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Charged Bond Correction to the Dispersion Curves of Diamond*

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1. INTRODUCTION

Phonon dispersion curves in directions of high symmetry have been previously measured for diamond,¹ silicon,² and germanium.³ The curves for silicon and germanium are nearly homologous, i.e., they differ from one another by a scale factor.⁴ Diamond, however is not homologous to silicon and germanium.⁵ A fit of the dispersion curves for germanium, (and hence silicon), by a general Born-von Karman model requires interactions out to at least sixth nearest neighbors.^{6,7} The need for so many neighbors comes about principally because the transverse acoustic branches are rather flat in the vicinity of the Brillouin zone boundary. The transverse acoustic branches of diamond are nowhere near as flat as those of silicon and germanium; one might hope to fit these dispersion curves with a Born-von Karman model involving fewer neighbors. A second neighbor model gives a good qualitative fit to the curves for diamond. See Fig. 1. The quantitative fit, however, cannot be considered satisfactory in view of the accuracy of the measurements. The application of an analysis similar to that given by Herman on germanium⁶ shows that the TA(111) branch is most sensitive to the range of the interactions required and indicates that an adequate fit to the data can only be obtained by going out to at least fifth neighbors. A Born-von Karman fifth neighbor model has 16 parameters and hence is physically objectionable.

Cochran's shell model, which accounts for the long range forces by including the interaction between electrical dipole moments induced on the atoms when they are displaced from their equilibrium positions, has been used by Dolling to fit the dispersion curves of silicon and germanium.² It is found that a quantitative fit to the data on silicon requires a second neighbor shell model involving eleven parameters. (In principle the second neighbor shell model involves nineteen parameters. This number is reduced to eleven

by the introduction of eight somewhat arbitrary restrictions.) The need for this many parameters is once again an indication of our lack of physical understanding.

In an attempt to find a model with fewer parameters than the shell model we noted that the charge density about any atom in a diamond-type lattice is not spherically symmetric. From X-ray diffraction studies it is known that some charge density is concentrated along the bonding directions.^{8,9} It has been estimated that in diamond perhaps .42 of an electron charge is in the region of the bond.⁸ There is less charge associated with the bonds in silicon and germanium. This suggested the following electrostatic model in the lowest order of approximation. The charge in the bond is replaced with a negative point charge, $-eZ$, which is constrained to remain midway between neighboring carbon nuclei. The carbon nucleus plus its associated spherically symmetric portion of the electron distribution is replaced by a positive point charge, $+eZ$, and a point mass M . Z^2 is treated as a parameter. Such a simple model can never lead to a stable crystal and therefore we introduced a general second neighbor Born-von Karman interaction between the point masses. This model then has six parameters.

Section II summarizes the well-known formulae for the second neighbor Born-von Karman model which forms the basis of our short range interaction. Section III describes how the calculation of the electrostatic contribution to the dynamical matrix was made, and how the parameters of the model were determined. The conclusions to be drawn from the calculation are given in Section IV.

2. SHORT RANGE INTERACTION

The short range interaction for this model is taken to be the same as that for the general second neighbor Born-von Karman model. Although this has been written down for diamond several times,^{6,7,10} it will be written down again for convenience of reference and explanation of our notation.

All quantities are made dimensionless for use with computers. Masses are scaled by the mass of carbon, $M = 1.9943 \times 10^{-23}$ gm. Lengths are scaled by the lattice constant of diamond, $a = 3.56718 \text{ \AA}$. Frequencies are scaled by $\sqrt{\frac{e^2}{M\nu}}$ where ν is the volume of the unit cell, $\nu = a^3/4$. e is the electronic charge. Energies are scaled by $e^2 a^2/\nu$; force constants by e^2/ν . In these units the equations of motion are

$$\ddot{u}_{\alpha}^{(\ell)} = - \sum_{\ell', \kappa', \beta} \Phi_{\alpha\beta}^{(\ell\ell', \kappa\kappa')} u_{\beta}^{(\ell')}$$

