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Relation between Photoelasticity, Electrostriction, and First-Order Raman Effect in Crystals of the Diamond Structure

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A lattice theory of the elasto-optic and electrostriction constants of crystals of the diamond structure is presented. The results of the theory relate these constants to the derivatives of the electronic polarizability which determine the intensity of the first-order Raman scattering of light by such crystals. Experimental values of the elasto-optic constants are used to estimate the electronic polarizability derivatives for diamond, germanium, and silicon.

I. INTRODUCTION

THE intensity of the first-order Raman scattering of light by the lattice vibrations of a crystal is determined essentially by the coefficients $\{P_{\mu\nu,\alpha}(l\kappa)\}$ which occur in the expansion of the electronic polarizability of the crystal in powers of the displacements of the atoms from their equilibrium positions,[1]

$$P_{\mu\nu}=P_{\mu\nu}^{(0)}+\sum_{l\kappa\alpha} P_{\mu\nu,\alpha}(l\kappa)u_\alpha(l\kappa)+\cdots. \qquad (1.1)$$

In this expression $u_\alpha(l\kappa)$ is the α Cartesian component of the displacement of the κth atom in the lth unit cell from its equilibrium position. In general, the expansion coefficients $P_{\mu\nu}^{(0)}$, $P_{\mu\nu,\alpha}(l\kappa)$, $\cdots$, are functions of the frequency of the incident light. However, in many applications the frequency of the incident light is small compared with the frequency of the electronic transitions in the crystal, and can be taken to be zero with little error. A consequence of this approximation, which we make in the remainder of this paper, is that $P_{\mu\nu}$ is a real operator which is symmetric in the indices μ and ν.

Homopolar crystals of the diamond structure display a first-order Raman effect. For such crystals symmetry arguments show that the elements of the tensor $P_{\mu\nu,\alpha}(l\kappa)$ can all be written in terms of a single parameter P as

$$P_{\mu\nu,\alpha}(01)=P|\epsilon_{\mu\nu\alpha}|=-P_{\mu\nu,\alpha}(02), \qquad (1.2)$$

when the crystal axes and the coordinate system coincide, where $\epsilon_{\mu\nu\alpha}$ is the Levi-Civita symbol. In writing Eq. (1.2) we have used the fact that, because of the periodicity of the crystal, $P_{\mu\nu,\alpha}(l\kappa)$ is independent of the cell index l, and have labeled the two atoms in a primitive unit cell by $\kappa=1, 2$. The calculation of the value of the coefficient P from first principles, for a given crystal possessing the diamond structure, while possible in principle, is nevertheless beset by serious computational difficulties, and has not been done yet. The lack of experimental values for the absolute intensity of light scattered from such crystals by one-phonon processes prevents the value of this parameter from being inferred from experimental scattering data. Consequently, all attempts to obtain values of P to date have proceeded indirectly.

In 1951, Theimer[2] related the parameter P to the elasto-optic constants of crystals of the diamond structure, and obtained an estimate of the value of the former coefficients from the experimental values of the latter for diamond. However, Theimer's calculation has been criticized by Born,[3] who pointed out that while the atomic coefficients $\{P_{\mu\nu,\alpha}(l\kappa)\}$ refer to a crystal with a fixed number of atoms, the elasto-optic constants are defined for a unit volume of the crystal, and that Theimer had overlooked the fact that an elastic deformation changes the number of atoms in a unit volume.

More recently Loudon[4] has derived a relation between the Raman tensor and the deformation potential for optical modes in homopolar semiconductors, and has used this result to obtain an order-of-magnitude estimate of the Raman efficiency for such crystals. [The Raman efficiency is defined as the ratio of the number of observed Raman photons produced per unit cross-sectional area of the crystal per unit time to the number of incident photons crossing unit area in unit time.]

In this paper we relate the elasto-optic and electrostriction constants of a crystal of the diamond structure to the coefficient P, from which estimates of the latter can be made. In doing so we correct the error in Theimer's paper. We use our results together with experimental values of the elasto-optic constants, to obtain values of P for diamond, silicon, and germanium. Knowledge of the first-order coefficients $\{P_{\mu\nu,\alpha}(l\kappa)\}$ enables one to predict the absolute intensity of the Raman scattering of light by one-phonon processes.

