sitive to the magnitude of Z_t in diamond, similar calculations of the normal modes of vibration for planar molecules (such as benzene) should test the validity of the present $Z_\sigma - Z_\pi$ model of sp^2 bonding. We also remark that the two-phonon induced infrared absorption in diamond[16] and benzene measures the magnitude and displacement of the bonding charges directly.

---

[16] R. Wehner, H. Borik, and W. Kress, Solid State Commun. **5**, 307 (1967).

Covalent Bond in Crystals. IV. Lattice Deformation Energies

J. C. PHILLIPS

Department of Physics and James Franck Institute, The University of Chicago, Chicago, Illinois 60637

(Received 3 August 1967)

A general method is described for calculating lattice deformation energies in covalent structures. The formulas are presented explicitly for harmonic energies in diamond-type crystals. The theory differs intrinsically from linear screening theories because of the inclusion of bond-stretching terms. These are calculated using a dynamical covalent sum rule. The results show that bond stretching leads to large bond-bond interaction energies that are similar to those in a nearest-neighbor classical shell model. The theory can be used to infer the covalent screening function from lattice vibration spectra measured by inelastic neutron scattering.

I. INTRODUCTION

IN the preceding papers of this series[1-3] we have developed the elements of a microscopic theory of covalent bonding with special reference to crystalline structures. At present the theory is axiomatic in character, but it is straightforward to calculate the total energy of the system as a functional of the structural parameters. Minimization of this energy with regard to these parameters yields a self-consistent theory. Several preliminary numerical estimates based on optical data suggested that the self-consistent theory will differ little from the *a posteriori* one with parameters determined from macroscopic dielectric properties.

The purpose of the present paper is to carry the axiomatic theory one step further and to present a simple prescription for lattice deformation energies. According to the usual theory of lattice dynamics[4] (based on the adiabatic approximation), nuclear motion can be described in terms of an effective potential energy function Φ. This function describes the change in electronic energy induced by the displacements $\mathbf{u}(l)$ and $\mathbf{u}(l')$ of the atoms with equilibrium sites at $\mathbf{r} = \mathbf{R}_l$ and $\mathbf{R}_{l'}$, respectively. If we know the lattice deformation

energies, $[\partial^2\Phi/\partial\mathbf{u}(l)\partial\mathbf{u}(l')]:\mathbf{u}(l)\mathbf{u}(l')$, then the lattice vibration frequencies can be obtained by a transformation to normal modes.

The method adopted in this paper follows closely the procedure which has proved successful in metals.[4-6] Briefly that method calculates lattice deformation energies using linear screening of the ion core potential $\tilde{v}_i(r)$. Such screening can easily be described[7] in terms of plane-wave screening of ion-core pseudopotential form factors $v_i(q)$. Our treatment reduces to the metallic one when $E_g = 0$.

In Sec. II we review the metallic theory.[8-11] In Sec. III the modifications of the metallic theory required when $E_g \neq 0$ are presented. It turns out that these can be described in terms of one additional axiom which expresses the effect of bond stretching on E_g. This is described in Sec. IV, and the contribution of a normal mode is derived in Sec. V. Electron-phonon interaction is discussed in Sec. VI and the relation to linear response theory is discussed in Sec. VII.

---

[1] J. C. Phillips, Phys. Rev. **166**, 832 (1968), I.

[2] J. C. Phillips, second preceding paper, Phys. Rev. **168**, 905 (1968), II.

[3] J. C. Phillips, first preceding paper, Phys. Rev. **168**, 912 (1968), III.

[4] W. Cochran, Rept. Progr. Phys. **26**, 1 (1963).

[5] T. Toya, J. Res. Inst. Catalys., Sapporo **6**, 183 (1958).

[6] T. Toya, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Oxford, 1965), p. 91.

[7] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961).

[8] A. O. E. Animalu, F. Bonsignori, and V. Bortolani, Nuovo Cimento **43B**, 159 (1966).

