	
GaAs	84	61,[a] 53,[b] 73,[c] 31[d]
GaP	43	40,[a] 30[e]
AlSb	77	

[a] Value obtained from the measured values of $\chi_E^{(2)}$ and $\chi_{EO}^{(2)}$ of Ref. 43 and the infrared data (Table I).

[b] Value obtained from the measured values of $\chi_E^{(2)}$ (Ref. 43) and C_1 (Ref. 42) and the infrared data (Table I).

[c] Value obtained from the measured values of $\chi_E^{(2)}$ (Ref. 45) and C_1 (Ref. 42) and the infrared data (Table I).

[d] See Ref. 41.

[e] Value obtained from the measured values of $\chi_E^{(2)}$ (Ref. 43) and C_1 (Ref. 10) and the infrared data (Table I).

TABLE V. Calculated optic-phonon interaction and damping coefficients of the III-V cubic compounds.

		Calc.		Expt.[b]	
Compound	$10^{-12}\, \tilde{\phi}^{(3)}$ (erg/cm^3)	$10\, \tilde{\mu}^{(2)}$[a] (esu/cm)	Γ/ω_T (300 °K)	Γ/ω_T	(temp)
InSb	−4.5	1.40	0.002	0.007[c]	(helium)
InAs	−7.5	2.48	0.004	0.007[c]	(helium)
InP	−13.5	2.89	0.009	0.04[c]	(room)
GaSb	−7.8	1.66	0.004	0.007[c]	(helium)
GaAs	−12	1.77	0.005	0.007[c]	(helium)
GaP	−21	2.33	0.013	0.01[d]	(room)
AlSb	−15	2.50	0.016	0.02[c]	(room)

[a] The axis conventions of Fig. 1 are used.

[b] No direct measurement of Γ exists for any of the studied compounds. The values given below were obtained by fitting the experimental results of reflectivity with an expression of the type (3.49).

[c] M. Haas and B. W. Henvis, J. Phys. Chem. Solids <u>23</u>, 1099 (1962).

[d] See Ref. 10.

tribute in GaP as well as in Si since both crystals have tetrahedral symmetry. The latter, however, is not the case. In the calculation of $\mu^{(2)}$ performed above for the III–V compounds the bonds were assumed to possess axial symmetry; hence the electronic bond dipole moment $\vec{p}$ was taken to have only an axial component p along the z-bond axis or $\vec{p}=(0,0,p)$ and the nonaxial (transverse) components were neglected. For an homopolar bond like the Si-Si bond in Si, however, the axial component p and its derivatives vanish identically and a nonzero $\mu^{(2)}$ will be obtained only if the nonaxial components are also taken into account. The nonaxial components contribute roughly by the same amount also in GaP but with a different order of magnitude than the axial components; the former arise from three-body interactions while the latter arise from two-body nearest-neighbors interaction. The fact that experimentally one finds much smaller values for α_{1r} in Si than in GaP indicates that this is the case and that the former are almost by an order of magnitude smaller than the latter and can be disregarded in a first approximation. Clearly, the nonaxiality of the bonds is related to the noncentral forces. The above discussion then indicates that the short-range noncentral forces contribute in the long-wavelength optic modes almost by an order of magnitude less than short-range central forces.

V. EFFECTIVE-BOND MODEL

The previous calculation shows that in the final analysis it is primarily the knowledge of some matrix elements and of their dependence on some few structural parameters that is required to calculate $\chi^{(2)}$. In order to exhibit this in a simpler but only qualitative way it is of some interest to consider the δ-function-bond model.[3,14] A short account of the model is given in Appendix E. This model can be solved[3] exactly and the expressions of α and β can be obtained in explicit form; here we shall use the expressions of these quantities obtained by the Unsöld approximation; they are given in Appendix E along with the moments $\langle z^n\rangle$ of the electronic density distribution of the bond. For the potential we adopt Lippincott's prescriptions (see Appendix E). Although the model is unidimensional, for our purposes this is not a serious drawback since, as we have seen, as far as the nonlinear properties are concerned the bonds of the III–V compounds behave as unidimensional.[8] It is sufficient then to derive the expressions of the quantities e_f^*, $\partial p/\partial R$, $\partial^2 p/\partial R^2$, $\partial\alpha/\partial R$, and $\partial^3\phi/\partial R^3$ since they completely determine the second-order polarizability per unit cell and consequently $\chi^{(2)}$. In this qualitative discussion we disregard local-field corrections.

Differentiating (E1)–(E3) and keeping terms up to e^{-2cR_0} $(cR_0>1)$ one obtains

$$\frac{\partial c}{\partial R}\equiv c^{(1)}=-\frac{cg}{e^2a_0}\,\frac{1-\mu^2}{\mu}\,e^{-2cR_0}\,,$$

$$\frac{\partial^2 c}{\partial R^2}\equiv c^{(2)}=\frac{2c^2g}{e^2a_0}\,\frac{1-\mu^2}{\mu}\,e^{-2cR_0}\,,$$

$$\frac{\partial\lambda}{\partial R}\equiv\lambda^{(1)}=-c\,\frac{1-\mu}{2\mu}\,e^{-cR_0}\,,$$

$$\frac{\partial^2\lambda}{\partial R^2}\equiv\lambda^{(2)}=2c^2\,\frac{1-\mu}{2\mu}\,e^{-cR_0}\,,$$

$$\frac{\partial}{\partial R}\left(\frac{N^2}{c}\right)=2c\,\frac{1-\mu}{2\mu}\,\left(\frac{N^2}{c}\right)^2\left(\frac{1-\mu}{2\mu}+2(1+cR_0)\right)e^{-2cR_0}\,.$$

The first two are analogous to (2.16) while the following two are analogous to (2.17). Using now the explicit expressions of p, α, and ϕ given by (E5), (E6), and (E9), respectively, one obtains successively

$$\frac{\partial p}{\partial R}=-e\left(\frac{q}{e}\right)\left[(1-\lambda^2)+cR_0(1-\lambda^2)\,\frac{1-\mu}{\mu}\,\left(\frac{N^2}{c}\right)\left(\frac{1-\mu}{2\mu}+2(1+cR_0)\,e^{-2cR_0}\right)+cR_0\left(\frac{1-\mu}{2\mu}\right)^2e^{-2cR_0}\right]\left(\frac{N^2}{c}\right)\,, \tag{5.1}$$

$$\frac{\partial^2 p}{\partial R^2}=-e\left(\frac{q}{e}\right)c(cR_0-1)\left(\frac{N^2}{c}\right)\left[(1-\lambda^2)\left(\frac{N^2}{c}\right)\frac{1-\mu}{\mu}\left(\frac{1-\mu}{\mu}+4(1+cR_0)\right)+\left(\frac{1-\mu}{\mu}\right)^2\right]e^{-2cR_0}\,, \tag{5.2}$$

$$\frac{\partial\alpha}{\partial R}=\left(\frac{q}{e}\right)^2\frac{R_0^3}{a_0}\left[1+\frac{2}{cR_0^3}-\frac{N^2}{c}\left(\frac{4cR_0}{3}\,e^{-cR_0}+\frac{N^2}{c}\,(\lambda^2-1)^2\right)\right]\left[2+cR_0\left(\frac{4cR_0}{3}-4+2(1-\lambda^2)\,\frac{1-\mu}{2\mu}\,\frac{N^2}{c}\right)\frac{N^2}{c}\,e^{-cR_0}\right]\,, \tag{5.3}$$

$$\frac{\partial^3\phi}{\partial R^3}=-\frac{2nD_e}{R_0^2}\,, \tag{5.4}$$

while from (E8) and (5.1) one obtains

$$e_f^*=\frac{M}{M_B}\,(Z_B-1)q-\frac{M}{M_A}\,(Z_A-1)\,q+\frac{\partial p}{\partial R}\,. \tag{5.5}$$

As it can be seen from (E7), (5.2), and (5.3), β^E, $\partial\alpha/\partial R$, and $\partial^2 p/\partial R^2$ are positive while $\partial^3\phi/\partial R^3$ is negative. This is in qualitative agreement with the results obtained previously through the detailed orbital description of the bonds. By proper choice of the parameters one can obtain numerical values from the above expressions.[38] This will not be pursued any further.

This simple δ-function-bond model illustrates in particular the transition from the orbital description of the bonds adopted here to the effective-bond model defined through the moments of the electronic density distribution; these later can be fitted, for instance, from experimental data. Such a phenomenological description of the bonding in III–V and II–VI compounds has been presented by Phillips and van Vechten and has been used[39] for the calculation of β_E. To extend this approach to calculate the additional contributions required in the infrared dispersion, one must introduce assumptions concerning the change with intrabond distance of the different parameters of the model. The main difficulty arises in finding an expression of p, the bond electronic dipole moment, in terms of the parameters of the model and in calculating the derivatives $\partial p/\partial R$ and $\partial^2 p/\partial R^2$. Clearly, this quantity must vanish for the two limiting cases of zero (united atoms) and infinite interatomic separation. A plausible assumption is to take $p \sim RC_{AB}$, where C_{AB} is a measure of the charge transfer that takes place within a bond.[15,39] After some simple approximations, this can be written

$$p = \delta e R(Z_A - Z_B)e^{-kR} ,$$

where k^{-1} is a Fermi-Thomas screening length; δ can be determined by fitting e_T^*, as given by (3.33a) and (3.15), to the experimental values with the additional assumption that $f = 1$. On the other hand, the expression (2.18) of the lattice potential or a similar one can still be used. Such an approach can be used for both III–V and II–VI compounds of zinc blende as well as wurzite structure. The numerical application of this approach will not be given here.