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[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 219.

[2] O. Theimer, Proc. Phys. Soc. (London) **65**, 38 (1952).

[3] Reference 1, p. 374.

[4] R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963).

The present calculations were motivated by two considerations. The first is that even if the absolute intensity of the Raman scattering of light by one phonon processes were determined experimentally, this information would yield only the magnitude of P, but not its sign. The calculations described in this paper yield both the magnitude and sign of P. Second, from a knowledge of these coefficients one can calculate the magnitude of the static electric field which is required to induce a measurable one-phonon infrared lattice-vibration absorption in homopolar crystals of the diamond structure.[5]

Recently, Anastassakis, Iwasa, and Burstein[6] have succeeded in inducing one-phonon lattice-vibration absorption at the Raman frequency of diamond by applying a static electric field of 1.2×10^5 V/cm to their sample. From the integrated absorption under the observed peak, these authors were able to infer a value of 4×10^{-16} cm^2 for the magnitude of the coefficient P. This result provides us with a check on the results of the present calculations. In addition, recent measurements of the first-order Raman spectra of silicon[7,8] and of germanium[8] have provided values of the ratios of $|P_{\mathrm{Si}}/P_{\mathrm{diamond}}|$ and of $|P_{\mathrm{Si}}/P_{\mathrm{Ge}}|$, which also serve as a check on the present calculations.

II. ELASTO-OPTIC AND ELECTROSTRICTION CONSTANTS

In this section we derive the formal expressions for the elasto-optic and electrostriction constants which provide the starting point for their calculation from a microscopic model of a crystal.

We began by considering an elastic dielectric which is subjected to a homogeneous deformation in the presence of an external electric field. We denote the position of some point in the undeformed medium, referred to some fixed Cartesian coordinate system, by the vector $\mathbf{X}$, and denote the position of the same point in the deformed medium, referred to the original coordinate system, by the position vector $\mathbf{x}$. The difference between these two points is the displacement $\mathbf{u}(\mathbf{X})$, which we express as a function of the coordinates of the point in the undeformed medium:

$$x_\alpha = X_\alpha + u_\alpha(\mathbf{X}), \quad \alpha = 1, 2, 3. \tag{2.1}$$

We define the position gradient $F_{\alpha\beta}$ by

$$F_{\alpha\beta} = \frac{\partial x_\alpha}{\partial X_\beta} = \delta_{\alpha\beta} + \frac{\partial u_\alpha(\mathbf{X})}{\partial X_\beta} \equiv \delta_{\alpha\beta} + \epsilon_{\alpha\beta}. \tag{2.2}$$

We will call the elements $\{\epsilon_{\alpha\beta}\}$ the deformation parameters. In the present work we will consider only homogeneous deformations so that $\epsilon_{\alpha\beta}$ is a constant, not a function of $\mathbf{X}$.

If the volume of some region of the undeformed medium is V_0, the volume V of the image of this region in the deformed medium is given by

$$V = JV_0, \tag{2.3}$$

where

$$J = \det\mathbf{F} > 0. \tag{2.4}$$

In terms of the deformation parameters $\{\epsilon_{\alpha\beta}\}$ we define the Lagrangian finite strain parameters $\{\eta_{\alpha\beta}\}$ by

$$\eta_{\alpha\beta} = \tfrac{1}{2}[\epsilon_{\alpha\beta} + \epsilon_{\beta\alpha} + \sum_\lambda \epsilon_{\lambda\alpha}\epsilon_{\lambda\beta}]. \tag{2.5}$$

Note that while $\epsilon_{\alpha\beta}$ has not been assumed to be symmetric in α and β, $\eta_{\alpha\beta}$ is by construction symmetric in these indices. The tensor $\boldsymbol{\eta}$ describes only pure strains, and vanishes if the deformation described by the $\{\epsilon_{\alpha\beta}\}$ is a pure rotation. Although $\eta_{\alpha\beta}$ is defined uniquely in terms of the parameters $\{\epsilon_{\alpha\beta}\}$, the reverse is not true: to any set of parameters $\{\eta_{\alpha\beta}\}$ there corresponds an infinite number of sets of $\{\epsilon_{\alpha\beta}\}$, which differ among themselves only in the orientation of the crystal relative to a fixed coordinate system which they describe.