[9] W. Cochran, Proc. Roy. Soc. (London) **A276**, 308 (1963).

[10] L. Sham, Proc. Roy. Soc. (London) **A283**, 33 (1965).

[11] W. A. Harrison, Phys. Rev. **139**, A179 (1965).

II. METALLIC SCREENING

Let the ions be given the static displacement

$$\mathbf{u}_n(l)=\sum_p \mathbf{e}_n{}^p(\mathbf{q})U^p(\mathbf{q})\exp[i\mathbf{q}\cdot\mathbf{R}_l]+\text{c.c.},\quad(2.1)$$

where l labels atomic cells, n labels atoms in the unit cell, and $\mathbf{e}$ is a unit polarization vector. The effective potential Φ_2 for harmonic ion motion in metals consists of three terms:

$$\Phi_2=\Phi_2{}^C+\Phi_2{}^R+\Phi_2{}^L,\quad(2.2)$$

which respectively represent $\Phi_2{}^C$: the ion-ion Coulomb interaction, derived from expanding $\tilde{v}_i(\mathbf{r}+\mathbf{u}_n(l)-\mathbf{R}_l+\mathbf{r}_n)$ to second order in $\mathbf{u}_n(l)$; $\Phi_2{}^R$: the Born-Mayer core-core repulsive term, which is negligible for light metals and semiconductors; and $\Phi_2{}^L$: the electronic energy arising from linear screening of the perturbation obtained from expanding $\tilde{v}_i$ to first order in $\mathbf{u}_n(l)$. There are two contributions to $\Phi_2{}^L$, from ion-electron and electron-electron interactions, and these are to be determined self-consistently.

The Coulomb interaction energy $\Phi_2{}^C$ may be evaluated by Ewald's method.[12] In elemental lattices the result is[4]

$$\Phi_2{}^C=\frac{4\pi N e^2}{3\Omega}\sum_p |\mathbf{U}^p(\mathbf{q})|^2+\Phi_2{}^E,\quad(2.3)$$

where N is the number of valence electrons per atom, Ω is the volume of the unit cell, and all atomic sites are assumed equivalent (as in the diamond crystal structure). The term $\Phi_2{}^E$ denotes an Ewald sum.[12]

The electronic energy deformation is derived from the perturbation potential

$$V_i{}'=-\sum_{l,n}\exp[i\mathbf{q}\cdot\mathbf{R}_l]\mathbf{U}_n(\mathbf{q})\tilde{v}_i{}'(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_n),\quad(2.4)$$

where

$$\tilde{v}_i{}'(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_n)\equiv\nabla\tilde{v}_i(\mathbf{r}-\mathbf{R}_l-\mathbf{r}_n).\quad(2.5)$$

The result is[10]

$$\Phi_2{}^L=\tfrac{1}{2}\sum_{q,p,p',n,n'}U^p(-\mathbf{q})U^{p'}(\mathbf{q})$$
$$\times\mathbf{e}_n{}^p(-\mathbf{q})\mathbf{e}_{n'}{}^{p'}(\mathbf{q}):\mathbf{X}_{nn'}(\mathbf{q}),\quad(2.6)$$

where the tensor

$$\mathbf{X}_{nn'}(\mathbf{q})=\sum_{G,G'}\{\mathbf{X}_{nn'}{}^{(0)}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')$$
$$-\mathbf{X}_{nn'}{}^{(0)}(\mathbf{G},\mathbf{G}')\}\quad(2.7)$$

is expressed in terms of the pseudopotential tensor

$$\mathbf{X}_{nn'}{}^{(0)}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')$$
$$=\{(4\pi e^2/|\mathbf{q}+\mathbf{G}|^2)[1-f(\mathbf{q}+\mathbf{G})]\}^{-1}$$
$$\times\{\epsilon^{-1}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G}')-\delta_{G,G'}\}(\mathbf{q}+\mathbf{G})(\mathbf{q}+\mathbf{G}')$$
$$\times v_{in}(-\mathbf{q}-\mathbf{G})v_{in'}(\mathbf{q}+\mathbf{G}').\quad(2.8)$$