VI. DISCUSSION

A. Comparison with Experiment

Experimental determination of the second-order partial susceptibilities $\chi_{H'}^{(2)}$, $\chi_{H''}^{(2)}$, and $\chi_N^{(2)}$ is still very scarce. This is in contrast to what the situation is for the purely electronic contribution $\chi_E^{(2)}$ where rather accurate experimental values exist for a fairly large class of materials. Since the pure electronic contribution $\chi_E^{(2)}$ is always present in any measurement of $\chi^{(2)}$ in the infrared-frequency region, it is convenient instead of the bare partial second-order susceptibilities to consider the ratios C_1, C_2, and C_3, respectively.

The most accurate determination of C_1 is the one performed by Faust and Henry[10] for GaP. These authors studied the dispersion of the second-order susceptibility $\chi^{(2)}(\omega, -\Omega)$ when Ω is near the reststrahlen frequency Ω_T of this compound while ω and $\omega - \Omega$ are well above Ω_T and they were able to fit their experimental results with a curve of the form

$$\chi^{(2)}(\omega, -\Omega) = \chi_E^{(2)}\left(1 + \frac{C}{1 - (\Omega/\Omega_T)^2 - i\,\Omega\Gamma/\Omega_T^2}\right) ,$$

where Γ^{-1} is a phenomenological phonon lifetime. For Ω well below the lattice frequency Ω_T, one obtains $\chi_E^{(2)}(1 + C)$ which is to be compared with the expression (3.39). The agreement between the experimental and the calculated values of C_1 for GaP as can be seen from Table II is satisfactory both in magnitude and sign. For the other compounds there is no similar study. The measured values of C for GaAs were obtained by comparing the experimental values of $\chi_{EO}^{(2)}$ and $\chi_E^{(2)}$ and through measurement of the absolute efficiencies of Raman scattering by longitudinal and transverse modes. Apart from some frequency and temperature factors the latter are determined[40] by (3.37) and (3.62), respectively, and hence their ratio gives a direct measurement of C. There are two slightly different values of C for GaAs by Moradian and McWorther[41] and by Kaminow and Johnston.[42] Here again the agreement is satisfactory both in sign and magnitude. Another experimental determination of C is provided through the measurement of $\chi_E^{(2)}$ and $\chi_{EO}^{(2)}$. Using the data of Ref. 43 for $\chi_E^{(2)}$ and $\chi_{EO}^{(2)}$ the values of C for GaAs and GaP thus obtained are again negative but somewhat larger in absolute magnitude than the ones given in Refs. 42 and 10, respectively.

The calculation gives that C_1 is negative for all III–V compounds. This seems to be the case also for the II–VI cubic compounds as it can be seen from the simplified effective-bond model discussed in Sec. V. The absolute magnitude of the calculated value of C_1 for GaP seems to be somewhat underestimated due to the overestimation[8] of $\chi_E^{(2)}$ while that of GaAs is somewhat overestimated due to the overestimation of $\tilde{\alpha}^{(1)}$ (see Table IV).

From the experimental values of $\chi_E^{(2)}$, C (or $\chi_{EO}^{(2)}$), and the infrared data, one can obtain the value of the Raman tensor $\tilde{\alpha}^{(1)}$ for these compounds; these values are given in Table IV. Due to the lack of accurate experimental values for $\chi_E^{(2)}$ and C (or $\chi_{EO}^{(2)}$) as it can be seen from Table IV the values of $\tilde{\alpha}^{(1)}$ thus obtained are uncertain. The agreement is satisfactory for the two compounds GaAs and GaP. The value of $\tilde{\alpha}^{(1)}$ for GaAs given in Ref. 41 is probably low. In general the present calculation somewhat overestimates $\tilde{\alpha}^{(1)}$.

Recently, Boyd *et al.*[43] have measured $\chi^{(2)}$ for GaP and GaAs in the microwave region; ω_1, ω_2, $\omega_1 + \omega_2 < \omega_T$. In this frequency region all four contributions in $\chi^{(2)}$ are present and their results have to be compared with the ones obtained by (3.46a); by substracting the pure electronic and first-hybrid contributions, $\chi_E^{(2)}$ and $\chi_{H'}^{(2)}$, respectively, one should be able to obtain $\chi_{H'}^{(2)}+\chi_N^{(2)}$. However, only the absolute magnitude of $\chi_M^{(2)}$ was determined in these measurements; lacking the sign of $\chi_M^{(2)}$ and an estimation of the experimental error one cannot unambiguously extract from their values of $\chi_M^{(2)}$ either the sign or the magnitude of $\chi_{H'}^{(2)}+\chi_N^{(2)}$ or equivalently those of $3C_2+C_3$. Since $C_1 \simeq -0.5$ the experimental results seem to be consistent with either $3C_2+C_3$ being positive and smaller than unity (if $\chi_M^{(2)}<0$) or positive and of the order of unity (if $\chi_M^{(2)}>0$) although the possibility of $3C_2+C_3$ being negative and small in absolute magnitude compared to unity cannot be altogether ruled out.

With the adopted lattice potential (3.18) our calculation gives that C_3 is negative while C_2 is positive and $3C_2+C_3$ is positive and smaller than unity thus favoring $\chi_M^{(2)}<0$. The experimental results of Ref. 43 do not permit one to determine the two contributions C_2 and C_3 separately and draw any conclusions about their magnitudes relative to each other. There is very little independent evidence concerning their relative magnitudes. The satisfactory order-of-magnitude agreement obtained for Γ (see Table V), where one of the coefficients enters, does not lead to any conclusions either. The experimental investigation of Geick[44] shows that the two coefficients are of comparable magnitude.

In general the calculated values of C_i given in Table II are affected both by the genuinely nonlinear coefficients $\chi_E^{(2)}$, etc., as well as by the linear ones e_T^* and ω_T. The abnormally high values of C_i for GaSb and AlSb clearly are due to the underestimation of $\chi_E^{(2)}$ by almost an order of magnitude[8] and the overestimation of the magnitude of e_T^* by almost 50%. In fact if the experimental values[45] of $\chi_E^{(2)}$ and e_T^* are used to calculate C_i for GaSb one obtains values showing the same trend as for the other III–V compounds studied here. The experimental value of $\chi_E^{(2)}$ for AlSb is not known but the same situation is expected here too. On the other hand, the values of C_i for InP are probably underestimated for the inverse reasons. From the values of C_i given in Table II one can estimate $\chi_M^{(2)}$. With the axes conventions of Fig. 1 one finds that $\chi_M^{(2)}$ is negative for GaAs the main contribution being the hybrid term $3C_1\chi_E^{(2)}$. The same is certainly the case for GaP although due to the underestimation of C_1 in our calculation the values of C_i of Table II would rather give the opposite sign. Probably the same is happening with all the other compounds.

B. General Remarks

The general expression of $\chi^{(2)}$ in the infrared-frequency region was also derived by Genkin, Fain, and Yaschin[5] using a phenomenological approach but no attempt was made either to derive it from a microscopic picture or to estimate the different contributions. The same remark applies for the more recent work of Garrett.[6]

A calculation of C_1 for the III–V compounds was performed in Ref. 7 adopting a method different from the one used in the present work. The approach used there amounts to replacing the short-range deformation mechanism that gives rise to $\alpha^{(1)}$ and ζ_d by an equivalent electrostatic one. More specifically it was argued there that since $e\zeta_d$ originates from a deformation of the electrons by the lattice displacements u_T, the corresponding dipole moment $\zeta_d\vec{u}$ can be written formally as $\alpha^E C_d E_\Omega$, where $C_d E_\Omega$ is an equivalent electric field that has the same effect on the valence electrons as the lattice-induced deformation. This same field then together with E_ω was assumed to give rise to $\chi_{H'}^{(2)}$ in the same way as $\chi_E^{(2)}$ is induced by E_ω and E_Ω the lattice being held fixed; C_d, which is a measure of the change of the electron-lattice potential, was calculated at a point using a particular choice of potentials and assuming point charges. Good agreement with experiment was obtained. These assumptions, however, do not take into account fully the essential characteristics of the bond which are its charge extension and asymmetry. Further, the replacement of the essentially nonuniform electric field is rather drastic. However, such an approach, when the above simplifications are replaced by more realistic assumptions, is of much value to the study of the lattice dynamics in these compounds. The above-described calculation predicts that $C_1 \simeq -0.5$ for all III–V and II–VI cubic compounds while for CuCl it predicts[46] $C_1 \simeq -1.2$.

Kelly[47] also performed a calculation of the electro-optic coefficient $\chi_{EO}^{(2)}$ for ZnS and CuCl using an ionic model for the electronic distribution in these compounds. He attributes the deformation of the electronic distribution to quadrupolar terms in the electron-lattice potential. This author predicts that C_1 is positive and larger than unity for both compounds.

