Kelley, *Selected Values of Thermodynamic Properties of Metals and Alloys* (Wiley, New York, 1963).
[15] J. A. Van Vechten, to be published.
[16] J. R. Arthur, J. Phys. Chem. Solids 28, 2257 (1967).
[17] C. D. Thurmond and J. D. Struthers, J. Phys. Chem. 57, 831 (1953).

Dominant Second-Order Dipole-Moment Contribution in the Infrared Absorption of III-V Compounds*

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

(Received 22 May 1972)

It is shown that a relationship exists between the coefficient describing the infrared lattice absorption and the ionic contribution to the second-order electric susceptibility in a polar noncentrosymmetric crystal. By analyzing the available data of the latter it is concluded that two-phonon sidebands in the infrared absorption are due to the second-order dipole moment in all the III-V compounds and to the third-order potential in ZnO and CdS. Further, the magnitude of the integrated infrared absorption coefficient in a cubic homopolar IV-IV semiconductor is discussed.

The infrared spectra of polar crystals consist of broad maxima corresponding to the fundamental phonon frequencies and somewhat weaker sidebands corresponding to combinations of two or three phonons.[1] The two-phonon infrared absorption responsible for the strongest of these sidebands is due to two mechanisms usually referred to as the third-order potential[2,3] and the second-order dipole moment,[3,4] respectively. At frequencies near the fundamental infrared-active lattice resonance, ω_T, one expects on general grounds that the third-order potential is more important than the second-order dipole moment and is responsible for the broadening of the main absorption peak. For frequencies not in the neighborhood of ω_T no such *a priori* argument can be given which allows one to ascertain the predominance of one mechanism over the other. Such knowledge, however, is of considerable interest for the description of the infrared properties and phonon coupling in these solids and their amorphous counterparts. Except for the general discussion of Szigeti,[5] all attempts until now to account for these subsidiary peaks have without exception explicitly or implicitly assemed that even there it is the third-order potential that contributes predominantly, and the second-order dipole moment was neglected.[6,7]

Here we want to show for the first time that independent and conclusive evidence about the relative magnitude of the two effects in crystals lacking a center of inversion can be obtained through an analysis of the infrared dispersion of the second-order susceptibilities in such compounds. In this Letter we use this relationship to discuss the origin of the two-phonon sidebands in the case of diatomic semiconducting compounds and we anticipate that both the theoretical values and the available experimental data indicate that these sidebands in III-V cubic compounds are due to the second-order dipole moment.

In these compounds the two-phonon sidebands arise from combinations of the three acoustic and the three optic modes. The latter are a doubly degenerate infrared- and Raman-active transverse mode (T) of frequency ω_T and a longitudinal (L) of frequency ω_L. As a rule the two-optic-mode combination bands are well separated[8,9] from the optic-acoustic combination bands. In the following we shall concern ourselves exclusively with the former.

In the high-temperature limit, using perturbation theory, the following formula was obtained[5] for $\omega\epsilon''(\omega)$, the infrared energy loss per unit time:

$$\omega\epsilon''(\omega)\,\delta\omega = \frac{\pi^2 kT}{36v}\sum\nolimits_{(\omega,\delta\omega)}^{\pm}\left(\frac{\omega}{\omega_\sigma\omega_{\sigma'}}\right)^2\left[3M_{\sigma\sigma'}{}^{(2)} - \frac{e_T{}^*\Phi_{T\sigma\sigma'}{}^{(3)}}{m(\omega_T{}^2-\omega^2)}\right]^2, \tag{1}$$

where $\sigma=\{s,\vec{q}\}$ (s labels the branch and $\vec{q}$ is the wave vector), $e_T{}^*$ is the transverse effective charge, m the effective mass, and v the unit cell volume. In (1) the summation goes over all those pairs of modes for which either $\omega_\sigma+\omega_{\sigma'}$ or $\omega_\sigma-\omega_{\sigma'}$ is in the interval $(\omega,\delta\omega)$. $M^{(2)}$ and $\Phi^{(3)}$ are the second-order dipole moment and third-order potential coefficients defined through the power series in lattice coordinates Q_σ of the lattice dipole moment $M(Q)$ and the potential energy $\Phi(Q)$, respectively;

$$M(Q) = \frac{1}{v} e_T{}^* Q_T + \frac{1}{2v} \sum_{\sigma,\sigma'} M_{\sigma\sigma'}{}^{(2)} Q_\sigma Q_\sigma,$$

$$\Phi(Q) = \frac{1}{2v} \sum_{\sigma} \omega_\sigma{}^2 Q_\sigma{}^2 + \frac{1}{6v} \sum_{\sigma,\sigma',\sigma''} \Phi_{\sigma\sigma'\sigma''}{}^{(3)} Q_\sigma Q_{\sigma'} Q_{\sigma''}.$$

