ELECTRO-OPTIC COEFFICIENTS IN III-V COMPOUNDS

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The electro-optic coefficients $\chi_{E0}^{(2)}$ for six III-V compounds InSb, InAs, InP, GaSb, GaAs, and GaP with the zinc-blende structure are calculated using an electrostatic point-charge model. An interpretation of the Faust-Henry result for GaP is presented and an approximate relation is shown to exist between the Faust-Henry coefficient C and the electronic deformation part of the transverse effective charge e_T^{+} in these compounds. The case of CuCl is also briefly discussed.

The linear electro-optic effect may be regarded as the second-order polarization $\vec{P}^{(2)}=\chi_{E0}^{(2)}\vec{E}_\omega\vec{E}_\Omega$ induced in the crystal under the action of a high-frequency field $\vec{E}_\omega$ and a low-frequency field $\vec{E}_\Omega$, where ω is a frequency well below the onset of electronic transitions but above the infrared lattice resonances while Ω is below the latter. The family of III-V compounds possessing the zinc-blende structure (point group symmetry $\bar{4}3m$) is the simplest crystalline class showing a nonvanishing linear electro-optic effect. These compounds are of cubic symmetry with two atoms per unit cell and they consequently have a threefold-degenerate infrared-active long-wavelength optic mode which in a crystal of finite dimensions is split into a doubly degenerate transverse mode Ω_T and a longitudinal mode Ω_L due to long-range electrical field effects.

In the present work we shall give a calculation of $\chi_{E0}^{(2)}$ in these compounds and relate these coefficients to $\chi_E^{(2)}$, the high-frequency second-order susceptibility.

The second-order polarization $\vec{P}^{(2)}$ has two contributions,[1] $\vec{P}_E^{(2)}$ and $\vec{P}_H^{(2)}$. In fact, the "static" field $\vec{E}_\Omega$ through its coupling with the electrons induces ionic displacements $\vec{u}_i^{\,T}=e_T^{+}\vec{E}_\Omega/M_i\Omega_T^{2}$ in the transverse mode where e_T^{+} is the transverse macroscopic effective charge and M_i is the mass of nucleus $i=\mathrm{III}$, V. The electronic distribution within a unit cell depends mainly on the relative positions of the ions in the cell and the displacements of these ions induce therefore a distortion of the electronic clouds. This short-range deformation field together with $\vec{E}_\omega$ induces the hybrid polarization $\vec{P}_H^{(2)}$. A further contribution $\vec{P}_E^{(2)}=\chi_E^{(2)}\vec{E}_\omega\vec{E}_\Omega$ comes from the direct coupling of the electrons with the two effective fields set up by $\vec{E}_\omega$ and $\vec{E}_\Omega$, respectively, the lattice being held fixed.

These same short-range forces are responsible also for the actual values of the effective charges e_T^{+} in ionic and covalent crystals as measured by infrared absorption.[2] In these crystals the effective charges are different from the formal atomic charges and this effect can be accounted for by assuming that the short-range forces[2,3] induce an electronic dipole moment $\vec{p}_H^{(1)}$ per unit cell in addition to that due to the long-range effective field set up in the crystal by $\vec{E}_\Omega$. Accordingly $\vec{p}_H^{(1)}$ and $\vec{P}_H^{(2)}$ must be considered concurrently.

The pure electronic contribution $\vec{P}_E^{(2)}=\chi_E^{(2)}\vec{E}_\omega\vec{E}_\Omega$ in III-V compounds has been successfully accounted for[4,5] by assuming that only the valence electrons of the four effectively localized tetrahedral bonds per unit cell contribute to $\chi_E^{(2)}$. It is clear that these same bonding electrons which reflect the structural features of the crystal will be most deformed by the displacements of the nuclei and contribute most to $\vec{P}_H^{(2)}$ as well.

To represent the charge distribution in a III-V compound we shall use a model analogous to the dielectric bond model discussed by Phillips[6,7] and applied to estimate the longitudinal macroscopic or Callen effective charge $e_C^{+}=e_T^{+}/\epsilon_\infty$, where ϵ_∞ is the high-frequency dielectric constant of the compound. Two positive charges Q_{III} and Q_{V} are located on the atomic sites III and V of a unit cell. These charges are neutralized by four negative bonding charges Q_c situated, respectively, on the four bonds tetrahedrally oriented around each atom. We assume point charges. The position of Q_c along the bond line is determined approximately by the condition[6,8]

$$V_{\mathrm{III}}(R_{\mathrm{III}})=V_{\mathrm{V}}(R_{\mathrm{V}}),\tag{1}$$

where $V_i(R)$ is the local potential, inside the bond, of the covalent atom i and R_i is the distance of the bonding charge Q_c from atom $i=\mathrm{III}$, V of the bond. This model has been used[9,10] to calculate the second-order electronic susceptibility $\chi_E^{(2)}$ in good agreement with experiment. We shall extend the simpler Levine approach which ascribes $\vec{P}_E^{(2)}$ to the anharmonic motion of the point bonding charges Q_c acted upon by the fields $\vec{E}_\omega$ and $\vec{E}_\Omega$[10] and we shall assume that $\vec{P}_H^{(2)}$ is due to the anharmonic motion of these same charges under the action of $\vec{E}_\Omega$ and the change of the potentials $V_i(R)$ due to the displacements $\vec{u}_i^T$.