Recently, Swanson and Maradudin[48] have performed a calculation of $\tilde{\alpha}^{(1)}$ for some diamond and zinc-blende crystals using the pseudopotential approach in band theory. The agreement is satisfactory.

In the present work the bond picture was used throughout the calculation. The dependence of the susceptibilities on the structural parameters of the electronic distribution within a unit cell and on the local-field corrections was clearly exhibited. In particular the microscopic picture adopted is consistent with the description of the linear properties of the crystal. However, some simplications and the approximate character of the wave functions used should be borne in mind. In particular the electron correlation is not taken into account adequately nor are any d states included and the local-field corrections were treated in a semiempirical way. As it can be seen from the expressions of $\chi^{(2)}$ in the different spectral regions the latter corrections are present in all the contributions and affect substantially their magnitude.[49] Further, the lattice potential was not derived consistently from the assumed electronic distribution of the bonds. In particular any directional effects arising from bond-bond interaction were altogether neglected. In covalent crystals like the ones considered here such effects can be important and probably account for the breakdown of the Cauchy relations observed in these crystals; their contribution, however, to the compressibility and to quantities related to the long-wavelength optic modes is relatively small. Intermediate electrostatic forces were not included explicitly although part of their effect was taken into account in the coefficients A and B in the terms in (3.44) originating from the local-field corrections. In general these forces are difficult to estimate although a clue is given by the work of Coulson and Doggett.[20] A study of the sign of $\chi^{(2)}$ in the whole infrared region could be of much value to determine some features of the internuclear potential and in particular the relative strength of the different parts in the potential. Further, it will give more insight into the relative magnitude of the two principal phonon-relaxation mechanisms. Apart from the experimental study of Geick[44] for GaAs, there is no independent evidence concerning the relative importance of these two mechanisms. In view of our results the experimental values of $\chi_M^{(2)}$ rather favor the fact that the second-order dipole-moment mechanism is slightly stronger than the anharmonic one; the electrons, especially the valence electrons, are easily deformable in III–V compounds and this is more strongly reflected in $\mu^{(2)}$ than in $\phi^{(3)}$. On the other hand for ionic crystals the anharmonic mechanism prevails. This could be the case of some II–VI compounds which were not considered here. In fact from the measured values[50] of ZnO (wurzite) and CdS (wurzite) given in Ref. 43 there is some evidence that at least $|3C_2+C_3|$ is large and $(3C_2+C_3)\chi_E^{(2)}$ probably negative[51] for these compounds. This can be accounted for in terms of the adopted potential (2.18). In fact these compounds are rather ionic and the potential is more realistic in this case than it is for the III–V compounds considered here. Further, it is more likely that $R/\rho \gtrsim 10$ in this case and as it can be seen from (4.7b) this enhances the value of the coefficient $\phi^{(3)}$ compared to what its value is for the covalent compounds while the other quantities β_E, $\alpha^{(1)}$, and $\mu^{(2)}$ are smaller, the crystals being rather ionic; hence $\chi_M^{(2)}$ will be negative[51] reflecting the sign of $\phi^{(3)}$ which is dominated by the short-range potential.

The interplay between long- and short-range forces mentioned previously is certainly crucial in order to account for the abnormally high values[43] of $\chi_M^{(2)}$ measured for the ferroelectrics. Such high values probably arise from the effective-field catastrophe[11] or equivalently from an infrared-active mode becoming soft, i.e., $\omega_T \to 0$. In fact as it can be seen from (3.34), ω_T is in general expressed as the difference of two positive terms and when they become roughly equal, ω_T tends to zero, and f_0, the local-field factor given by (3.30), becomes large. This effect enhances the values of the contributions in $\chi^{(2)}$ that display a dispersion characteristic of the lattice. Clearly, the ones associated with the soft mode will be the dominant ones and the crystal will behave effectively as a one-mode crystal like the III–V compounds. Further $\chi_M^{(2)}$ will be dominated by $\chi_N^{(2)}$ or $\chi_M^{(2)} \simeq \chi_N^{(2)} = \phi^{(3)}(e_T^*/M\omega_T^2)^3$, where T refers now to the soft mode. The quantity $\delta_N = \chi_M^{(2)}/[(\epsilon_0-\epsilon_\infty)/4\pi]^3$ then will only depend on $\tilde{\phi}^{(3)}$ but not on ω_T^{-2}. Since $\tilde{\phi}^{(3)}$ arises from higher-order derivatives than the ones occurring in ω_T^2, the near cancellation of the different parts occurring in the latter will not necessarily occur in the former too. Rather one of the contributions, either the short range or the long range, will become the dominant one and hence one expects values for δ_N of the same order of magnitude as for the semiconductors. This is indeed the case for the oxygen-bonded ferroelectrics while for the hydrogen-bonded ones the small values of δ_N indicate a small $\tilde{\phi}^{(3)}$. This simplified discussion permits one to extract the right order of magnitude of $\chi_M^{(2)}$ for the ferroelectrics but not the sign and other finer details which require one to carefully take into account the crystal symmetry and the lattice potential.[36] Although the ferroelectrics have drastically different polarization properties from the cubic semiconductors, the approach outlined in the present work seems to be that most indicated to account for $\chi^{(2)}$ in the former class of crystals. In particular any attempt to calculate $\chi^{(2)}$ must proceed through a reproduction of the linear dielectric properties in these crystals.

Note added in proof. After the present work was sent in for publication our attention was called to the work of M. A. Pollack and E. H. Turner, Phys. Rev. B 4, 4578 (1971). These authors have determined the sign of $\chi_M^{(2)}$ and found it positive with the axes convention of Fig. 1. This confirms our prediction concerning the sign of $\chi_M^{(2)}$. (See Sec. VI A; in the last column of Table II the lower value of $3C_2+C_3$ corresponds to $\chi_M^{(2)}<0$.) The author is indebted to Dr. G. D. Boyd and Dr. M. A. Pollack for calling his attention to this work.

ACKNOWLEDGMENTS

The author is very indebted to Professor N. Bloembergen and Professor C. L. Tang for discussions and comments. He gratefully acknowledges a very illuminating discussion with Professor M. Karplus.

APPENDIX A: MICROSCOPIC POLARIZABILITIES

Here we give a brief summary of the method employed in Ref. 3 to derive the expression of $\beta(\omega_1, \omega_2)$ in the Born-Oppenheimer approximation for a neutral system of nuclei and electrons confined in a volume small compared to the wavelengths. In the Born-Oppenheimer approximation the states of the system are described by the wave functions

$$\psi_{ev} = \chi_{ev}(\vec{X})\phi_e(\vec{x}, \vec{X}) , \tag{A1}$$

where $\vec{x}$ and $\vec{X}$ denote collectively the electronic and nuclear coordinates, respectively; $\phi_e(\vec{x}, \vec{X})$ is the wave function of the electrons in the field of the nuclei which are held fixed in an arbitrary position $\vec{X}$, e being the corresponding quantum number with eigenvalue $E_e(\vec{X})$ a function of $\vec{X}$; $\chi_{ev}(\vec{X})$ represents a wave function for the nuclei moving in the effective potential $E_e(\vec{X})$ the corresponding eigenvalues being ϵ_{ev}. We denote by $E_0(\vec{X})$ the energy of the ground electronic state and by $\vec{X}_0$ the equilibrium nuclear configuration obtained by the requirement that $E_0(\vec{X})$ must have a minimum; then $E_0(\vec{X})$ can be expanded in power series in the deviations $u = \vec{X} - X_0$ from this equilibrium position. Introducing the normal coordinates q_σ this expansion can be written

$$E_0(\vec{X}) = E_0(\vec{X}_0) + \frac{1}{2!} \sum_\sigma \omega_\sigma^2 q_\sigma q_\sigma + \frac{1}{3!} \sum_{\sigma, \sigma', \sigma''} \Phi^{(3)}_{\sigma\sigma'\sigma''} q_\sigma q_{\sigma'} q_{\sigma''} . \tag{A2}$$

The dipole moment operator of the system is

$$\vec{M}(\vec{x}, \vec{X}) = -\textstyle\sum_i e\vec{x}_i + \sum_k e Z_k \vec{X}_k , \tag{A3}$$

where i runs over the electrons, k over the nuclei, and Z_k is the charge of nucleus k. We define also the lattice dipole moment for the ground electronic state

$$\vec{M}(\vec{X}) = \int \phi_e(\vec{x}, \vec{X})(-\textstyle\sum_i e\vec{x}_i + \sum_k e Z_k \vec{X}_k)\, \phi_e(\vec{x}, \vec{X})\, d\vec{x} ,$$

which for small displacements of the nuclei from their equilibrium positions can also be expanded in powers of the normal coordinates or

$$\vec{M}(\vec{X}) = \vec{M}(\vec{X}_0) + \sum_\sigma \vec{M}^{(1)}_\sigma q_\sigma + \tfrac{1}{2} \sum_{\sigma, \sigma'} \vec{M}^{(2)}_{\sigma\sigma'} q_\sigma q_{\sigma'} . \tag{A4}$$