The relative contribution of the two mechanisms in (1) is measured by the dimensionless quantity

$$\Theta_{\sigma\sigma'} = -e_T{}^* \Phi_{T\sigma\sigma'}{}^{(3)} / 3m\omega_T{}^2 M_{\sigma\sigma'}{}^{(2)}$$

which, because of the flatness of the optic modes, can be replaced[5] by its value at the center of the Brillouin zone,

$$\Theta_{\sigma\sigma'} \simeq \Theta_{ss'} = -e_T{}^* \Phi_{Tss'}{}^{(3)} / 3m\omega_T{}^2 M_{ss'}{}^{(2)}. \tag{2}$$

Because of the presence of the resonant term $D_T(\omega) = [1 - (\omega/\omega_T)^2]^{-1}$ in (1), the third-order potential predominates near ω_T. Away from ω_T, however, neither the selection rules nor the temperature dependence allow one to distinguish between the two mechanisms. Further, since $3M_{\sigma\sigma'}{}^{(2)}[1 + \Theta_{\sigma\sigma'} D_T(\omega)]$ occurs squared in expression (1), the expression is insensitive to the absolute signs of the two coefficients $M^{(2)}$ and $\Phi^{(3)}$, and, although it will vanish for a frequency ω_0 either above or below ω_T depending on whether $\Theta_{\sigma\sigma'}$ is positive or negative, respectively, such a criterion is of little use in practice because of the lack of detailed and accurate phonon dispersion curves.

Yet the determination of the signs of these two coefficients and of $1 + \Theta_{ss'}$ clearly is sufficient to determine which of the two mechanisms, $M^{(2)}$ or $\Phi^{(3)}$, is dominant. Such information can be directly obtained from a study of the infrared behavior of the second-order susceptibility $\chi^{(2)}(\omega_1, \omega_2)$. This quantity relates the Fourier component of the sum frequency of the induced polarization to the Fourier components of two incident fields: $\vec{P}_{(\omega_1+\omega_2)}{}^{(2)} = \underline{\chi}^{(2)}(\omega_1, \omega_2) \cdot \vec{E}(\omega_1) \cdot \vec{E}(\omega_2)$, where the fields can be either longitudinal or transverse. In the Born-Oppenheimer approximation the expression for $\chi^{(2)}$ for induced transverse polarization at frequencies below the electronic transitions and above the elastic resonances of the sample can be written[10,11]

$$\begin{aligned}\chi^{(2)}(\omega_1, \omega_2) = \chi_E{}^{(2)}[1 &+ C_T D_T(\omega_1+\omega_2) + C_s D_s(\omega_1) + C_{s'} D(\omega_2) + C_{Ts} D_T(\omega_1+\omega_2) D_s(\omega_1) \\ &+ C_{Ts'} D_T(\omega_1+\omega_2) D_{s'}(\omega_2) + C_{ss'} D_s(\omega_1) D_{s'}(\omega_2) + C_{Tss'} D_T(\omega_1+\omega_2) D_s(\omega_1) D_{s'}(\omega_2)] \eta_s \eta_{s'}.\end{aligned} \tag{3}$$

where s and s' stand for L- or T-optic modes, $\chi_E{}^{(2)}$ is the purely electronic second-order susceptibility,