In practice, local-field corrections are neglected in metals so that $\mathbf{G}=\mathbf{G}'$ and

$$\epsilon^{-1}(\mathbf{q}+\mathbf{G},\,\mathbf{q}+\mathbf{G})=\epsilon_f{}^{-1}(\mathbf{q}+\mathbf{G})\quad(2.9)$$

is simply the plane-wave dielectric function in the Hartree approximation. The factor $f(\mathbf{q}+\mathbf{G})$ in (28) corrects the Hartree approximation to include roughly the effects of exchange and correlation. Further small modifications of (2.8) are needed[8] to correct for the orthogonality hole.

III. DEFORMATION ENERGIES IN THE PRESENCE OF COVALENT BONDS

In covalent crystals Φ_2 becomes

$$\Phi_2=\Phi_2{}^C+\Phi_2{}^R+\Phi_2{}^M+\Phi_2{}^S+\Phi_2{}^L,\quad(3.1)$$

where the first two terms have the same interpretation as in metals. The change in Madelung energy of the lattice (denoted by E_3 in I) with charges

$$Z_a=-4Z_b\quad(3.2)$$

at the atomic sites and

$$2Z_b=-[2|e|/|\epsilon_s(0)|]\quad(3.3)$$

at the bonding sites is denoted by $\Phi_2{}^M$. Holding Z_b fixed, we can calculate this change by Ewald techniques.[12]

Because $\epsilon_s(0)$ is a function of N, according to (3.3) displacement of an atom must change Z_b. In equilibrium E_g and Z_b are related, and this means that the screening function $\epsilon_s(x; N,E_g)$ is changed by lattice deformations. The valence energy E_v (see I) depends on E_g; the second-order correction to E_v arising from changes in E_g is denoted by $\Phi_2{}^S$.

IV. CHANGE OF GAP PARAMETER WITH BOND STRETCHING

The effect of bond stretching on $\epsilon_s(0)$ to first order, i.e., the hydrostatic derivative

$$N[\partial\epsilon_s(0)/\partial N]=\epsilon_s{}'(0)\quad(4.1)$$

has been measured.[13] In principle $\epsilon_s{}'(0)$ can also be calculated by the self-consistent methods of I. From (3.3) and (4.1) we see that Z_b changes when the bond length τ changes. We must also determine the change in Z_a. To this end we assume the validity of the following relation

$$Z_a(l,n)=-\sum_c Z_b(\tau_c),\quad(4.2)$$

which we call the *covalent sum rule* [the dynamical generalization of (3.2)]. In (4.2) the sum extends over the covalent bonds $c=c(l,n)$ which are adjacent to the atomic site at $\mathbf{R}_l+\mathbf{r}_n$ and τ_c is the nearest-neighbor separation along each of these bonds.

[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954); E. W. Kellerman, Phil. Trans. Roy. Soc. (London) **A238**, 513 (1940).

[13] D. F. Gibbs and G. J. Hill, Phil. Mag. **9**, 367 (1964).

We may now write

$$\frac{Z_b(\tau_c)}{|e|} = \frac{-1}{\epsilon_s(0)} + a_1(\delta\tau_c) + a_2\tfrac{1}{2}(\delta\tau_c)^2, \qquad (4.3)$$

where experimental values may be used for

$$a_1 = -\{3\epsilon_s'(0)/\tau_c[\epsilon_s(0)]^2\}. \qquad (4.4)$$

The value of a_2 can be calculated self-consistently from minimizing $E_v(N,E_g)$, i.e., evaluating $\partial^2 E_v/\partial N \partial E_g$. For a simple trial calculation a_2 can be taken as an adjustable parameter.