The quantum-mechanical expressions of the linear and second-order polarizabilities for the ground electronic state of the above described system are

$$\alpha_{ij}(\omega) = \sum_{e; v_0 v_e} \rho^{(0)}_{v_0 v_0} \left(\frac{\langle e_0 v_0 | M_i(\vec{x}, \vec{X}) | e v_e \rangle \langle e v_e | M_j(\vec{x}, \vec{X}) | e_0 v_0 \rangle}{(E_{e v_e} - E_{e_0 v_0} - \hbar\omega)} + \frac{\langle e_0 v_0 | M_j(\vec{x}, \vec{X}) | e v_e \rangle \langle e v_e | M_i(\vec{x}, \vec{X}) | e_0 v_0 \rangle}{E_{e v_e} - E_{e_0 v_0} + \hbar\omega} \right) , \tag{A5}$$

$$\beta_{ijk}(\omega_1, \omega_2) = \tfrac{1}{2} \mathcal{S}_3 \sum_{e' e''; v_0 v_{e'} v_{e''}} \rho^{(0)}_{v_0 v_0} \left(\frac{\langle e_0 v_0 | \tilde{M}_i(\vec{x}, \vec{X}) | e' v_{e'} \rangle \langle e' v_{e'} | \tilde{M}_j(\vec{x}, \vec{X}) | e'' v_{e''} \rangle \langle e'' v_{e''} | \tilde{M}_k(\vec{x}, \vec{X}) | e_0 v_0 \rangle}{[E_{e' v_{e'}} E_{e_0 v_0} - \hbar(\omega_1 + \omega_2)](E_{e'' v_{e''}} - E_{e_0 v_0} - \hbar\omega_2)} \right) , \tag{A6}$$

where $\mathcal{S}_3$ means summation over all possible permutations of the pairs $(i, -\omega_1 - \omega_2)$, (j, ω_1), and (k, ω_2) and $\tilde{\vec{M}} = \vec{M} - \langle 0 | \vec{M} | 0 \rangle$ and $\rho^{(0)}_{v_0 v_0}$ are the density matrix elements of the vibrational modes for the ground state.

With respect to the two infinite summations over the intermediate states $|e'\rangle | v_{e'}\rangle$ and $|e''\rangle | v_{e''}\rangle$, β can be split into three parts or

$$\beta_{ijk}(\omega_1, \omega_2) = \beta'_{ijk}(\omega_1, \omega_2) + \beta''_{ijk}(\omega_1, \omega_2) + \beta'''_{ijk}(\omega_1, \omega_2) \tag{A7}$$

that correspond to the following three cases: (a) $|e'\rangle$ and $|e''\rangle$ are different from the ground electronic state $|e_0\rangle$; (b) $|e'\rangle = |e_0\rangle$ but $|e''\rangle \neq |e_0\rangle$ and vice versa; and (c) $|e_0\rangle = |e'\rangle = |e''\rangle$. Then the detailed analysis of Ref. 3 shows that the first case gives

$$\beta'_{ijk}(\omega_1, \omega_2) \simeq \beta^E_{ijk} = \frac{1}{2!} \mathcal{S}_3 \sum_{e', e''} \frac{\langle e | \tilde{m}_i | e' \rangle \langle e' | \tilde{m}_j | e'' \rangle \langle e'' | \tilde{m}_k | e \rangle}{(E_{e'} - E_0)(E_{e''} - E_0)} , \tag{A8}$$

where $\vec{m} = -\sum_i e\vec{x}_i$, $\tilde{\vec{m}} = \vec{m} - \langle e_0 | \vec{m} | e_0 \rangle$; in (A8) only moments and states of the electronic system appear, the lattice being held fixed in its equilibrium position $\vec{X}_0$ and the frequencies were assumed well below the onset of electronic transitions, $\omega_i \ll E_e - E_0$. The second case gives

$$\beta''_{ijk}(\omega_1, \omega_2) = \beta''_{ijk}(\omega_1, \omega_2) = \tfrac{1}{2} \sum_\sigma \left(\frac{M_i^{(1)}(\sigma) \alpha^{(1)}_{jk}(\sigma)}{\omega_\sigma^2 - (\omega_1 + \omega_2)^2} + \frac{M_j^{(1)}(\sigma) \alpha^{(1)}_{ki}(\sigma)}{\omega_\sigma^2 - \omega_1^2} + \frac{M_k^{(1)}(\sigma) \alpha^{(1)}_{ij}(\sigma)}{\omega_\sigma^2 - \omega_2^2} \right) , \tag{A9}$$

where again the frequencies were neglected with respect to electronic transition energies and $\alpha^{(1)}_{ij}(\sigma)$ is the Raman tensor of the system for the mode σ. Finally, the third case gives two terms or

$$\beta'''_{ijk}(\omega_1, \omega_2) = \beta^{H''}_{ijk}(\omega_1, \omega_2) + \beta^{N}_{ijk}(\omega_1, \omega_2) , \qquad \text{(A10)}$$

with

$$\beta^{H''}_{ijk}(\omega_1, \omega_2) = \tfrac{1}{2} \sum_{\sigma,\sigma'} \left(\frac{M^{(2)}_i(\sigma,\sigma') M^{(1)}_j(\sigma) M^{(1)}_k(\sigma')}{(\omega^2_\sigma - \omega^2_1)(\omega^2_{\sigma'} - \omega^2_2)} + \frac{M^{(1)}_i(\sigma) M^{(2)}_j(\sigma,\sigma') M^{(1)}_k(\sigma')}{[\omega^2_\sigma - (\omega_1+\omega_2)^2](\omega^2_{\sigma'} - \omega^2_2)} + \frac{M^{(1)}_i(\sigma) M^{(1)}_j(\sigma') M^{(2)}_k(\sigma,\sigma')}{[\omega^2_\sigma - (\omega_1+\omega_2)^2](\omega^2_{\sigma'} - \omega^2_1)} \right) ,$$

$$\beta^{N}_{ijk}(\omega_1, \omega_2) = -\tfrac{1}{2} \sum_{\sigma,\sigma',\sigma''} \phi^{(3)} \times \frac{M^{(1)}_i(\sigma) M^{(1)}_j(\sigma') M^{(1)}_k(\sigma'')}{[\omega^2_0 - (\omega_1+\omega_2)^2](\omega^2_{\sigma'} - \omega^2_1)(\omega^2_{\sigma''} - \omega^2_2)} .$$

Consequently the second-order polarizability for frequencies well below the onset of electronic transitions can be written

$$\beta_{ijk}(\omega_1, \omega_2) = \beta^E_{ijk} + \beta^{H'}_{ijk}(\omega_1, \omega_2) + \beta^{H''}_{ijk}(\omega_1, \omega_2) + \beta^{N}_{ijk}(\omega_1, \omega_2) . \qquad \text{(A11)}$$

We have formally denoted[52] by β^E the purely electronic term, by $\beta^{H'}$ and $\beta^{H''}$ the hybrid terms which arise from cross terms of the electronic and nuclear coordinates, and by β^N the purely ionic term. However, even in this term the electronic contribution is substantial since (A2) contains electron interactions as well.

A similar analysis of $\alpha_{ij}(\omega)$ gives[4] that, for frequencies below the onset of electronic transitions,

$$\alpha_{ij}(\omega) = \alpha^E_{ij} + \alpha^N_{ij}(\omega) , \qquad \text{(A12)}$$

where

$$\alpha^N_{ij}(\omega) = \sum_\sigma \frac{M^{(1)}_i(\sigma) M^{(1)}_j(\sigma)}{\omega^2_\sigma - \omega^2}$$

and

$$\alpha^E_{ij}(\omega) = 2 \sum_e \frac{\langle e_0 | m_i | e \rangle \langle e | m_j | e_0 \rangle}{E_e - E_0}$$

and the ionic and electronic contributions, respectively. However, here too, the electronic contribution is substantial even in the first term as it can be seen from (A4).

For the case of the zinc-blende structure we have a single mode which we denote by s. Using the notations of the text, the expressions of the microscopic polarizabilities α and β for a unit cell are

$$\alpha(\omega) = \alpha^E + \frac{(\mu^{(1)})^2}{M(\omega^2_s - \omega^2_1)} , \qquad \text{(A13)}$$

$$\beta(\omega_1, \omega_2) = \beta^E + \frac{1}{2M} \left(\frac{\alpha^{(1)}\mu^{(1)}}{\omega^2_s - (\omega_1+\omega_2)^2} + \frac{\mu^{(1)}\alpha^{(1)}}{\omega^2_s - \omega^2_1} + \frac{\mu^{(1)}\alpha^{(1)}}{\omega^2_s - \omega^2_2} \right) + \frac{1}{2M^2} \left(\frac{\mu^{(2)}\mu^{(1)}\mu^{(1)}}{[\omega^2_s - (\omega_1+\omega_2)^2](\omega^2_s - \omega^2_2)} + \frac{\mu^{(2)}\mu^{(1)}\mu^{(1)}}{[\omega^2_s - (\omega_1+\omega_2)^2](\omega^2_s - \omega^2_1)} + \frac{\mu^{(2)}\mu^{(1)}\mu^{(1)}}{(\omega^2_s - \omega^2_1)(\omega^2_s - \omega^2_2)} \right) - \tfrac{1}{2}\phi^{(3)} \frac{\mu^{(1)}\mu^{(1)}\mu^{(1)}}{M^3[\omega^2_s - (\omega_1+\omega_2)^2](\omega^2_s - \omega^2_1)(\omega^2_s - \omega^2_2)} . \qquad \text{(A14)}$$

In the previous discussion we have not included local-field corrections. These will renormalize the different quantities which occur in (A14) (see Sec. III) and in particular will modify ω_s to ω_T which is the true lattice eigenfrequency.