$$C_s = \frac{e_s{}^* \tilde{\alpha}_s{}^{(1)}}{2mv\omega_s{}^2 \chi_E{}^{(2)} \eta_s}, \quad C_{ss'} = \frac{e_s{}^* e_{s'}{}^* M_{ss'}{}^{(2)}}{2m^2 v \omega_s{}^2 \omega_{s'}{}^2 \chi_E{}^{(2)} \eta_s \eta_{s'}}, \quad C_{Tss'} = -\frac{e_T{}^* e_s{}^* e_{s'}{}^* \Phi_{Tss'}{}^{(3)}}{2m^3 v \omega_T{}^2 \omega_s{}^2 \omega_{s'}{}^2 \chi_E{}^{(2)} \eta_s \eta_{s'}}, \tag{4}$$

with $\alpha_s{}^{(1)}$ and $e_s{}^*$ the Raman tensor and effective charge for the s mode, respectively. $\eta_s = \epsilon_\infty{}^{-m_s}$, where $m_s = 1$ if $s = L$ and $m_s = 0$ if $s = T$.

We consider first the purely transverse case, $s = s' = T$, and we define $M^{(2)} = M_{TT}{}^{(2)}$, $\Phi^{(3)} = \Phi_{TTT}{}^{(3)}$, C_1 $C_2 = C_{TT}$, $C_3 = C_{TTT}$, and $\Theta = \Theta_{TT} = C_3/3C_2$. We see from (3) that

$\chi^{(2)} = \chi_E{}^{(2)}$ for $\omega_1, \omega_2, \omega_1 + \omega_2 > \omega_T$ (mixing in the visible),

$\chi^{(2)} = \chi_E{}^{(2)}(1 + C_1)$ for $\omega_1, \omega_1 + \omega_2 > \omega_T > \omega_2$ (electro-optic effect),

$\chi^{(2)} = \chi_E{}^{(2)}(1 + 3C_1 + 3C_2 + C_3)$ for $\omega_1, \omega_2, \omega_1 + \omega_2 < \omega_T$ (microwave).

Hence by measuring the magnitude and sign of $\chi^{(2)}$ in these three frequency regions the magnitudes and signs of $\chi_E{}^{(2)}$, C_1, and $3C_2 + C_3 = 3C_2(1 + \Theta)$ can be obtained and, as will be seen below, this is sufficient to extract $1 + \Theta$ as well. Therefore we present here an analysis of (1) in terms of these quantities.

We assume that the valence electrons are located on tetrahedral bonds which we assume to possess axial symmetry, and we describe them with wave functions $\psi = \psi_{\mathrm{V}} + \lambda\psi_{\mathrm{III}}$ constructed[12] with sp^3 Slater orbitals. The core electrons, on the other hand, are assumed rigidly bound to the nuclei, canceling part of their positive charge and leaving positive charges $3e$ and $5e$ on sites III and V, respectively.

For the lattice potential we assume that it can be written in the form $\varphi = \varphi_L + \varphi_S$, where $\varphi_L = \pm (Ze)^2/R$, $\varphi_S = Be^{-R/\rho}$, with Ze an apparent static charge and B the strength and ρ the range of the short-range forces; ρ is a measure of the extension of the electronic distribution around each atom and is taken as $\rho^{-1} \simeq \frac{1}{2}(\zeta_{\text{III}} + \zeta_{\text{V}})$, where the ζ_i are the Slater coefficients of the Slater orbitals used[12,13] to form ψ. In connection with the imposed axiality of the bonds, we neglect for the moment noncentral forces; the latter are three-body forces and act only beyond nearest neighbors. No attempt is made here to derive all these forces consistently from the electronic wave functions.

The calculation of the bond polarizabilities and dipole moments and their derivatives was performed[11,13] using the wave functions ψ while ω_T^2 and $\Phi^{(3)}$ were calculated using standard lattice-sum techniques.[14] The local field corrections were taken into account in a semiempirical way as in Ref. 13.

