Bond Charge, Bond Polarizability, and Phonon Spectra in Semiconductors

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A nonlinear extension of the bond-charge model is used for the analysis of the infrared and Raman spectra because of phonons in diamond, silicon, and germanium. The infrared absorption of these crystals is explained by the anharmonic coupling between the bond charges and their neighboring ions. The first- and second-order Raman spectra are described successfully by means of bond polarizabilities. The relation of the model parameters to the photoelastic constants and band structures is discussed.

In recent years the bond-charge model (BCM) introduced by Phillips[1] was used for the description of the lattice vibrations in covalent crystals by Martin.[2] Very recently the model has been modified by Weber[3] to include the adiabatic motion of the bond charge (Fig. 1). The bond charge arises from the off-diagonal part of the dielectric matrix[2, 5, 6] and corresponds formally to the acoustic sum rule.[7] This BCM is in many respects analogous to the rigid-ion model of ionic solids[8] which accounts quite satisfactorily for the infrared absorption in ionic crystals via the anharmonic forces between the ions.[9] In a similar way we may expect that the "anharmonic" forces between the bond charge and the ions are responsible for the infrared absorption in covalent crystals.

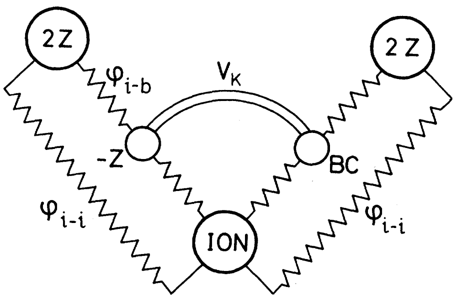

FIG. 1. Bond-charge model (after Ref. 3). $\varphi_{i-i}(r)$, central potential between nearest-neighbor ions. $\varphi_{i-b}(r)$, central potential between ions and bond charges. V_K, bond-bending potential (Keating, see Ref. 4) between neighboring bonds. $2Z, -Z$, values of ion and bond charges which determine the Coulomb forces.

The infrared absorption is generally described by the imaginary part of the dielectric susceptibility,[10, 11]

$$\chi_{\alpha\alpha}''(\omega) = (4\pi\hbar/N\Omega_0)\sum_{\vec{q}\,j_1 j_2} |M_\alpha^{(2)}(\vec{q}, j_1; -\vec{q}, j_2)|^2(n_1+n_2+1)\delta(\omega-\omega_1-\omega_2). \tag{1}$$

Here, n_1 and n_2 denote the thermal occupation numbers of phonons $(\vec{q}, j_1)$ and $(-\vec{q}, j_2)$, respectively, and $\underline{M}^{(2)}$ means the second-order dipole moment. In the BCM we determine the matrix elements of $\underline{M}^{(2)}$ from the cubic anharmonic expansion term of $\varphi_{i-b}(r)$ (Fig. 1) which we denote by $\underline{\phi}^3$. There are three independent parameters, $\alpha = \phi^3{}_{xxx}$, $\beta = \phi^3{}_{xxy}$, and $\gamma = \phi^3{}_{xyz}$. These parameters contribute to the matrix elements of the second-order dipole moment as follows:

$$\underline{M}^{(2)} = (N/2)Z\omega_{\rm el}^{-1}\underline{\phi}^{(3)}:\vec{U}^+\vec{U}^-, \tag{2}$$

where the hypervectors $\vec{U}^+$ and $\vec{U}^-$ are built of elements $\vec{U}_{\kappa\kappa'}{}^+ = \vec{U}^\kappa - \vec{U}^{\kappa'}$ and $\vec{U}_{\kappa\kappa'}{}^- = \vec{U}^\kappa + \vec{U}^{\kappa'} - 2\vec{U}^b$, respectively. Here, the local displacements are decomposed into those of even parity (where neighboring ions are moving symmetrically against the bond charge at rest) $\vec{U}^\kappa - \vec{U}^{\kappa'}$, and those of odd parity $\vec{U}^\kappa + \vec{U}^{\kappa'} - 2\vec{U}^b$, with the bond charge moving against the two ions in phase. Only the odd displacements $(\vec{U}^-)$ carry dipole moments of bond charges while the even displacements $(\vec{U}^+)$ lead to a modulation of these dipole moments via the potential φ_{i-b} (Fig. 1). With the help of α, β, γ, a very good fit of the infrared spectra in C, Si, and Ge[12] is obtained.