In the diatomic crystals with the zinc-blende structure e_T^+ is a scalar and $\chi_{E0}^{(2)}$ as well as $\chi_E^{(2)}$ has only one component. We take, for convenience, the electric fields $\vec{E}_\omega$ and $\vec{E}_\Omega$ along the crystalline 111 axis. We assume that the effective field inside the crystal can be written $\vec{E}_{\text{eff}} = \vec{E} + \mathcal{L}\vec{P}$, where $\mathcal{L}$ is a generalized Lorentzian factor taken constant over the unit cell and $\vec{P}$ is the polarization set up in the crystal. The linear macroscopic polarization $\vec{P}^{(1)}$ due uniquely to $\vec{E}_\Omega$ is

$$\vec{P}^{(1)} = N(Q_{\text{III}}\vec{u}_{\text{III}}^{\,T} + Q_{\text{V}}\vec{u}_{\text{V}}^{\,T} + \vec{p}_H^{(1)}) + N\alpha_E(\vec{E}_\Omega + \mathcal{L}\vec{P}^{(1)}), \tag{2}$$

where α_E, a scalar, is the linear high-frequency microscopic polarizability per unit cell and N is the number of unit cells per unit volume. For a transverse optic mode we have $M_{\text{III}}\vec{u}_{\text{III}}^{\,T} + M_{\text{V}}\vec{u}_{\text{V}}^{\,T} = 0$ and since $\vec{p}_H^{(1)}$ is a dipole moment due to the coupling of the ionic displacements and the electronic polarization we may write

$$\vec{p}_H^{(1)} = Q_d\vec{u}^T, \tag{3}$$

where $\vec{u}^T = \vec{u}_{\text{III}}^{\,T} - \vec{u}_{\text{V}}^{\,T} = (\epsilon_0 - \epsilon_\infty)\vec{E}_\Omega/4\pi e_T^+ N$, Q_d is an apparent deformation bonding charge which measures also the strength of the short-range deformation forces, and ϵ_0 is the static dielectric constant of the compound. After some reshuffling of the terms in (2) we obtain[11]

$$\begin{aligned}\vec{P}^{(1)} &= NfQ_f\vec{u}^T + N\alpha_E f\vec{E}_\Omega \\ &= Ne_T^+\vec{u}^T + \frac{\epsilon_\infty - 1}{4\pi}\vec{E}_\Omega,\end{aligned} \tag{4}$$

where $f = 1/(1 - \mathcal{L}N\alpha_E)$ is the effective-field factor, $fQ_f = e_T^+$, and

$$Q_f = Q_L + Q_d = \frac{M}{M_{\text{III}}}(Q_{\text{III}} + Q_d) - \frac{M}{M_{\text{V}}}(Q_{\text{V}} - Q_d). \tag{5}$$

Q_L is the static ionic charge of the unit cell and $M^{-1} = M_{\text{III}}^{-1} + M_{\text{V}}^{-1}$.

The second-order polarization on the other hand is written

$$\begin{aligned}\vec{P}^{(2)} &= \chi_E^{(2)}\vec{E}_\omega\vec{E}_\Omega + \vec{P}_H^{(2)} \\ &= Nf^3\beta_E\vec{E}_\omega\vec{E}_\Omega + \vec{P}_H^{(2)},\end{aligned} \tag{6}$$

where β_E is the second-order electronic polarizability per unit cell for fields along the 111 axis and the effective field corrections were taken explicitly into account.[12]