It should be remarked that the approximation made in assuming (4.2) is essentially one of neglecting the effect of changes in bond-bond interactions on Z_b. This is similar in some respects to determining the bonding sites from $O_2(\mathbf{r})$ rather than $O_\infty(\mathbf{r})$, as discussed in Sec. VIII of I. We saw in II that the error involved in this approximation is small compared to the chemical shifts in physical properties (e.g., from Si to Ge) associated with changes in $v_i(q)$.

From the relations (3.3), (4.2) and

$$\epsilon_s(0) = 1 + (\hbar\omega_p/E_g)^2 C, \qquad (4.5)$$

one can deduce $E_g(l,n)$ by relating it to $Z_a(l,n)$ and thence to an effective $Z_b(l,n)$ defined by (3.2). The result is

$$\frac{E_g(l,n)}{E_{g0}} = \left[\frac{(1-\alpha)^{-1} - \epsilon_s^{-1}(0)}{1 - \epsilon_s^{-1}(0)}\right]^{-1/2} \qquad (4.6)$$

$$\alpha = \frac{\epsilon_s(0)}{4|e|} \sum_c \left[a_1\delta\tau_c + \tfrac{1}{2}a_2(\delta\tau_c)^2\right]. \qquad (4.7)$$

We can simplify (4.6) materially by neglecting $[\epsilon_s(0)]^{-2}$ compared to 1. This gives

$$\frac{E_g(l,n)}{E_{g0}} = 1 - \tfrac{1}{2}[1 + \epsilon_s^{-1}(0)]\alpha - \tfrac{1}{8}[1 - 2\epsilon_s^{-1}(0)]\alpha^2. \quad (4.8)$$

In the harmonic approximation only terms of order $(\delta\tau_c)^2$ need be retained in (4.8), so that

$$\alpha^2 = \left(\frac{\epsilon_s(0)}{4|e|}\right)^2 \left(\sum_c a_1\delta\tau_c\right)^2. \qquad (4.9)$$

The cross terms of the form $\delta\tau_c\delta\tau_{c'}$ in (4.9) represent the effect of bond-bond interactions. The expansion for $E_g(l,n)$ is thus

$$\frac{E_g(l,n)}{E_{g0}} = 1 + b_1 \sum_c \delta\tau_c + \tfrac{1}{2}b_2 \sum_c (\delta\tau_c)^2$$

$$+ b_3 \sum_{c,c'} \delta\tau_c\delta\tau_{c'}(1 - \delta_{cc'}), \qquad (4.10)$$

with

$$b_1 = -\frac{\epsilon_s(0)}{8|e|}[1 + \epsilon_s^{-1}(0)]a_1 \qquad (4.11)$$

$$b_2 = -\frac{\epsilon_s(0)}{8|e|}[a_2[1 + \epsilon_s(0)]^{-1}$$

$$+ \frac{\epsilon_s(0)}{2|e|}[1 - 2\epsilon_s^{-1}(0)]a_1^2] \quad (4.12)$$

$$b_3 = -\left(\frac{\epsilon_s(0)}{4|e|}\right)^2 [1 - 2\epsilon_s^{-1}(0)]a_1^2. \qquad (4.13)$$

V. BOND STRETCHING BY PHONONS

If the bond vector τ_c connects ions (l,n) and (l',n') the bond stretching associated with the displacements $\mathbf{u}_n(l)$ and $\mathbf{u}_{n'}(l')$ is determined from the identity

$$(\tau_c + \delta\tau_c)^2 = |\tau_c + \mathbf{u}_n(l) - \mathbf{u}_{n'}(l')|^2. \qquad (5.1)$$