The results of a one-parameter fit ($\alpha = \beta = 0$, $\gamma \neq 0$) for diamond are shown in Fig. 2. A comparison with the seven-parameter fit of Kress, Borik, and Wehner,[14] using the formal expansion in terms of $\underline{M}^{(2)}$, shows that the physical origin of the formal parameters is a strongly localized nonlinear electron-ion interaction.

The Raman scattering in covalent crystals exhibits a one-phonon line with symmetry $\Gamma_{25}{}^+$ and two-phonon spectra of symmetry Γ_1^+, Γ_{12}^+, and Γ_{25}^+. The second-order Raman scattering tensor is given by (Stokes part)[15]

$$I_{\alpha\beta\gamma\delta}(\Omega)=2\sum_{\vec{q}j_1j_2} P_{\alpha\beta}(\vec{q},j_1;-\vec{q},j_2)P_{\gamma\sigma}^*(\vec{q},j_1;-\vec{q},j_2)(n_1+1)(n_2+1)\delta(\Omega-\omega_1-\omega_2). \tag{3}$$

The polarizability tensor $\underline{P}$ may be expanded in powers of the ionic and bond-charge displacements in ordinary space as was done for the nonlinear dipole moment $\underline{M}^{(2)}$ in Eq. (2):

$$\underline{P}=\underline{P}^0+\underline{P}^1\cdot\vec{U}^+ +(\tfrac{1}{2})\underline{P}^2:(\vec{U}^+\vec{U}^+ +\vec{U}^-\vec{U}^-). \tag{4}$$

The contribution of $\underline{\phi}^3$ to the Raman spectra analogous to Eq. (2) for $\underline{M}^{(2)}$ cannot account for the second-order Raman scattering since it leads to a very weak change of the crystal polarizability. Instead, we followed the concept of bond polarizabilities (BP)[16-18] and represented the polarizability of the covalent crystal $\underline{P}$ by a sum of independent BP's each of which depends only on the bond length R^b of two neighboring ions. Under this assumption $\underline{P}$ is given by[12]

$$P_{\alpha\beta}\{R^b\}=\sum_b[\hat{R}_\alpha{}^b\hat{R}_\beta{}^b\alpha_\parallel(R^b)+(\delta_{\alpha\beta}-\hat{R}_\alpha{}^b\hat{R}_\beta{}^b)\alpha_\perp(R^b)], \tag{5}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the longitudinal and transverse components of the BP. The expansion coefficients of $\underline{P}$ defined in Eq. (4) are then simple linear combinations of $\alpha_\parallel$, $\alpha_\perp$, and their derivatives:

$$\alpha_v=4(\alpha_\parallel+\alpha_\perp)/3\Omega_0,\quad \alpha_q=4(\alpha_\parallel-\alpha_\perp)/3\Omega_0,\quad \alpha_1=r_0\alpha_v',$$

$$\alpha_1'=r_0^2\alpha_v'',\quad \alpha_{25}=r_0\alpha_q[\ln|\alpha_q/(R^b)^2|]^1,\quad \alpha_{25}'=r_0^2\{\alpha_q[\ln|\alpha_q/(R^b)^2|]'\}';$$

r_0 is the equilibrium bond length. Thus,

$$\begin{aligned}&P^0{}_{\alpha\beta}=\Omega_0\alpha_v\delta_{\alpha\beta}=(\Omega_0/4\pi)(\epsilon_{00}-1)\delta_{\alpha\beta},\quad P^1{}_{\alpha\beta\mu}(\Gamma_{25}^+)=(\Omega_0/r_0\sqrt{3})\alpha_{25}\epsilon_{\alpha\beta\mu},\\&P^2{}_{\alpha\alpha\mu\nu}(\Gamma_1^+)=(\Omega_0/12r_0^2)[-\alpha_1'+(1-3\delta_{\mu\nu})\alpha_1],\\&P^2{}_{\alpha\beta\mu\nu}(\Gamma_{12}^+)=(\Omega_0/24r_0^2)(2\alpha_{25}+3\alpha_q\delta_{\mu\nu})(2-\bar{\epsilon}_{\alpha\beta\mu}-\bar{\epsilon}_{\alpha\beta\nu}),\\&P^2{}_{\alpha\beta\mu\nu}(\Gamma_{25}^+)=(\Omega_0/12r_0^2)[-\alpha_{25}'-3\alpha_{25}(\delta_{\mu\nu}+1-\epsilon_{\alpha\beta\nu}-\epsilon_{\alpha\beta\mu})-9\alpha_q(1-\delta_{\mu\nu})(1-\epsilon_{\alpha\beta\mu}-\epsilon_{\alpha\beta\nu})],\end{aligned} \tag{6}$$