To simplify the calculations and keep in sight the most important features which are likely to affect the estimation of the short-range interaction polarization we have assumed that $V_i(R_i) = \frac{1}{4}(Q_i/R_i)f_{\text{TF}}$ ($i = \text{III, V}$), where f_{TF} is the Thomas-Fermi screening factor taken approximately constant; further we have implicitly assumed that only $\frac{1}{4}Q_i$ of each covalent atom is effective inside the bond, the rest being neutralized by the other three adjacent negative bonding charges; this takes into account partially bond-bond repulsion interactions within a unit cell and amounts to treating the bonds inside the crystal as neutral molecules.[8] With this choice of the potentials $V_i(R_i)$ the calculation of the change of these potentials at the position of the bonding charges because of the atomic displacements $\vec{u}_i^T$ reduces to that of the electric field $\vec{E}_d = C_d\vec{E}_\Omega$ due to the electric dipoles $\frac{1}{4}Q_{\text{III}}f_{\text{TF}}\vec{u}_{\text{III}}^{\,T}$ and $\frac{1}{4}Q_{\text{V}}f_{\text{TF}}\vec{u}_{\text{V}}^{\,T}$ at the position of the bonding charge. Expressing $\vec{u}_i^T$ in terms of $\vec{u}^T$ and using (1) we obtain

$$C_d = -\frac{512}{3\sqrt{3}}Q_c^3\left(\frac{M}{M_{\text{III}}}Q_{\text{III}}^{-2} - \frac{M}{M_{\text{V}}}Q_{\text{V}}^{-2}\right) \times f_{\text{TF}}\frac{\epsilon_0 - \epsilon_\infty}{4\pi e_T^+}. \tag{7}$$

It is this equivalent electrical field which induces $\vec{p}_H^{(1)}$ and together with $\vec{E}_\omega$ induces $\vec{p}_H^{(2)}$. Accordingly we may write

$$\vec{p}_H^{(1)} = \alpha_E\vec{E}_d. \tag{8}$$

Expression (2) can be rewritten then as follows

$$\vec{P}^{(1)} = NfQ_L\vec{u}^T + N\alpha_E(1 + C_d)f\vec{E}_\Omega. \tag{9}$$

Similarly $\vec{P}_H^{(2)}$ can be expressed in terms of β_E in the same way as $\vec{P}_E^{(2)}$. Taking into account the effective field factors we obtain from (6)

$$\begin{aligned}\vec{P}^{(2)} &= Nf^3\beta_E(1 + C_d)\vec{E}_\omega\vec{E}_\Omega \\ &= \chi_E^{(2)}(1 + C_d)\vec{E}_\omega\vec{E}_\Omega.\end{aligned} \tag{10}$$

Comparing (3) with (8) we obtain within this simple point-charge model the following relation between C_d and Q_d:

$$C_d = \frac{Q_d}{Q_f}\,\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_\infty - 1}. \tag{11}$$

This expression, which does not contain explicitly the effective field factor, permits us to determine the sign of C_d with respect to that of Q_d and Q_f. Once C_d has been calculated, $\chi_{E0}^{(2)}$

can also be calculated by

$$\chi_{E0}^{(2)}=(1+C_d)\chi_E^{(2)}, \tag{12}$$

where $\chi_E^{(2)}$ are the values given by Levine.[10] Similarly, once Q_d has been calculated, Q_f can also be calculated by $Q_f=Q_L+Q_d$ and an effective field factor can be determined by requiring that $e_T^+=fQ_f$ is equal to its experimentally determined value.[13] These values of f are to be considered as rough estimates rather than the actual values of the effective field.

The charges $Q_{\rm III}$ and $Q_{\rm V}$ were taken equal to $\epsilon_\infty e_{\rm III}^+$ and $\epsilon_\infty e_{\rm V}^+$, respectively, where $e_{\rm III}^+$ and $e_{\rm V}^+$ are slightly different from the screened valence charges given by Phillips[6] and assumed independent of the crystalline environment; their values are $e_{\rm In}^+=0.13$, $e_{\rm Ga}^+=0.18$, $e_{\rm Sb}^+=0.40$, $e_{\rm As}^+=0.55$, and $e_{\rm P}^+\simeq 0.74$.

The results of the calculation for C_d and f for InSb, InAs, InP, GaSb, GaAs, and GaP are given in Table I. The values for the effective field factor f thus obtained are in general smaller than the ones corresponding to the full Lorentzian correction $f_L=\frac{1}{3}(\epsilon_\infty+2)$ but are still substantially larger than unity. They are in fair agreement, except for GaSb, with those obtained in Ref. 5.