In the diamond lattice the four nearest neighbors of an ion (l,n) consist of one neighbor (l,n') with bond vector τ_c in the same unit cell, and three neighbors (l',n') in adjacent unit cells with bond vectors $\tau_{c'}$. The three lattice vectors connecting (l,n) with (l',n) satisfy the relation

$$\mathbf{R}_{l'} - \mathbf{R}_l = \tau_c - \tau_{c'}, \qquad (5.2)$$

with $c' \neq c$. Substitution of (2.1) in (5.1) yields [in a form symmetrical between (n,n') and (c,c')] the relation

$$\delta\tau_c = |\tau_c \cdot \delta\tau_c|/\tau, \qquad (5.3)$$

with

$$\delta\tau_c = \sum_p \mathbf{e}_n{}^p(\mathbf{q})U^p(\mathbf{q})\exp(-i\mathbf{q}\cdot\tau_c)$$

$$- \sum_{p'} \mathbf{e}_{n'}{}^{p'}(\mathbf{q})U^{p'}(\mathbf{q})\exp(i\mathbf{q}\cdot\tfrac{1}{2}\tau_c), \quad (5.4)$$

where $U^p(\mathbf{q})$ and $U^{p'}(\mathbf{q})$ are real. Note that

$$(\delta\tau_c)^2 = |\sum_p \mathbf{e}_n{}^p(\mathbf{q})U^p(\mathbf{q})|^2 + |\sum_p \mathbf{e}_{n'}{}^p(\mathbf{q})U^p(\mathbf{q})|^2$$

$$- 2\sum_{pp'} \mathbf{e}_n{}^p(\mathbf{q}) \cdot \mathbf{e}_{n'}{}^{p'}(\mathbf{q})U^p(\mathbf{q})U^{p'}(\mathbf{q})\cos\mathbf{q}\cdot\tau_c. \quad (5.5)$$

The first two terms on the rhs of (5.5) alter Φ_2 in an intra-atomic way similar to the terms that occur in a linear screening theory [cf. Eq. (2.3)]. The third term, proportional to $U^p(\mathbf{q})U^{p'}(\mathbf{q})$, does not arise in the linear theory.

By substituting (5.3)–(5.5) in (4.10) we can compute $\Phi_2{}^A$, $\Phi_2{}^B$, and $\Phi_2{}^D$ by applying the chain rule to E_1, E_2, and E_4. For example the change in one-electron

energies associated with bond stretching is given by

$$\Phi_2{}^A = E_{g0}\frac{\partial E_1}{\partial E_g}[\tfrac{1}{2}b_2\sum_c(\delta\tau_c)^2 + b_3\sum_{c'c}\delta\tau_c\delta\tau_{c'}(1-\delta_{cc'})]$$

$$+E_{g0}{}^2\left(\frac{\partial^2 E_1}{\partial E_g{}^2}\right)b_1{}^2(\sum_c\delta\tau_c)^2. \quad (5.6)$$

Note that all the terms include bond-bond interactions. We stress this point to show that the covalent sum rule (4.2) does not eliminate such terms from the theory. A classical shell model including only nearest-neighbor forces also contains such terms, but they depend on many parameters. The present theory contains only one disposable parameter, a_2.

To conclude this section we remark that $\Phi_2{}^Q$ contains two kinds of terms. The induced quadrupole-quadrupole interaction depends only on a_1. On the other hand, the induced quadrupole interacts with Z_a and Z_b to yield terms which depend on both a_1 and a_2.

VI. ELECTRON-PHONON INTERACTIONS

The bare electron-phonon interaction V_i' in metals, Eq. (2.4), can be regarded as a special case of the covalent theory with $E_{g0}=0$. If we fix E_g, the same perturbation potential is obtained for $E_{g0}\neq0$. Then the formulas (2.6)–(2.8) still hold for $\Phi_2{}^L$, but in (2.9) we must use

$$\epsilon^{-1}(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G}) = \epsilon_s{}^{-1}(\mathbf{q}+\mathbf{G}). \quad (6.1)$$

This simple result for electron-phonon interaction energies illustrates the advantages of our *a posteriori* model. All the characteristic covalent effects are described by the difference between (6.1) and (2.9), as well as the bond stretching terms discussed in the preceding sections.