APPENDIX B: MICROSCOPIC COEFFICIENTS

We derive here the expressions of the microscopic coefficients for a unit cell required for the determination of α and β (see Appendix A).

(a) The linear and second-order microscopic polarizabilities per unit cell in terms of the corresponding bond polarizabilities are given by

$$\alpha_{ij} = \textstyle\sum_\kappa \alpha^\kappa_{lm} a^\kappa_{il} a^\kappa_{jn} , \qquad \text{(B1)}$$

$$\beta_{ijk} = \textstyle\sum_\kappa \beta^\kappa_{lmn} a^\kappa_{il} a^\kappa_{jm} a^\kappa_{kn} , \qquad \text{(B2)}$$

where κ runs over the four bonds of the unit cell and a^κ_{ij} are the direction cosines of the κ-bond axes $Oxyz$ with respect to the crystalline axes $KXYZ$; i, j, k run over the crystallographic coordinates X, Y, Z while l, m, n over the bond coordinates x, y, z. Both the bond polarizabilities and the direction cosines are functions of the nuclear configuration. For small displacements of the atoms from their equilibrium position R_0 these quantities can be developed in powers of $\vec{u} = \vec{R} - \vec{R}_0$. Here we need the zero- and first-order terms of α and the zero-order term of β. Expressing the cosines in terms of the nuclear coordinates, assuming that the bonds are deformed only by stretching and inserting the numerical values of the direction cosines corresponding to the undistorted cell, one obtains

$$\alpha_{ij} = \alpha^E \delta_{ij} + \alpha^{(1)} \epsilon_{ijk} u_k + \cdots$$

and

$$\beta_{ijk} = \beta^E \epsilon_{ijk} + \cdots ,$$

where

$$\alpha^E = \tfrac{4}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) , \tag{B3}$$

$$\alpha^{(1)} = \frac{4}{3\sqrt{3}} \left(\frac{\partial \alpha_{zz}}{\partial R} - \frac{\partial \alpha_{xx}}{\partial R} - \frac{2}{R_0}(\alpha_{zz} - \alpha_{xx})\right) , \tag{B4}$$

$$\beta^E = \frac{4}{3\sqrt{3}} (\beta_{zzz} - 3\beta_{xzx}) , \tag{B5}$$

and δ_{ij} and ϵ_{ijk} are the Kronecker and Levi-Civita tensors, respectively.

(b) Similarly the electronic dipole moment of the unit cell for an arbitrary nuclear configuration $\vec{R}$ is given in terms of the bond dipole moments by the expression

$$\pi_i = \sum_\kappa p_l^\kappa a_{il}^\kappa . \tag{B6}$$

Developing in powers of the small displacements $\vec{u} = \vec{R} - \vec{R}_0$ of the atoms from their equilibrium configuration $\vec{R}_0$, one obtains to terms up to the second order

$$\pi_i = \pi_i^{(0)} + \pi_{ij}^{(1)} u_j + \tfrac{1}{2} \pi_{ijk}^{(2)} u_j u_k ,$$

where

$$\pi_i^{(0)} = 0 , \tag{B7}$$

$$\pi_{ij}^{(1)} = \frac{4}{3} \left(\frac{\partial p}{\partial R} + 2 \frac{p_0}{R_0}\right) \delta_{ij} , \tag{B8}$$

and

$$\pi_{ijk}^{(2)} = \frac{4}{3\sqrt{3}} \left[\frac{\partial^2 p}{\partial R^2} + \frac{1}{R_0} \left(3 \frac{p_0}{R_0} - \frac{\partial p}{\partial R}\right)\right] \epsilon_{ijk} , \tag{B9}$$

where p_0 is the nonzero component of the bond dipole moment along the bond axis.

(c) Finally we need the expressions of the coefficients $\phi_{ij}^{(2)}$ and $\phi_{ijk}^{(3)}$: For this purpose we have to calculate the change of the potential ϕ between an atom and any other atom and sum over the lattice; the sum of all ϕ for the equilibrium configuration is (2.18). The potential ϕ consists of two parts, one long range and another short range or $\phi = \phi_L + \phi_S$; we shall derive separately their contributions to $\phi^{(2)}$ and $\phi^{(3)}$.

The short-range interactions are limited between an atom and its four nearest neighbors; a straightforward application of symmetry operations gives

$$\phi_S = \phi_S^{(0)} + \tfrac{1}{2} \phi_{ij,S}^{(2)} u_i u_j + \tfrac{1}{6} \phi_{ijk,S}^{(3)} u_i u_j u_k ,$$

where

$$\phi^{(0)} = n_0 \phi_S(R_0) \equiv \Phi_S(R_0) ,$$

$$\phi_{ij,S}^{(2)} = \frac{4}{3} \left(\frac{\partial^2 \phi_S}{\partial R^2} + \frac{2}{R_0} \frac{\partial \phi_S}{\partial R}\right) \delta_{ij} , \tag{B10}$$

$$\phi_{ijk,S}^{(3)} = \frac{4}{3\sqrt{3}} \left[\frac{\partial^3 \phi_S}{\partial R^3} + \frac{3}{R_0} \left(\frac{1}{R_0} \frac{\partial \phi_S}{\partial R} - \frac{\partial^2 \phi_S}{\partial R}\right)\right] \epsilon_{ijk} . \tag{B11}$$

The long-range potential falls slower with distance than the short-range potential; further, the number of atoms within a shell of radius R and $R + \Delta R$ around any atom increases as R^2. Accordingly, interactions of this atom with both nearest and more distant neighbors must be included in the calculation of $\phi^{(2)}$ and $\phi^{(3)}$. To carry out the pertinent summations we need to specify the coordinate system.[4,47] Using the conventions of Fig. 1, we chose as origin a III atom. Then the other III atoms lie on the sites of the corresponding face-centered cubic sublattice. The face-centered sublattice formed by the V atoms is displaced from the previous one by an amount $a(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. If there is a V atom at lattice site (R_1, R_2, R_3), one can easily see that there will be a layer of identical ions at $(R_1, -R_2, -R_3)$, $(-R_1, -R_2, R_3)$, and $(-R_1, R_2, -R_3)$, and eight more sites obtained from those four by cyclic permutation of the indices; further, one can show that in the case of uniform displacements considered here interactions between atoms of the same sublattice will not contribute in the sums. Straightforward use then of $\bar{4}3m$ point-group symmetry operations gives

$$\phi_L = \phi_L^{(0)} + \tfrac{1}{2} \phi_{ij,L}^{(2)} u_i u_j + \tfrac{1}{6} \phi_{ijk,L}^{(3)} u_i u_j u_k ,$$

where

$$\begin{aligned} \phi_L^{(0)} &= \alpha_M \phi_L(R_0) \equiv \Phi_L(R_0) , \\ \phi_{ij,L}^{(2)} &= 0 , \end{aligned} \tag{B12}$$

$$\phi_{ijk,L}^{(3)} = +15(ze)^2 \sum_n n_R \frac{R_1 R_2 R_3}{R^7} \epsilon_{ijk} , \tag{B13}$$

where n_R is the number of atoms (generally 12) on the layer of radius R around the origin and the summation is extended over all layers including the one with nearest neighbors at distance $R = R_0$ and in which case $n_R = n_0$.

The unit-cell coefficients $\phi^{(2)}$ and $\phi^{(3)}$ are then obtained by summing the two contributions or

$$\phi_{ij}^{(2)} = \phi_{ij,S}^{(2)} \equiv \phi^{(2)} \delta_{ij} , \tag{B14}$$

$$\phi_{ijk}^{(3)} = \phi_{ijk,S}^{(3)} + \phi_{ijk,L}^{(3)} \equiv \phi^{(3)} \epsilon_{ijk} . \tag{B15}$$

All the derivatives are evaluated at $R = R_0$.

For completeness we give also the formulas for the case of intermediate-range electrostatic or dispersion-type interactions which although not important at very large distances extend, however, to atoms more distant than nearest neighbors and accordingly their changes can be appreciable. Denoting by ϕ_I their contribution to ϕ and assuming this quantity to be a function of R, one has

$$\phi_{ij,I}^{(2)} = \sum_R n_R \left[\left(\frac{\partial^2 \phi_I}{\partial R^2} - \frac{1}{R} \frac{\partial \phi_I}{\partial R}\right) \frac{R_i R_j}{R^2} + \frac{1}{R} \frac{\partial \phi_I}{\partial R}\right] \delta_{ij} ,$$

$$\phi_{ij,I}^{(3)} = \sum_R n_R \left[\frac{\partial^3 \phi_I}{\partial R^3} + \frac{3}{R} \left(\frac{\partial \phi_I}{\partial R} - \frac{\partial^2 \phi_I}{\partial R^2}\right)\right] \frac{R_1 R_2 R_3}{R^3} \epsilon_{ijk} .$$

If in particular $\phi_I = D/R^m$, where $m > 1$, one obtains

$$\phi^{(2)}_{ij,I} = mD\sum_R n_R\left(\frac{m+2}{R^{m+2}}\ \frac{R_iR_j}{R^2} - \frac{1}{R^{m+2}}\right)\delta_{ij}\ ,$$

$$\phi^{(3)}_{ijk,I} = -\,m(m+2)(m+4)D\sum_R n_R\ \frac{R_1R_2R_3}{R^{m+6}}\ \epsilon_{ijk}\ ;$$

for $D < 0$ attractive intermediate-range forces, their contributions will have the same sign as the corresponding contributions of ϕ_L but opposite to those of ϕ_S. For the more general case these forces are actually angle and direction dependent and the corresponding formulas of $\phi^{(2)}$ and $\phi^{(3)}$ are slightly more complicated.