where the subindices α, β refer to the Cartesian coordinates of the dielectric tensor and its derivative; μ, ν are the coordinates of the differences in the displacement of near-neighbor atoms; $\epsilon_{\alpha\beta\mu}$, the Levi-Civita tensor, is given by $\epsilon_{\alpha\beta\mu}=(1-\delta_{\alpha\beta})(1-\delta_{\alpha\mu})(1-\delta_{\beta\mu})$; and $\bar{\epsilon}_{\alpha\beta\mu}=(1-\delta_{\alpha\beta})\times(1+\delta_{\alpha\mu})(1-{}_{\beta\mu})$.

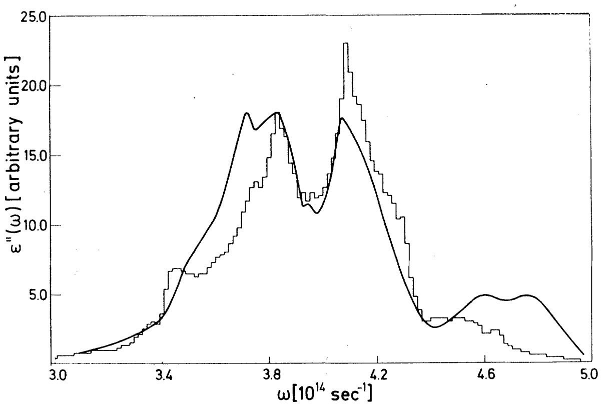

FIG. 2. Infrared absorption $\epsilon''(\omega)$ of diamond at 296 K. The solid line is the experimental curve of Ref. 13. The histogram is the absorption spectrum calculated with only one parameter (γ).

Calculations of the first- and second-order Raman spectra of C, Si, and Ge were carried out with the five fitting parameters α_q, α_1, α_1', α_{25}, and α_{25}'. α_v was obtained from ϵ_∞. The dominant component of the experimental spectra is that of Γ_1^+ symmetry accompanied by a weaker Γ_{25}^+ quadrupole and a very weak Γ_{12}^+ scattering. These facts are well reproduced by our model in all three substances. Preliminary results for silicon were shown elsewhere.[12] Here, we focus on the situation in diamond.

In Fig. 3 the three spectra of diamond are compared with our calculations. The two prominent spectra with Γ_1^+ and Γ_{25}^+ symmetry are practically determined by α_1' and α_{25}', respectively, which are approximately equal. This corresponds to a very low value of $\alpha_\perp$ as compared to $\alpha_\parallel$ in diamond ($\alpha_q\approx\alpha_v$) and indicates a simple (longitudinal) charge-transfer mechanism in this crystal. Since the intensity of the measured Raman spectra is only known in arbitrary units we determined α_q from the photoelastic constants $p_{11}+2p_{12}$.[17] The nonfitted photoelastic constants p_{11}

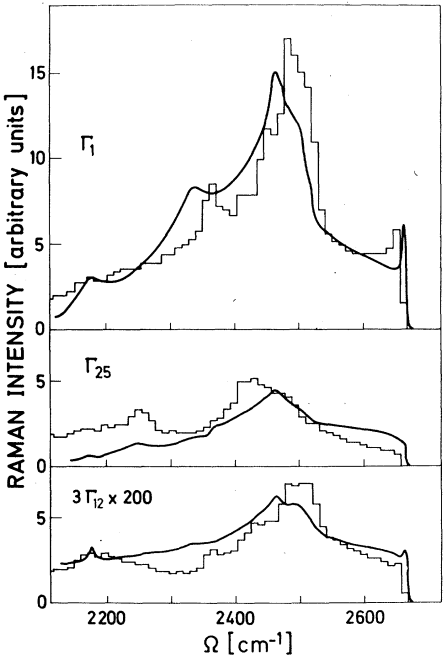

FIG. 3. Second-order Raman spectra of diamond at 300 K. The solid lines are the experimental spectra of Ref. 19. The histograms are the calculated spectra.