VII. RELATION TO LINEAR RESPONSE THEORY

In the evaluation of (2.8) in metals it is customary[8] to neglect the umklapp terms $(\mathbf{G}\neq\mathbf{G'})$ in $\epsilon^{-1}(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G'})$. It has sometimes been suggested that if these terms were included in the theory, an accurate treatment of the lattice-vibration spectra of covalent crystals could be obtained. It is argued that an infinitesimal displacement of the ion cores is equivalent to application of an external potential, and that the response to this weak potential can be obtained in the linear approximation, using the dielectric function of the static lattice. Apart from off-energy shell corrections to the pseudopotential form factors, such a theory, it is argued, should be exact.

The viewpoint taken here is rather different. We find that in addition to the terms in Φ_2 depending on $\epsilon_s{}^{-1}(\mathbf{q}+\mathbf{G}, \mathbf{q}+\mathbf{G})$, there are a number of new and unexpected terms. These arise because the deformation of the lattice changes the screening function $\epsilon_s(x,N,E_g)$ through changes in E_g. These changes in turn alter the self-energy of the occupied valence states. Such changes

are absent in the linear screening theory which calculates Φ_2 only to order $|\tilde{v}_i|^2$. It is not clear how such interactions could be extracted from the umklapp terms, and at present it appears that the applicability of linear response theory to covalent crystals remains to be established.

VIII. CONCLUSIONS

In this paper we have shown that the *a posteriori* model of covalent bonding proposed in the preceding papers of this series can be extended to give a complete and internally consistent model for the lattice vibrations of covalent crystals. Previously models of lattice vibrations of both ionic and covalent crystals have utilized a classical approach based on a multipole expansion of the electrostatic energy of polarizable nonoverlapping ions.[14] A number of authors (Darwin,[15] Nozieres and Pines,[16] Cochran,[17] Leigh and Szigeti[18]) have suggested that the valence electrons in covalent crystals are not acted on by the Lorentz local field; because they are nonlocalized and interpenetrating they "see" only the macroscopic field. Thus Cochran anticipated[17] that a radical revision of the shell-model theory would be required to describe covalent crystals.

We believe that the present model represents a realization of these suggestions. Because the bonding charges are not situated at atomic sites, the irrelevance to this model of the Lorentz field is manifest. The theory reduces to the metallic one in the limit $E_g \to 0$, but it contains qualitatively new terms. These are found to be self-energy effects associated with bond-stretching. It is hoped that numerical calculations based on the formalism presented here will yield dispersion curves which can be compared with those measured by neutron scattering. If the electron-phonon harmonic energy $\Phi_2{}^L$ is not too small compared to the remaining terms in (3.1), such a comparison should enable us to explore $\epsilon_s(x,N,E_g)$ and compare the results with Penn's expression[19] $\epsilon_p(x,N,E_g)$. Such a comparison has already been made[20] using the semiclassical shell model. For the reasons mentioned at the end of Sec. V, we believe that the present theory is likely to be more accurate and more informative.

After completion of this paper an interesting paper

[14] V. S. Mashkevich and K. B. Tolpygo, Zh. Eksperim. i Teor. Fiz. **32**, 520 (1957) [English transl.: Soviet Phys.—JETP **5**, 435 (1957)].

[15] C. G. Darwin, Proc. Roy. Soc. (London) **146A**, 17 (1934). This paper contains an amusing discussion of the extent to which local field corrections are influenced by the model chosen.

[16] P. Nozieres and D. Pines, Phys. Rev. **109**, 762 (1958). These authors show that when $\hbar w_p > E_g$, only the macroscopic field acts on the electrons. According to (4.5), this is equivalent to $\epsilon(0) > 2$, which is true for all covalent crystals.

[17] W. Cochran, Rept. Progr. Phys. **26**, 1 (1963); W. Cochran and R. A. Cowley, Handbuch der Physik (Springer-Verlag, Heidelberg, 1967), XXV 2a, p. 99.

[18] R. S. Leigh and B. Szigeti, Phys. Rev. Letters **19**, 566 (1967).