The trial solution is

$$u_{\alpha}^{(\ell)} = w_{\alpha}^{(\kappa)} \exp \left\{ i [q \cdot r(\ell) - \omega t] \right\},$$

where

$$r_{\kappa}^{(\ell)} = \underline{r}(\ell) + \underline{r}(\kappa), \quad \kappa = 1, 2, \quad \text{are the positions of the carbon nuclei.}$$

This solution leads to the set of homogeneous equations

$$\sum_{\kappa', \beta} [\Phi_{\alpha\beta}^{(\underline{q}, \underline{r}_{\kappa\kappa'})} - \omega^2 \delta_{\kappa, \kappa'} \delta_{\alpha, \beta}] w_{\beta}^{(\kappa')} = 0,$$

where

$$\Phi_{\alpha\beta}^{(\underline{q}, \underline{r}_{\kappa\kappa'})} = \sum_{\ell'} \Phi_{\alpha\beta}^{(\ell\ell', \kappa\kappa')} \exp [i q \cdot r(\ell' - \ell)].$$

The ω^2 's are determined by the vanishing of the secular determinant associated with the above set of homogeneous equations. For $\underline{q}$ in the (100) or (111)

directions, ω^2 takes on the following simple forms because of symmetry.

In the (100) direction

$$\omega_L^2(q) = \Phi_{11}(\vec{q}_1) \pm |\Phi_{11}(\vec{q}_2)|$$

$$\omega_T^2(q) = \Phi_{22}(\vec{q}_1) \pm |\Phi_{22}(\vec{q}_2) + \Phi_{23}(\vec{q}_2)|$$

In the (111) direction

$$\omega_L^2(q) = \Phi_{11}(\vec{q}_1) + 2\Phi_{12}(\vec{q}_1) \pm |\Phi_{11}(\vec{q}_2) + 2\Phi_{12}(\vec{q}_2)|$$

$$\omega_T^2(q) = \Phi_{11}(\vec{q}_1) - \Phi_{12}(\vec{q}_1) \pm |\Phi_{11}(\vec{q}_2) - \Phi_{12}(\vec{q}_2)|$$

The transverse branches are doubly degenerate. Let

$$\Phi_{\alpha\beta}(\vec{q}_{KK}) = {}^s\Phi_{\alpha\beta}(\vec{q}_{KK}) + {}^c\Phi_{\alpha\beta}(\vec{q}_{KK})$$

"s" stands for shortranged part and "c" for Coulomb part.

In the (100) direction, with $q = (2\pi\xi, 0, 0)$, $0 \leq \xi \leq 1$

$${}^s\Phi_{11}(\vec{q}_1) = 4\alpha + 8\mu (1 - \cos \pi \xi)$$

$${}^s\Phi_{11}(\vec{q}_2) = -2\alpha (1 + \exp[-i\pi\xi]) = {}^s\Phi_{22}(\vec{q}_2)$$

$${}^s\Phi_{22}(\vec{q}_1) = 4\alpha + 4(\lambda + \mu) (1 - \cos 2\pi\xi)$$

$${}^s\Phi_{23}(\vec{q}_2) = -2\beta (1 - \exp[-i\pi\xi])$$

In the (111) direction, with $q = \pi\xi(1,1,1)$, $0 \leq \xi \leq 1$

$${}^s\Phi_{11}(\vec{q}_1) = 4\alpha + 2(2\mu + \lambda) (1 - \cos \pi\xi)$$

$${}^s\Phi_{11}(\vec{q}_2) = -\alpha (1 + 3 \exp[-i\pi\xi])$$

$${}^s\Phi_{12}(\vec{q}_1) = 2\nu (1 - \cos \pi\xi)$$

$$\phi_{12}(\vec{q}) = -\beta (1 - \exp [-i\pi \xi])$$

The notation is the same as F. Herman's, but the force constants are now dimensionless.⁶ The Born-von Karman fit shown in Fig. 1 was obtained using above short range portion of the interaction. The five parameters were determined by requiring the dispersion curves to give the measured values, ω_{LA} , ω_{TA} , ω_{TO} at the zone boundary in the (100) direction, ω_{RAMAN} at the zone center, and $\omega_{TO}^2 + \omega_{TA}^2$ at the zone boundary in the (111) direction.