APPENDIX C: MACROSCOPIC RAMAN TENSOR

Here we show that the macroscopic Raman tensor conventionally defined through the third-order susceptibility $\chi^{(3)}$ is the same as the one derived in (3.37). The third-order susceptibility is formally defined[53] by

$$P^{(3)}_i(\omega_1+\omega_2+\omega_3) = D_3\chi^{(3)}_{ijkl}(\omega_1,\omega_2,\omega_3) \times E_j(\omega_1)E_k(\omega_2)E_l(\omega_3)\ , \qquad \text{(C1)}$$

where $\vec{P}^{(3)}(\omega_1+\omega_2+\omega_3)$ is the Fourier component at frequency $\omega_1+\omega_2+\omega_3$ of the induced third-order polarization, D_3 is equal to the number of distinct permutations of $(\omega_1, \omega_2, \omega_3)$, and $\vec{E}(\omega_i)$ are the applied fields. We formally introduce the third-order macroscopic polarizability per unit cell $\tilde{\gamma}$ by

$$\chi^{(3)}_{ijkl}(\omega_1,\omega_2,\omega_3) = (1/v)\tilde{\gamma}(\omega_1,\omega_2,\omega_3)\ , \qquad \text{(C2)}$$

where v is the volume of the unit cell. For crystals of the zinc-blende structure below the onset of electronic transitions and not in the neighborhood of the lattice resonance ω_T, $\tilde{\gamma}$ has two independent components $\tilde{\gamma}_{xxxx}$ and $\tilde{\gamma}_{xyxy}$. Here we are interested in the case where $\omega_1 = \omega_3$ and $\omega_2 < 0$, with ω_1, $-\omega_2 > \omega_T$, but $\omega_1+\omega_2 < \omega_T$ and all three frequencies $2\omega_1+\omega_2$, ω_1, and $-\omega_2$ are below the electronic gap. Then on purely phenomenological grounds and symmetry reasons one can show[54] that

$$\tilde{\gamma}_{xxxx} = \tilde{\gamma}^E_{xxxx} \qquad \text{(C3)}$$

and

$$\tilde{\gamma}_{xyxy} = \tilde{\gamma}^E_{xyxy} + \frac{(\tilde{\alpha}^{(1)}_{xyz})^2}{3M[\omega_T^2-(\omega_1+\omega_2)^2]}\ , \qquad \text{(C4)}$$

where $\tilde{\gamma}^E$ is the purely electronic third-order macroscopic polarizability and $\tilde{\alpha}^{(1)}_{xyz}$ the macroscopic Raman tensor of a unit cell. Presently we shall derive the expression of $\tilde{\gamma}$ from the microscopic description and the assumptions concerning the effective field adopted in the main text. More specifically we are interested in the component $\tilde{\gamma}_{xyxy}$ and we shall neglect $(\omega_1+\omega_2)$ compared to ω_T. For this purpose we take for convenience $\vec{E}(\omega_1)$ along the y direction and $\vec{E}(\omega_2)$ along the x direction and we derive the expression of the x component of $\vec{P}$ at frequency $2\omega_1+\omega_2$ including terms up to the third order on the fields. Taking into account the positions of the involved frequencies with respect to ω_T, one has

$$\begin{aligned}\vec{P}_x(2\omega_1+\omega_2) = {}& N\alpha^E[E_x(2\omega_1+\omega_2)+LP_x(2\omega_1+\omega_2)] + 2N\beta^{\mathrm{EO}}_{xyz}[E_y(\omega_1)+LP_y(\omega_1)]\,[E_z(\omega_1+\omega_2)+LP_z(\omega_1+\omega_2)]\\ &+3N[\gamma^E_{xyxy}+\tfrac{1}{3}(\alpha^{(1)})^2/M\omega_s^2]\,[E_y(\omega_1)+LP_y(\omega_1)]\,[E_x(\omega_2)+LP(\omega_2)]\,[E_y(\omega_1)+LP_y(\omega_1)]\\ ={}& P^{(1)}_x(2\omega_1+\omega_2)+P^{(2)}_x(2\omega_1+\omega_2)+P^{(3)}_x(2\omega_1+\omega_2)\ ,\end{aligned} \qquad \text{(C5)}$$

where

$$P^{(3)}_x(2\omega_1+\omega_2) = 2N(\beta^E+\tfrac{1}{2}\alpha^{(1)}\,e_f^*/M\omega_s^2)f^2E_y(\omega_1)LP^{(2)}_z(\omega_1+\omega_2) + 3N[\gamma^E_{xyxy}+\tfrac{1}{3}(\alpha^{(1)})^2/M\omega_s^2]f^4E_y(\omega_1)E_x(\omega_2)E_y(\omega_1)\ ,$$

and where γ^E_{xyxy} is the purely electronic third-order microscopic polarizability of a unit.

Replacing $P^{(2)}(\omega_1+\omega_2)$ by [compare (3.41)]

$$P^{(2)}_z(\omega_1+\omega_2) = 2N(\beta^E+\tfrac{1}{2}\alpha^{(1)}\,e_f^*/M\omega_s^2)f_0ffE_y(\omega_1)E_x(\omega_2)\ ,$$

one obtains finally

$$\begin{aligned}P^{(3)}_x&(2\omega_1+\omega_2)\\ &=4N^2(\beta^E+\tfrac{1}{2}\alpha^{(1)}\,e_f^*/M\omega_s^2)^2f^4f_0LE_y(\omega_1)E_x(\omega_2)E_y(\omega_1)\\ &\quad+3N(\gamma^E_{xyxy}+\tfrac{1}{3}(\alpha^{(1)})^2/M\omega_s^2)f^4E_y(\omega_1)E_x(\omega_2)E_y(\omega_1)\ .\end{aligned} \qquad \text{(C6)}$$

By straightforward algebra where use is made of (3.27), (3.30), (3.33a), and (3.33b) one obtains finally

$$\tilde{\gamma}_{xyxy} = \tilde{\gamma}^F_{xyxy} + \frac{1}{3}\ \frac{\tilde{\alpha}^{(1)}_{xyz}\,\tilde{\alpha}^{(1)}_{xyz}}{M[\omega_T^2-(\omega_1+\omega_2)^2]}\ ,$$

where

$$\tilde{\gamma}_{xyxy} = (\gamma^E_{xyxy}+\tfrac{4}{3}\beta_E^2NLf)f^4$$

and

$$\tilde{\alpha}^{(1)}_{xyz} = (\alpha^{(1)}+2NLe^*\beta_E)f^2\ .$$

This last expression is identical with the one derived in (3.37) as required.

APPENDIX D: EQUATION-OF-MOTION APPROACH

The equation of motion of the relative displacement coordinate $\vec{u}$ including nonlinear terms is

$$\ddot{u}_i + \omega_s^2 u_i + \tfrac{1}{2}\phi^{(3)}_{ijk} u_j u_k = e_f^*(E_i + LP_i) + \tfrac{1}{2}\mu^{(2)}_{ijk} u_j (E_k + LP_k) + \tfrac{1}{2}\alpha^{(1)}_{ijk}(E_j + LP_j)(E_k + LP_k) \; . \qquad \text{(D1)}$$

The total polarization, on the other hand, is

$$P_i = N[e_f^* u_i + \tfrac{1}{2}\mu^{(2)}_{ijk} u_j u_k + \alpha^E (E_i + LP_i) + \alpha^{(1)}_{ijk} u_j (E_k + LP_k) + 2\beta_{ijk}(E_j + LP_j)(E_k + LP_k)] \; , \qquad \text{(D2)}$$

where $\vec{E}$ here is the total macroscopic field and the different coefficients are defined in the text. Expression (D2) can also be written as follows:

$$P_i = N[e_T^* u_i + \tfrac{1}{2} f \mu^{(2)}_{ijk} u_j u_k + f\alpha^E E_i + f\alpha^{(1)}_{ijk} u_j (E_k + LP_k) + 2f\beta_{ijk}(E_j + LP_j)(E_k + LP_k)] \; . \qquad \text{(D3)}$$

After substitution of this expression in (D1) rearrangement of the terms and use of (3.33a), (3.33b), (3.37), (3.43), and (3.44) one obtains

$$\ddot{u}_i + \omega_T^2 u_i + \tilde{\phi}^{(3)}_{ijk} u_j u_k = e_T^* E_i + \mu^{(2)}_{ijk} u_j E_k + \tfrac{1}{2}\tilde{\alpha}^{(1)}_{ijk} E_j E_k \; . \qquad \text{(D4)}$$

If this equation is solved iteratively for each different Fourier component up to the second order on the electric fields and its solution replaced in (D3), one obtains

$$P_i = \chi^{(1)}_{ii} E_i + \chi^{(2)}_{ijk} E_j E_k \; ,$$

where $\chi^{(2)}_{ijk}$ is given by (3.47) and $\chi^{(1)}$ by (2.2b). In this phenomenological approach the finite lifetime of the phonons can be taken into account by introducing a linear velocity-dependent term γu_i in the right-hand side of Eq. (D1).