[19] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[20] W. Cochran and J. C. Phillips, Phys. Rev. **134**, 1402 (1964).

on the lattice dynamics of white Sn appeared.[21] There it is shown that conventional linear screening theory leads to $\omega^2(q)<0$ for transverse acoustic modes and q near Brillouin zone faces. This instability arises from neglect of terms associated with electronic energy gaps near Brillouin zone faces, and it is corrected by adding short-range bond-stretching forces parametrically. The present paper provides the first *microscopic* explanation of the origin of these forces in terms of dielectric screening theory.

ACKNOWLEDGMENTS

APPENDIX: EFFECTS OF BOND BENDING

In general one might expect that the bonding charge Z_b would depend both on the bond length τ_b and on changes in $\tau_b \cdot \tau_{b'}$ associated with changes in $\phi_{bb'}$. We show here that in the elastic limit a consistent microscopic model is obtained with Z_b a function of τ_b only. This provides formal justification for the expression for $\Phi_2{}^S$ given in Eq. (3.4).

Our discussion is based on the photoelastic constants p_{ijkl} which provide the connection between the strain tensor e_{kl} and the change in the dielectric tensor $\Delta\epsilon_{ij}$. The experimental values for these constants in diamond and Si satisfy[22] a relation first derived for the ordinary elastic constants by Keating.[23] Keating's model involves two parameters, α and β. The hydrostatic photoelastic constant, $p_{11}+2p_{12}$, is proportional to $3\alpha-\beta$,

while $\alpha-3\beta$ describes the effects of pure bond bending depending on changes in $\phi_{bb'}$ only.

To utilize the photoelastic constants, we note that changes in bond charge must be described by changes in a scalar. The appropriate scalar is

$$\bar{\epsilon}=\tfrac{1}{3}\operatorname{Tr}\varepsilon. \tag{A1}$$

From cubic symmetry we see tha $\bar{\epsilon}$ is unchanged by a shear strain e_{xy}. Inspection of the diamond structure shows that of the four bonds attached to each atom, two are stretched by e_{xy}, and two shortened by the same amount. Thus the dynamical sum rule (4.2) is satisfied if we interpret Z_a as

$$Z_a(l,n)=Z/\bar{\epsilon}. \tag{A2}$$

On the other hand, e_{xx} changes $\bar{\epsilon}$ only in proportion to $p_{11}+2p_{12}$, i.e., in proportion to $3\alpha-\beta$. Because of linearity, (A2) will be consistent with (4.2) for any combination of strains. Only e_{xx} gives information about changes in Z_b so that the photoelastic constants (because of linearity) can be used once. Bond stretching is the dominant effect (because it changes the long-range forces) so that (4.1), (4.2), and (A2) should describe the most important changes in Z_b.

The third-order photoelastic constants (which should be measurable by an extension[22] of present techniques) should be dominated by anharmonic bond stretching, the parameter a_2 in Eq. (4.3). Keating has shown[24] that anharmonic bond stretching makes the dominant contribution to the third-order elastic constants.

The last question concerns the completeness of our microscopic model. What is there in our model corresponding to changes in charge distribution produced by bond bending? The answer, of course, is that such changes alter

$$\epsilon_{ij'}=\epsilon_{ij}-\bar{\epsilon}\delta_{ij}. \tag{A3}$$

In the uniaxial case ϵ_{ij}' is connected directly with the quadrupole moments $Q_{a\,p}$ discussed in Sec. III of Ref. 3. In the linear limit ϵ_{ij}' and ε determine Q_{ij} completely.

[21] E. G. Brovman and Y. Kagan, Zh. Eksperim. i Teor. Fiz. **52**, 557 (1967) [English transl.: Soviet Phys.—JETP **25**, 365 (1967)].

[22] J. C. Phillips, Phys. Letters, **25A**, 727 (1967).

[23] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[24] P. N. Keating, Phys. Rev. **149**, 674 (1966).