The values of the parameters in c.g.s. units are:

$$\alpha = 1.569 \times 10^5 \text{ dynes/cm}$$

$$\beta = .457$$

$$\mu = .236$$

$$\nu = .255$$

$$\lambda = .222$$

3. THE COULOMB INTERACTION AND TEST OF MODEL

The treatment of the Coulomb interaction is reasonably straightforward but too lengthy to be given in detail here. We will indicate how the problem was set up, what methods were used in performing the summations and give tables for the required functions, ${}^c\phi_{\alpha\beta}(\frac{q}{KK'})$.

If $\underline{x}_K^{(\ell)} = \underline{r}_K^{(\ell)} + \underline{u}_K^{(\ell)}$ are the positions of carbon nuclei, then the positions and charges of the point charges in this model are

$$\underline{X}_1^{(\ell)} = \underline{x}_1^{(\ell)} \quad , \quad Z_1 = Z$$

$$\underline{X}_2^{(\ell)} = \underline{x}_2^{(\ell)} \quad , \quad Z_2 = Z$$

$$\underline{X}_3^{(\ell)} = \frac{1}{2} [\underline{x}_1^{(\ell)} + \underline{x}_2^{(\ell)}] \quad , \quad Z_3 = -\frac{1}{2}Z$$

$$\underline{X}_4^{(\ell)} = \frac{1}{2} [\underline{x}_1^{(\ell_1+1, \ell_2, \ell_3)} + \underline{x}_2^{(\ell)}] \quad , \quad Z_4 = -\frac{1}{2}Z$$

$$\underline{X}_5^{(\ell)} = \frac{1}{2} [\underline{x}_1^{(\ell_1, \ell_2+1, \ell_3)} + \underline{x}_2^{(\ell)}] \quad , \quad Z_5 = -\frac{1}{2}Z$$

$$\underline{X}_6^{(\ell)} = \frac{1}{2} [\underline{x}_1^{(\ell_1, \ell_2, \ell_3+1)} + \underline{x}_2^{(\ell)}] \quad , \quad Z_6 = -\frac{1}{2}Z$$

The last four equations express the idea that the charge in the bond is constrained to remain midway between the carbon nuclei. In dimensionless units the Coulomb energy is

$${}^c\phi(\dots \underline{x}_K^{(\ell)} \dots) = \frac{v}{2a^3} \sum_{m, \lambda} \sum_{m', \lambda'} \frac{Z_\lambda Z_{\lambda'}}{|\underline{X}_\lambda^{(m)} - \underline{X}_{\lambda'}^{(m')}|}$$

The interaction constants are

$${}^c\phi_{\alpha\beta}(\frac{\ell, \ell'}{K, K'}) = \left. \frac{\partial^2 {}^c\phi}{\partial x_{\alpha}^{(\ell)} \partial x_{\beta}^{(\ell')}} \right|_{\underline{x} = \underline{r}}$$

We see that

$$\Phi_{\alpha\beta}(\ell, \ell') = \sum_{\substack{m, \lambda, \gamma \\ m', \lambda', \delta}} \frac{\partial^2 c \Phi}{\partial X_{\gamma}^{(m)} \partial X_{\delta}^{(m')}} \bigg|_{x=r} \frac{\partial X_{\gamma}^{(m)}}{\partial x_{\alpha}^{(\ell)}} \frac{\partial X_{\delta}^{(m')}}{\partial x_{\beta}^{(\ell')}}.$$

Define

$$F_{\alpha\beta}(|\underline{x}|) = -\frac{\nu}{a^3} \frac{1}{|\underline{x}|^3} \left[\frac{3x_{\alpha} x_{\beta}}{|\underline{x}|^2} - \delta_{\alpha, \beta} \right],$$