The only existing reliable experimental value for C is that of Faust and Henry[14] for GaP; these authors studied the dispersion of the second-order susceptibility near the Reststrahlen frequency Ω_T and were able to fit their experimental results with a curve of the form $\chi^{(2)}=\chi_E^{(2)}\{1+C/[1-(\Omega/\Omega_T)^2]\}$. For Ω well below the lattice frequency Ω_T one obtains $\chi_E^{(2)}(1+C)$ which is to be compared with expression (12). The agreement between the experimental and the theoretical value for this compound is satisfactory both with respect to magnitude and sign. For the other compounds there is no similar study. The measured value for GaAs was obtained by comparing the experimental values of $\chi_{E0}^{(2)}$ and $\chi_E^{(2)}$[15]; here again the agreement seems to be satisfactory. Actually the calculation shows that C_d is negative for all six III-V compounds considered; Q_f was found to be negative while Q_d is positive. Due to the fact that C_d and Q_d are both lattice-induced quantities, they show the characteristic dispersion behavior near Ω_T and a systematic experimental study of the dispersion of $\chi^{(2)}$ near Ω_T similar to that conducted by Faust and Henry for GaP combined with relation (11) may also give some valuable information about Q_d which cannot be obtained otherwise by infrared absorption since Q_d cannot be separated from the rigid ionic component Q_L.

Table I. Calculated values of the Faust-Henry coefficient $C=(\chi_{E0}^{(2)}-\chi_E^{(2)})/\chi_E^{(2)}$ and the effective field factor f.

	C		
	Calc	Exp	f
InSb	−0.36		3.8
InAs	−0.61		2.3
InP	−0.52		1.3
GaSb	−0.21		6.
GaAs	−0.55	−0.60[a]	3.
GaP	−0.51	−0.53[b]	1.7

[a] See Ref. 15.

[b] See Ref. 14.

The same model may be used for II-VI compounds like ZnS but due to the large admixture of covalent and ionic binding in these compounds additional interactions may be present which will invalidate the above simple considerations. For I-VII compounds like CuCl on the other hand the ionic binding is predominant and the shell model[3] seems to be more adequate. The short-range interaction polarization is due then to the repulsion between closed-shell electron configurations. Assuming $f=f_L=\frac{1}{3}(\epsilon_\infty+2)$ and taking $Q_{\rm I}=-Q_{\rm VII}=e$ in (2), Q_f may be identified then with the Szigeti charge e_S^+; relation (11) still holds since one can always define an equivalent electrical field by (8). The fact that $e_S^+=Q_f$ is larger than unity for this compound seems to indicate that for this compound C_d is positive and approximately equal to 0.2.

A different approach has been used by Kelly[16] for the calculation of $\chi_{E0}^{(2)}$ in CuCl and ZnS assuming pure ionic binding. Our approach stresses explicitly the fact that the hybrid term $\vec{P}_H^{(2)}$ as well as $\vec{p}_H^{(1)}$ has its origin in the electrons and arises from the coupling of the ionic displacements and the electronic polarization of the bonds, a coupling beyond the one due to the long-range effective field. This is due to the change of the potential felt by electrons inside the unit cell. Any improvements must take into account explicitly the bond-bond interactions and replace the point charges, which are not adequate when nonuniform short-range forces are considered by more realistic extended distributions. This can be done only with rigorous quantum mechanical calculations or with a more sophisticated shell model instead of the electrostatic point-charge model used here.

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ELECTRODISINTEGRATION OF ^{3}H AND ^{3}He

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Two- and three-body electrodisintegration cross sections for ^{3}H and ^{3}He are calulated with nucleon-nucleon interactions represented by nonlocal, separable forms. Good agreement with experiment is obtained with Tabakin's ground state for the range of incident energies 250 to 550 MeV.

During the past several years, considerable attention has been given to the study of inelastic electron scattering from ^{3}H and ^{3}He in order to investigate their structure. Experimental effort has involved high- and low-energy electrons at various electron-scattering angles,[1] including an experiment where the fast proton was detected in coincidence with the scattered electron.[2] Theoretical effort has been devoted mainly to the coincidence cross section for two-body breakup of ^{3}He with the ground state represented by an analytic form containing one or two parameters which are determined from photodisintegration and/or form-factor data.[3] However, a pole-model calculation for comparison with the first high-energy data where only the electron is detected (hereafter called the inelastic cross section as opposed to the coincidence cross section) has been carried out.[4] The constant vertex parameters of this model were determined from the coincidence data with the result that the inelastic cross sections were 30 to 70% too high. A reanalysis of the coincidence data resulted in qualitative agreement, but is limited due to the ambiguities in interpreting the experimental data and the lack of an accurate calculation of the three-body coincidence cross section. Thus these circumstances, along with the availability of more recent inelastic cross-section data,[5] indicate the importance of an accurate three-body coincidence calculation and of a calculation of the inelastic cross sections without use of the coincidence data. The purpose of this Letter is to report the results of such work for the processes

$$e + {}^3\mathrm{He} \to e' + p + \mathrm{D} \qquad (1a)$$

$$\to e' + p + n + p \qquad (1b)$$

and

$$e + {}^3\mathrm{H} \to e' + n + \mathrm{D} \qquad (2a)$$

$$\to e' + n + n + p, \qquad (2b)$$