The calculated values of C_1, $3C_2 + C_3$, and $\Theta = C_3/3C_2$ are displayed in Table I along with the existing experimental values. The calculation showed that e_T^* and $\chi_E^{(2)}$ have opposite signs; $\alpha_T^{(1)}$ was found to be positive. Accordingly C_1 is negative[15] for all compounds considered. $M^{(2)}$ was found to be positive while $\Phi^{(3)}$ was found to be negative. The sign of the latter quantity is determined by the sign of the short-range contribution, $\varphi_S^{(3)}$, to $\varphi^{(3)}$. As was mentioned previously, in adopting this form for the potential we have not taken explicitly into account intermediate-range electrostatic forces, although part of them are introduced through the local field corrections. 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 the interionic distance 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. As a matter of fact, although the attractive part will give by far the largest contribution to the cohesive energy, the first derivatives of the two parts must cancel each other, as is required by the equilibrium condition, and ω_T^2 must be positive, reflecting the fact that the repulsive part changes more rapidly with distance than the attractive part; one expects that the same trend will be followed by the third-order derivatives; accordingly $\Phi^{(3)}$, and hence C_3, will be negative.

TABLE I. Calculated values of C_1, $3C_2 + C_3$, and $\Theta = C_3/3C_2$.

		Calculated		Expt.
Compound	C_1	$3C_2 + C_3$	Θ	$3C_2 + C_3$ [a]
InSb	-0.66	0.15	-0.17	
InAs	-0.28	0.22	-0.12	
InP	-0.14	0.23	-0.11	
GaSb			-0.16	
GaAs	-0.83	0.35	-0.17	0.4 ± 0.1
GaP	-0.37	0.27	-0.15	0.3 ± 0.1
AlSb			-0.10	

[a] Ref. 16.

On the other hand C_2 was found to be positive. The calculation shows that $3C_2 + C_3$ is also positive, the same sign as C_2, in agreement with the experimental data.[16] The experimental values, then, favor the fact that the second-order dipole moment is the dominant mechanism in the two-phonon sidebands in the III-V compounds.

When longitudinal phonons are involved in (1) the pertinent quantities are given by[11,17]

$$M_{ss'}^{(2)} = M^{(2)}[1 - (\kappa_s + \kappa_{s'})C_1/C_2 + \kappa_s\kappa_{s'}/C_2], \quad \text{(5a)}$$

$$\Phi_{Tss'}^{(3)} = \Phi^{(3)}\left[1 - (\kappa_s + \kappa_{s'})\frac{C_2}{C_3} + \kappa_s\kappa_{s'}\frac{C_1}{C_3}\right], \quad \text{(5b)}$$

an analogous expression for $\Theta_{ss'}$; here $\kappa_s = (\omega_s^2 - \omega_T^2)/\omega_T^2$. Expressions (5a) and (5b) are generalizations[11] to the nonlinear regime of the Lyddane-Sachs-Teller relations $e_L^* = e_T^*/\epsilon_\infty$ and $\omega_L^2 = (\epsilon_0/\epsilon_\infty)\omega_T^2$. Using the values of C_i given in Table I one can compute the coefficients (5a) and (5b). The conclusion is again that the second-order dipole moment is the dominant mechanism.

A similar investigation for CdS and ZnO shows that for these compounds the anharmonic potential is the predominant mechanism.

In the past, quantitative arguments were given[6,8] supporting the assumption that the third-order potential is the dominant mechanism in III-V compounds and in particular GaP. This was based on the following: (a) The integrated absorption coefficient in the infrared, $\alpha^{\text{IR}} = (2/\pi)\int[\epsilon''(\omega)/\omega]d\omega$ for Si, which is due entirely to the second-order moment [$e_T^* = 0$ in (1)], is at least an order of magnitude smaller than that in GaP where both $M^{(2)}$ and $\Phi^{(3)}$ contribute; and (b) it was assumed that the same $M^{(2)}$ processes contributed in GaP as well as in Si. The latter however is not the case.