Then

$$\frac{\partial^2 c \Phi}{\partial X_{\gamma}^{(m)} \partial X_{\delta}^{(m')}} \bigg|_{x=r} = Z_{\lambda} Z_{\lambda'} F_{\gamma\delta}(|\underline{x}_{\lambda}^{(m')} - \underline{x}_{\lambda}^{(m)}|) \bigg|_{x=r}$$

for

$$(\underline{m}) \neq (\underline{m}').$$

$$\frac{\partial^2 c \Phi}{\partial X_{\gamma}^{(m)} \partial X_{\delta}^{(m')}} \bigg|_{x=r} = - \sum_{\substack{m' \neq m \\ \lambda' \neq \lambda}} Z_{\lambda} Z_{\lambda'} F_{\gamma\delta}(|\underline{x}_{\lambda}^{(m')} - \underline{x}_{\lambda}^{(m)}|) \bigg|_{x=r}$$

One must now re-express everything in terms of the independent variables

$r_K^{(\ell)}$. It can be shown that $c\Phi_{\alpha\beta}(\ell\ell')$ can be cast into the form,

$$c\Phi_{\alpha\beta}(\ell\ell') = Z^2 \sum_{j=1}^{25} C^{(KK')}_j F_{\alpha\beta}(|\underline{r}^{(\ell\ell')} - \underline{r}^{(KK')}_j|)$$

for $(\underline{\ell}) \neq (\underline{\ell}')$. Since for cubic symmetry and Coulomb forces it can be shown that $\Phi_{\alpha\beta}(\ell\ell) = 0$, we need not consider this case. $\Phi_{\alpha\beta}(\underline{q}, \underline{r})$ now takes the form

$$\Phi_{\alpha\beta}(\underline{q}, \underline{r}) = Z^2 \sum_{j=1}^{25} C^{(KK')}_j \exp[iq \cdot \underline{r}^{(KK')}_j] F_{\alpha\beta}(q, r^{(KK')}_j)$$

where

$$F_{\alpha\beta}(\underline{q}, \underline{r}) = \sum'_{\ell'} F_{\alpha\beta}(|\underline{r}(\ell') - \underline{r}|) \exp \{ \underline{q} \cdot [\underline{r}(\ell') - \underline{r}] \}$$

The prime on the summation means that the $\ell'=0$ term is omitted when $\underline{r}=0$

$F_{\alpha\beta}(\underline{q}, \underline{r})$ is most quickly evaluated by the Ewald method.¹¹ There are several alternative forms of the method. The one used here is due to Adler.¹²

The final expression for $F_{\alpha\beta}(\underline{q}, \underline{r})$ is

$$F_{\alpha\beta} = \left\{ \sum'_{\ell'} \left[-\frac{v}{3a^3} Y_{\alpha\beta}(|\underline{r}(\ell') - \underline{r}|) g_{\epsilon}(|\underline{r}(\ell') - \underline{r}|) \exp \{ i \underline{q} \cdot [\underline{r}(\ell') - \underline{r}] \} \right] \right. \\ \left. + \sum_h \left[\frac{4\pi}{3} Y_{\alpha\beta}(|\underline{K}(h) + \underline{q}|) \exp \left(-|\underline{K}(h) + \underline{q}|^2 / 4\epsilon^2 \right) \right. \right. \\ \left. \left. \times \exp \left(i \underline{K}(h) \cdot \underline{r} \right) \right] \right\}$$

where

$$\frac{1}{3} g_{\epsilon}(|\underline{x}|) = \frac{1 - \text{erf}(\epsilon|\underline{x}|)}{|\underline{x}|^3} + \frac{2\epsilon}{\sqrt{\pi}} \left(\frac{1}{|\underline{x}|^2} + \frac{2\epsilon^2}{3} \right) \exp \left[-\epsilon^2 |\underline{x}|^2 \right],$$

$$Y_{\alpha\beta}(|\underline{x}|) = \frac{3x_{\alpha}x_{\beta}}{|\underline{x}|^2} - \delta_{\alpha\beta},$$

$\underline{K}(h)$ is a reciprocal lattice vector and ϵ is a parameter used to make the summations converge most rapidly. The results are given in Tables I and II.