TABLE I. Values of quantities calculated in this paper. The experimental values are given in brackets.

	C	Si	Ge
ϵ_∞	(5.86)	(11.7)	(16.3)
α_1/α_q	·4.13	−46.16	−57.45
α_1'/α_q	284.65	−180.02	−288.22
α_{25}/α_q	2.13	−23.08	−24.39
α_{25}'/α_q	255.6	0.0	−248.78
$p_{11}+2p_{12}$	−0.16	−0.058	−0.28
	(−0.16)[a]	(−0.058)[b]	(−0.28)[c]
$p_{11}-p_{12}$	−0.283	0.013	0.016
	(−0.293)[a]	(−0.167)[a]	(−0.0095)[a]
			(0.011)[d]
p_{44}	−0.172	−0.0076	0.019
	(−0.172)[a]	(−0.082)[a]	(−0.074)[a]
			(0.012)[d]
α_v	0.387	0.851	1.218
α_q	0.387	−0.069	−0.167
$\alpha_\parallel$ (Å^3)	3.293	6.006	9.89
$\alpha_\perp$ (Å^3)	0.0	7.749	15.49
$P^{(1)}$ (Å^2)	3.5	13.95	43.1
	−1.82[e]	6.73[e]	40.53[e]
	(±4)		
I_1/I_2[f]	334	93.4	52
	(250)	(35)	(60)

[a] Ref. 20.
[b] Ref. 21.
[c] Ref. 22.
[d] Ref. 23.
[e] Ref. 24.
[f] Ratio of the first- to second-order Raman intensity.

$-p_{12}$, p_{44} agree for diamond very well with the experimental values (Table I).

A feature of particular interest is the peak at the cutoff of the two-phonon spectra which often is attributed to a two-phonon bound state.[19] Since our calculation represents well the frequency of the experimental peak (slightly above $2\omega_{\text{Raman}}$) as well as its shape we believe that our result does explain the two-phonon spectrum of diamond without invoking a bound state. A certain "overbending" of the LO mode in the [100] direction above the Raman frequency with a subsequent extension of the density of states in this frequency region was first proposed by Musgrave and Pople.[25] Thus within our model the peak would be due to an overtone volume scattering, in agreement with the conjecture of Uchinokura, Sekine, and Matsuura.[26]

For germanium and silicon a large increase in α_1 is observed (Table I). Our calculated first-order Raman tensor agrees quite well with that calculated by Swanson and Maradudin,[24] while for diamond our value has the opposite sign. This discrepancy might be due to the strong dependence of the Raman tensor on δ in Swanson and Maradudin's calculation. We note that the p_{11} $-p_{12}$ and p_{44} calculated with our model for germanium have opposite signs to those observed experimentally. This rather disturbing fact is a consequence of our assumption of simple bond polarizabilities which is good for diamond. For germanium, however, it is known[23] that two main mechanisms contribute to the polarization: the average band gap E_2 ("Penn" gap) and the lowest direct gap E_0. While ϵ_∞ is determined mainly by E_2, in the differential parameters one encounters equal contributions of both mechanisms which can even have opposite sign.[27] The shear photoelastic constants, determined at long wavelength by E_0 and E_2, reverse sign near E_0 because of the increasing contribution of this gap. The first-order Raman tensor of germanium, however, is mainly determined by E_0 and no antiresonance cancellation occurs.[28] $p_{11}+2p_{12}$ is determined for long wavelength by E_2 and so should be the Γ_1^+ scattering.[23] Within this model, and assuming that the quadrupolar (Γ_{12}^+ and Γ_{25}^+) scattering is produced mainly by the E_0 gap, a fact which seems to agree with experiment, we conclude that the calculated $p_{11}-p_{12}$ and p_{44} represent only the E_0 contribution to these quantities. We have also listed in Table I, footnote d, the contributions of E_0 to $p_{11}-p_{12}$ as extracted by Cardona.[23] The proximity of these contributions to the values calculated with our BP model is quite satisfactory. For silicon the situation is somewhat more complicated and shall be discussed elsewhere together with the details of the present work.

In spite of the qualitative nature of these considerations we believe they go far in elucidating the microscopic physics behind the BP model. They can, alternatively, be discussed by relating the increase of $\alpha_\perp$ when going from diamond to germanium to a breakdown of the sp^3 hybridization in the bonds due to a strong lowering of the $\Gamma_2{}'$ band at the Γ point.

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