$M^{(2)}$ arises exclusively from the distortion of the electronic distribution by two phonons. Above, it was calculated by assuming that the bonds possess axial symmetry, and hence the bond dipole moment $\vec{p}$ has a single nonzero component, namely, along the bond axis (z axis), or $\vec{p}=(0,0,p)$; for a homopolar bond like Si-Si in silicon, p and its derivatives and hence $M^{(2)}$ vanish identically. Actually, because of bond-bond interaction and the different orientations of the two adjacent bond triplets at the end points of each bond, a nonaxiality and twisting of the bond electron distribution is introduced resulting in small nonaxial components to $\vec{p}$ [or $\vec{p}=(p_x, p_y, p)$] which are nonzero even for the homopolar bond where $p=0$; they give rise to a nonzero $M_{\text{Si}}^{(2)}$ in Si and to an additional contribution $M_{na}^{(2)}$ in GaP so that $M_{\text{GaP}}^{(2)} = M_a^{(2)} + M_{na}^{(2)}$, where $M_a^{(2)}$ is the axial contribution calculated previously. Since the same nonaxial processes are operative in both cases, $M_{\text{Si}}^{(2)} \cong M_{na}^{(2)}$. For the heteropolar case, using the Mulliken-Löwdin approximation,[18] one obtains the crude estimate $|M_{na}^{(2)}/M_a^{(2)}| \simeq S_1/S_0 \leqslant 0.15$, where S_0 and S_1 are the overlap integrals between nearest and next-nearest neighbors, respectively, as calculated using the Slater orbitals. Hence $|M_{\text{Si}}^{(2)}/M_{\text{GaP}}^{(2)}| \simeq 0.15$ or $\alpha_{\text{Si}}^{\text{IR}}/\alpha_{\text{GaP}}^{\text{IR}} \simeq 0.02$; experimentally one finds[8] ~ 0.08.

The nonaxiality of the bonds is closely related to the noncentral forces. The above argument indicates that these contribute 10–15% to the coefficients of the optic modes of the III-V compounds. They are of course crucial for assuring lattice stability against shear stresses.

The present calculation gives no direct information concerning the shape of the absorption spectrum. With the availability, however, of infrared lasers the parallel study of $\chi^{(2)}$ and $\omega\epsilon''(\omega)$ may prove to be a valuable tool for a quantitative study of phonon coupling in solids. In particular, the relations (5a) and (5b) may be used to determine the relative ordering of the combination bands since the intensities of the latter are proportional to the squares of $M^{(2)}$ or $\Phi^{(3)}$.

The author is indebted to Professor N. Bloembergen for a most suggestive discussion.

---

*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, Université de Paris-Sud, Centre d'Orsay, 91-Orsay, France.

[1] See for instance, E. Burstein, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 276.

[2] M. Born and M. Blackman, Z. Phys. 82, 551 (1933).

[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford Univ. Press, Oxford, England, 1954).

[4] M. Lax and E. Burstein, Phys. Rev. 97, 39 (1955).

[5] B. Szigeti, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, New York, 1965), p. 337, and Proc. Roy. Soc., Ser. A 252, 217 (1959), and 258, 377 (1960).

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

[7] J. N. Neuberger and R. D. Hatcher, J. Chem. Phys. 34, 1733 (1961); V. V. Mitskevich, Fiz. Tverd. Tela 3, 3036 (1960), and 4, 3035 (1962) [Sov. Phys. Solid State 3, 2211 (1962), and 4, 2224 (1963)].

[8] D. A. Kleinman and W. G. Spitzer, Phys. Rev. 118, 160 (1960).

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

[10] For a semiclassical approach see G. M. Genkin, V. M. Fain, and E. G. Yaschin, Zh. Eksp. Teor. Phys. 52, 897 (1967) [Sov. Phys. JETP 25, 592 (1967)].

[11] C. Flytzanis, to be published.

[12] C. Coulson, L. Rédei, and D. Stocker, Proc. Roy. Soc., Ser A 270, 276 (1962).

[13] C. Flytzanis and J. Ducuing, Phys. Rev. 178, 1218 (1969).

[14] K. S. Krishnan and S. Kumar Roy, Proc. Roy. Soc., Ser. A 207, 447 (1954).

[15] W. L. Faust and C. M. Henry, Phys. Rev. Lett. 17, 1265 (1966); I. P. Kaminow and W. D. Johnston, Phys. Rev. 188, 1209 (1969).

[16] G. D. Boyd, J. J. Bridges, M. A. Pollack, and E. M. Turner, Phys. Rev. Lett. 26, 387 (1971). M. A. Pollack and E. H. Turner, Phys. Rev. B 4, 4578 (1971).

[17] It is important to notice from (5a) and (5b) that when LO phonons are involved, the Raman coefficient provides an additional phonon coupling contribution. This has always been ignored in the existing theories (Refs. 2–6).

[18] J. Cižek, Mol. Phys. 6, 19 (1963).