Two tests were made of the model. In the (100) direction the five parameters α , β , μ , ν , Z^2 were determined algebraically from ω^2 at 5 points. This resulted in $Z^2 = -22.73$ which is physically impossible. As a second test the TA(111) branch was set up for a least squares computer fit with the requirement that $Z^2 \geq 0$. The result was $Z^2 = 0$.

4. CONCLUSIONS

Therefore it must be concluded that no positive value of Z^2 will improve the fit to the data over the fit obtained by a straight second neighbor Born-von Karman model. The charge in the bonds cannot be used to explain the long range forces in covalent materials. In fact the inclusion of the charge bond contribution would worsen the agreement of the theory with experiment. One might try to explain the lack of homology of diamond with silicon and germanium on the basis of this model by noting that the amount of charge in the diamond bond is approximately three times that in the silicon bond.⁸ However, the ratio of the Raman frequencies for the two substances is also of the order of three and hence it is not clear that the lack of homology can be explained in this way. A detailed calculation would probably be necessary. Since there is at present no really satisfactory basic model, such a calculation would not be too meaningful at this time.

TABLE I. $c_{\alpha\beta}^{(q)}(K, K')$ for $\underline{q} = \frac{2\pi}{a} (\zeta, 0, 0)^{a, b}$

ζ	$c_{11}^{(q)}(1, 1)$	$c_{11}^{(q)}(1, 2)$	$c_{22}^{(q)}(1, 1)$	$c_{22}^{(q)}(1, 2)$	$c_{23}^{(q)}(1, 2)$
.0	.000	.000 - i .000	.000	.000 + i .000	.000 + i .000
.1	.023	.004 - i .001	-.012	-.002 + i .000	.946 + i 5.971
.2	.091	.014 - i .005	-.045	-.007 + i .002	3.689 + i 11.352
.3	.198	.028 - i .014	-.099	-.014 + i .007	7.955 + i 15.613
.4	.337	.039 - i .028	-.169	-.019 + i .014	13.322 + i 18.336
.5	.495	.043 - i .043	-.248	-.022 + i .022	19.259 + i 19.259
.6	.658	.040 - i .054	-.329	-.020 + i .027	25.182 + i 18.296
.7	.810	.029 - i .057	-.405	-.014 + i .028	30.514 + i 15.547
.8	.932	.015 - i .047	-.466	-.008 + i .024	34.737 + i 11.287
.9	1.013	.004 - i .027	-.506	-.002 + i .013	37.444 + i 5.931
1.0	1.040	.000 - i .000	-.520	.000 + i .000	38.377 + i .000

TABLE II. $c_{\alpha\beta}^{(q)}(K, K')$ for $\underline{q} = \frac{\pi}{a} (\zeta, \zeta, \zeta)^{a, b}$

ζ	$c_{11}^{(q)}(1, 1)$	$c_{11}^{(q)}(1, 2)$	$c_{12}^{(q)}(1, 1)$	$c_{12}^{(q)}(1, 2)$
.0	.000	.000	.000	.000 + i .000
.1	.000	.000	.015	.475 + i 2.985
.2	.000	.000	.058	1.853 + i 5.673
.3	.000	.000	.125	3.994 + i 7.798
.4	.000	.000	.210	6.684 + i 9.152
.5	.000	.000	.304	9.655 + i 9.606
.6	.000	.000	.398	12.616 + i 9.119
.7	.000	.000	.483	15.277 + i 7.744
.8	.000	.000	.551	17.383 + i 5.619
.9	.000	.000	.594	18.732 + i 2.951
1.0	.000	.000	.609	19.196 + i 2.825

^aTo get the proper Coulomb contributions the numbers in this table must be multiplied by Z^2 .

^bTo express these numbers in c.g.s. units, multiply by e^2/v

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Figure 1

Fit of a second neighbor Born-von Karman model to the phonon dispersion curves of diamond in the (001) and (111) directions. Dots are transverse phonons. Triangles are longitudinal phonons.

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