The previous discussion referred to the purely transverse polarization. The same procedure can be used for the longitudinal polarization; one only needs to replace E by $E - 4\pi P_L$ in (D1)–(D3) whenever the field is longitudinal. For the case of all fields and polarizations being longitudinal the equation of motion for a longitudinal mode, then, becomes simply

$$\ddot{u}_i + \omega_L^2 u_i + \tilde{\phi}^{(3)}_{L,ijk} u_j u_k = e_L^* E_i + (\tilde{\mu}_{L,ijk}/\epsilon_\infty) u_j E_k + \tfrac{1}{2}(\tilde{\alpha}^{(1)}_{L,ijk}/\epsilon_\infty^2) E_j E_k \; , \qquad \text{(D5)}$$

where $\tilde{\alpha}^{(1)}_{L,ijk} = \tilde{\alpha}^{(1)}_L \epsilon_{ijk}$, $\tilde{\mu}_{L,ijk} = \tilde{\mu}^{(1)}_L \epsilon_{ijk}$, and $\tilde{\phi}^{(3)}_{L,ijk} = \tilde{\phi}^{(3)}_L \epsilon_{ijk}$, and $\tilde{\alpha}^{(1)}_L$, $\tilde{\mu}^{(2)}_L$, and $\tilde{\phi}^{(3)}_L$ are given by (3.62), (3.65a), and (3.65b), respectively. We note that it is the frequency of the longitudinal mode ω_L that now determines the dispersion.

APPENDIX E: δ-FUNCTION-BOND MODEL

The δ-function-bond model[14] consists of a one-electron unidimensional Schrödinger equation with

$$H_0 = -\frac{\hbar^2}{2m}\frac{d^2}{d^2 z} + V(z)$$

and

$$V(z) = -g_a \delta(z + \tfrac{1}{2}R_0) - g_b \delta(z - \tfrac{1}{2}R_0) \; ,$$

where z is the coordinate of motion along the internuclear axis directed from A to B, $R_0 = 2d$ is the δ-function spacing, g_a and g_b are the δ-function strengths for nucleus a and b, respectively, and $\delta(x)$ is the Dirac function.

The ground-state wave function is of the form $N(\psi_B + \lambda\psi_A)$ and its explicit form is

$$\psi_{\rm I} = N e^{cz}(e^{cd} + \lambda e^{-cd}) \; , \quad -\infty < z \le -\tfrac{1}{2}R_0 \quad \text{region I}$$

$$\psi_{\rm II} = N e^{-cd}(e^{-cz} + \lambda e^{cz}) \; , \quad -\tfrac{1}{2}R_0 < z \le \tfrac{1}{2}R_0 \quad \text{region II}$$

$$\psi_{\rm III} = N e^{-cz}(e^{-cd} + \lambda e^{cd}) \; , \quad \tfrac{1}{2}R_0 < z < \infty \quad \text{region III}$$

with

$$c = \tfrac{1}{2}\{g_a + g_b + [(g_a + g_b)^2 - 4(1 - e^{-2cR_0}) g_a g_b]^{1/2}\} \frac{1}{e^2 a_0} = g\{1 + [\mu^2 + (1 - \mu^2) e^{-2cR_0}]^{1/2}\} \frac{1}{e^2 a_0} \; , \qquad \text{(E1)}$$

$$\lambda = \left(\frac{1 - c/g_b}{1 - c/g_a}\right)^{1/2} \; , \qquad \text{(E2)}$$

$$\frac{N^2}{c} = \frac{1}{1 + \lambda^2 + 2\lambda e^{-cR_0}(1 + cR_0)} \; , \qquad \text{(E3)}$$

where $2g = g_a + g_b$ and $2\mu g = g_a - g_b$ with $g_b > g_a$.

In the presence of an electric field with a component E_z along the bond, the perturbing potential is

$$H' = -qzE_z \; , \qquad \text{(E4)}$$

where q is the electronic charge in this model.

It was shown in Ref. 3 that the Dalgarno-Lewis equation (4.3) which solves the perturbation problem for (E4) can be solved exactly. The different moments $\langle z^n \rangle$ of the electronic distribution can be obtained from

$$\langle e^{ikz} \rangle = \frac{4cN^2}{k^2 + 4c^2}\left(e^{-ikd} + \lambda^2 e^{ikd} + 2\lambda e^{-2cd} \times \frac{kd\cos kd + 2cd \sin kd}{kd}\right) .$$

In particular the electronic bond dipole moment is

$$p = 2q\langle z \rangle = -qR(1 - \lambda^2)N^2/c \; . \qquad \text{(E5)}$$

In the Unsöld approximation the linear and second-order polarizabilities along the bond are

$$\alpha_{\parallel} = \left(\frac{q}{e}\right)^2 \frac{R^4}{2a_0}\left[1 + \frac{2}{(cR)^2} - \frac{N^2}{c}\left(\frac{4cR}{3} e^{-cR} + \frac{N^2}{c}(1 - \lambda^2)^2\right)\right]^2 , \qquad \text{(E6)}$$

$$\beta_{\parallel}=\frac{3}{16}\left(\frac{q}{e}\right)^3\frac{R^7}{ea_0^2}(1-\lambda^2)\frac{N^2}{c}\times\left[1+\frac{2}{(cR)^2}-\frac{N^2}{c}\left(\frac{4cR}{3}e^{-cR}+\frac{N^2}{c}(\lambda^2-1)^2\right)\right]^2\times\left[1+\frac{2}{(cR)^2}-\frac{N^2}{c}\left(2cRe^{-cR}+\frac{N^2}{c}(1-\lambda^2)^2\right)\right]. \tag{E7}$$

With the two strengths of the δ functions, g_a and g_b, one can associate the nuclear charges Z_Aq and Z_Bq defined by

$$Z_Aq=g_a \text{ and } Z_Bq=g_b . \tag{E8}$$

The g_i are obtained through the electronegativity scale.

All the above expressions follow directly from the knowledge of the exact wave function of the model. The potential, however, cannot be derived from the latter without further assumptions. We adopt Lippincott's prescriptions[14] which amount to assuming

$$\phi(R)=D_e(1-e^{-n\,\Delta R^2/2R}), \tag{E9}$$

where D_e is the dissociation energy of the bond, $\Delta R=R-R_0$ and $n=n_0(I/I_0)_A^{1/2}(I/I_0)_B^{1/2}$, with $(I/I_0)_i$ the ionization potential of $i=A, B$, relative to that of the corresponding atom in the same row and first column of the Periodic Table and n_0 is a constant. Requiring that, at equilibrium, the first derivative vanishes and that the second-order derivative $\phi''=k_e$, the stretching force constant of the bond, one obtains

$$D_e=k_eR_0/n . \tag{E10}$$

---

*Research supported in part by the Joint Services Electronics Program under Contract No. N00014-67-A-0298-0006.

†On leave from Laboratoire d'Optique Quantique, Institut d'Optique, Université de Paris-Sud, Centre d'Orsay, 91-Orsay, France.

[1] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. 127, 1918 (1962).

[2] P. N. Butcher and T. B. McLean, Proc. Phys. Soc. (London) 81, 219 (1962).

[3] J. Ducuing and C. Flytzanis, in *Optical Properties of Solids*, edited by F. Abélès (North-Holland, Amsterdam, 1971).

[4] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1954).

[5] G. M. Genkin, V. M. Fain, and E. G. Yaschin, Zh. Eksperim. i Teor. Fiz. 52, 897 (1967) [Sov. Phys. JETP 25, 592 (1967)].

[6] C. G. B. Garrett, J. Quantum Electron. QE-4, 70 (1968).

[7] C. Flytzanis, Phys. Rev. Letters 23, 1336 (1969).

[8] C. Flytzanis and J. Ducuing, Phys. Rev. 178, 1218 (1969). The expression (2.5) of the coefficient $\chi_{14}^{(2)}$ derived there is by a factor 2 larger than $\chi_E^{(2)}$ used in the present work; accordingly the values of $\chi_{14}^{(2)}$ given there are those of the quantity $2\chi_E^{(2)}$ in the present work.

[9] S. Jha and N. Bloembergen, Phys. Rev. 171, 891 (1968).

[10] W. L. Faust and C. H. Henry, Phys. Rev. Letters 17, 1265 (1966).

[11] W. Cochran, Advan. Phys. 9, 387 (1960).

[12] K. Huang, Report No. L/T 239 of the British Electrical and Allied Industries Research Association, 1950 (unpublished); Proc. Roy. Soc. (London) A208, 352 (1951).

[13] B. Szigeti, Trans. Faraday Soc. 45, 155 (1949).

[14] A. A. Frost, J. Chem. Phys. 25, 1150 (1954); E. R. Lippincott, *ibid.* 23, 603 (1955).

[15] J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970); J. A. van Vechten, Phys. Rev. 182, 891 (1969); 187, 1007 (1969).

[16] T. Kurosawa, J. Phys. Soc. Japan 16, 1298 (1961).

[17] R. H. Lyddane, R. G. Sachs, and E. Teller, Phys. Rev. 59, 643 (1941).

[18] This statement and expression (2.13) below are valid only for long-wavelength $(\vec{k}\simeq 0)$ phonons where the polarization vectors for acoustic modes tend to zero; this remark applies to all similar expressions which will be given below.

[19] C. A. Coulson, L. B. Rédei, and D. Stocker, Proc. Roy. Soc. (London) 270, 357 (1962).

[20] C. A. Coulson and G. Doggett, Intern. J. Quantum Chem. 2, 825 (1968).

[21] E. N. Korol and K. B. Tolpygo, Phys. Status Solidi (b) 45, 71 (1971); see also V. S. Mashkevich and K. B. Tolpygo, Dokl. Akad. Nauk SSSR 1, 575 (1956) [Sov. Phys. Doklady 1, 690 (1956)].

[22] M. J. P. Musgrave and J. A. Pople, Proc. Roy. Soc. (London) A268, 474 (1962).

[23] For a simple calculation of such forces in molecular systems, see E. S. Rottner, J. Chem. Phys. 19, 1030 (1951).

[24] See, for instance, B. Szigeti, Proc. Roy. Soc. (London) A204, 51 (1950).

[25] K. S. Krishnan and S. K. Roy, Proc. Roy. Soc. (London) A207, 447 (1951).

[26] The division of e_f^* into a rigid and a deformation part is reminiscent, but not equivalent, of the one used in shell models or deformation dipole models used in ionic crystals. For a detailed discussion and literature, see D. Dick, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 159.

[27] The true eigenfrequency of the system is ω_T and not ω_S.

[28] For conventions and notations concerning macroscopic second-order susceptibilities, see G. D. Boyd and D. A. Kleinman, J. Appl. Phys. 39, 3597 (1968), Appendix 2.

[29] The first term in the expression of $\tilde{\alpha}^{(1)}$ apparently originating from purely electronic processes is not equivalent to the one considered by F. Matossi and R. Mayer, Phys. Rev. 74, 449 (1948) to explain some peculiarities of the Raman effect.

[30] H. Poulet, Ann. Phys. (Paris) 10, 908 (1955); see also R. Loudon, Advan. Phys. 13, 423 (1964).

[31] I. Kaminow, in *Ferroelectricity*, edited by E. F. Weller (Elsevier, Amsterdam, 1967); see also I. S. Zheludev, Usp. Fiz. Nauk 88, 253 (1966) [Sov. Phys. Usp. 9, 97 (1966)].

[32] M. Born and M. Blackman, Z. Physik 82, 551 (1933);

M. Blackman, *ibid.* 86, 421 (1933); see also J. Neuberger and R. D. Hatcher, J. Chem. Phys. 34, 1733 (1961).

[33] B. Szigeti, Proc. Roy. Soc. (London) A252, 217 (1959); A258, 377 (1960); in Ref. 26, p. 377.

[34] D. Kleinman, Phys. Rev. 118, 118 (1960).

[35] V. V. Mitskevitch, Fiz. Tverd. Tela 3, 3036 (1961); 4, 3035 (1962) [Sov. Phys. Solid State 3, 2211 (1962); 4, 2224 (1963)].

[36] C. Flytzanis (unpublished); see also, C. Flytzanis, in *Treatise in Quantum Electronics*, edited by H. Rabin and C. L. Tang (Wiley, New York, to be published), Vol. I.

[37] A. Dalgarno and J. Lewis, Proc. Roy. Soc. (London) A233, 701 (1956); C. Schwartz, Ann. Phys. (N. Y.) 6, 156 (1959); see also M. Karplus and J. Kolker, J. Chem. Phys. 39, 2011 (1963).

[38] For a calculation of the Raman tensor of diatomic molecules with this model see T. Veach Long and R. A. Plane, J. Chem. Phys. 43, 457 (1965); for a more detailed discussion of different calculations of $\alpha^{(1)}$ for molecules see also J. Tang and A. C. Albrecht, *ibid.* 49, 1144 (1968).

[39] C. L. Tang and C. Flytzanis, Phys. Rev. B 4, 2520 (1971).

[40] S. Ushioda, A. Pinczuk, W. Taylor, and E. Burstein, in *II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1968).

[41] A. Moradian and A. L. McWhorter, in *Proceedings of the International Conference on Light Scattering in Solids, New York University*, edited by G. B. Wright (Springer-Verlag, New York, 1968).

[42] I. P. Kaminow and W. D. Johnston, Phys. Rev. 188, 1209 (1969).

[43] G. D. Boyd, T. J. Bridges, M. A. Pollack, and E. H. Turner, Phys. Rev. Letters 26, 387 (1971). The separation out of $\chi_M^{(2)}$ of the contribution $\chi_H^{(2)}, +\chi_N^{(2)}$ given there is not altogether correct since a contribution $2C_1\chi_E^{(2)}$ is included which is of an entirely different nature [compare (3.39) with (3.46b)].

[44] R. Geick, Phys. Rev. 138, A1495 (1965).

[45] J. J. Wynne and N. Bloembergen, Phys. Rev. 188, 1211 (1969).

[46] In Ref. 7, using an old value for $e_S^* = [3/(\epsilon_\infty + 2)]\, e_T^* = 1.2$, it was found that $C_1 \simeq 0.2$ for CuCl. This value for e_S^*, however is incorrect; e_T^* has been remeasured recently by Iwasa [thesis (University of Pennsylvania) (unpublished)] and found $e_T^* = 1.2$ which gives $e_S^* = 0.5$ ($\epsilon_\infty = 3.5$ and $\epsilon_0 = 6.5$). With e_S^* smaller than unity repeating the argument of Ref. 7 one obtains $C_1 \simeq -1.2$; for this crystal e_T^* is positive or equivalently Cu behaves as a positive ion. A simple calculation predicts, then, that the signs of C_i alternate. Further, due to the *d* states it is predicted (Refs. 3 and 39) that $\chi_E^{(2)}$ is negative for this compound. The simple calculation, then, predicts that $\chi_M^{(2)} > 0$ with the axis conventions of Fig. 1 and almost by an order of magnitude larger than $-\chi_E^{(2)}$.

[47] R. L. Kelly, Phys. Rev. 151, 721 (1966).

[48] L. R. Swanson and Maradudin, Solid State Commun. 8, 589 (1970).

[49] We point out that in the case of purely ionic cubic crystals like NaCl, where the effective field factor $f = (\epsilon_\infty + 2)/3$ can be used, the expressions for e_T^*, ω_T, $\mu^{(2)}$, and $\phi^{(3)}$ derived in the present work reduce to the ones given by Szigeti, Refs. 13. 24, and 34, respectively. However, this author does not take into account the contributions in $\mu^{(2)}$ and $\phi^{(3)}$ originating from β_E and $\alpha^{(1)}$ and which provide additional phonon interaction terms (see Ref. 36).

[50] We restrict ourselves to the coefficient $\chi_{zzz}^{(2)}$ in these compounds; the *z* axis in wurzite structure is equivalent to one of the [111] directions in the zinc-blende structure and the axis convention of Fig. 1 is still valid.

[51] This statement is correct only if $e_T^* < 0$ with the axis conventions adopted. This seems to be confirmed by the sign of the experimental values of $\chi_{\mathrm{EO}}^{(2)} - \chi_E^{(2)}$.

[52] Slightly different classification is used in Ref. 3.

[53] P. D. Maker and R. W. Terhune, Phys. Rev. 137, A801 (1965).

[54] E. Yablonovitch, C. Flytzanis, and N. Bloembergen, in Seventh International Quantum Electronics Conference, Montreal, Canada, 1972 (unpublished); and (unpublished).

PHYSICAL REVIEW B VOLUME 6, NUMBER 4 15 AUGUST 1972

Raman Scattering from ZnS Polytypes[*]

J. Schneider[†] and R. D. Kirby[‡]
Department of Physics and Materials Research Laboratory, University of Illinois,
Urbana, Illinois 61801

(Received 17 February 1972)

The Raman spectra of the 2*H* and 4*H* structures of ZnS have been measured between room temperature and 60 K, and compared with the spectra from zinc blende ZnS. The observed phonons in each case are in good agreement with those expected from the known structural differences.

ZnS is known[1] to crystallize in many different crystal structures belonging to the cubic, hexagonal, and rhombohedral space groups. All such ZnS polytypes[1] can be constructed from alternating zinc and sulphur planes which are perpendicular to the cubic [111] or hexagonal [0001] axis, with the various polytypes being distinguished only by the stacking sequence of the planes. The most important characteristic which distinguishes one polytype from another is then the length *c* of the funda-