We can rewrite Eq. (2.5) in matrix form as

$$\boldsymbol{\eta} = \tfrac{1}{2}(\mathbf{C} - \mathbf{I}), \tag{2.6}$$

where

$$\mathbf{C} = \mathbf{F}^T\mathbf{F}. \tag{2.7}$$

Since the determinant of the transpose of a matrix equals the determinant of the matrix itself, we can use Eqs. (2.4), (2.6), and (2.7), to express J alternatively as

$$\begin{aligned} J^2 &= \det\mathbf{F}\,\det\mathbf{F} = \det\mathbf{F}^T\,\det\mathbf{F} \\ &= \det\mathbf{F}^T\mathbf{F} = \det\mathbf{C} = \det(\mathbf{I} + 2\boldsymbol{\eta}), \end{aligned}$$

so that

$$J = [\det(\mathbf{I} + 2\boldsymbol{\eta})]^{1/2}. \tag{2.8}$$

At the same time that we introduce the Lagrangian finite strain parameters $\{\eta_{\alpha\beta}\}$ in terms of the deformation parameters, we must introduce the contravariant components of the electric field, $\mathcal{E}_\mu$, which are defined in terms of the true field components E_μ by

$$\mathcal{E}_\mu = \sum_\rho F_{\rho\mu}E_\rho = E_\mu + \sum_\rho \epsilon_{\rho\mu}E_\rho. \tag{2.9}$$

The physical interpretation of the components $\{\mathcal{E}_\alpha\}$ is that, apart from factors which depend on the primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ of the undeformed crystal and on the Lagrangian strain parameters $\{\eta_{\alpha\beta}\}$, they are the components of the applied electric field with respect to the primitive translation vectors of the de-

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[5] E. Burstein and S. Ganesan, J. Phys. (Paris) **26**, 637 (1965).

[6] E. Anastassakis, S. Iwasa, and E. Burstein, Phys. Rev. Letters **17**, 1051 (1966).

[7] J. P. Russell, Appl. Phys. Letters **6**, 223 (1965).

[8] J. H. Parker, Jr., D. W. Feldman, and M. Ashkin, Phys. Rev. (to be published).

formed crystal, $\mathbf{A}_1$, $\mathbf{A}_2$, $\mathbf{A}_3$, which are given by

$$A_\mu^\alpha = a_\mu^\alpha + \sum_\beta \epsilon_{\alpha\beta} a_\mu^\beta \quad \alpha,\beta = x,y,z$$
$$\mu = 1,2,3.$$

Finally, we need the fact that the position gradient $F_{\alpha\beta}$ is compounded of a pure rotation of the medium and of a pure strain:

$$\begin{aligned} F_{\alpha\beta} &= \sum_\lambda R_{\alpha\lambda} (\mathbf{C}^{1/2})_{\lambda\beta} \\ &= \sum_\lambda R_{\alpha\lambda} [(\mathbf{I} + 2\boldsymbol{\eta})^{1/2}]_{\lambda\beta}, \end{aligned} \tag{2.10}$$

where $\mathbf{R}$ is the rotation tensor.

Let us denote by $W = \hat{W}(\mathbf{F},\mathbf{E},\mathbf{X})$ the potential energy *per unit undeformed volume* of the medium. If the energy is invariant against rigid body rotations of the medium, there exists a function $\tilde{W}$ such that

$$W = \tilde{W}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}},\mathbf{X}). \tag{2.11}$$

If we wish to refer the energy to unit volume of the deformed crystal, we denote this function by $\hat{w}$, where

$$\hat{w} = J^{-1}\hat{W}, \tag{2.12}$$

so that

$$\tilde{W}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}},\mathbf{X}) = J\tilde{w}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}},\mathbf{X}). \tag{2.13}$$

In what follows, because we consider only homogeneous deformations, we will suppress the dependence of $\hat{W}$ and $\tilde{W}$ on $\mathbf{X}$.

That $\mathbf{E}$ and $\boldsymbol{\eta}$ together do not unambiguously describe a thermodynamic state of the system of medium plus field follows from the fact that the strain parameters $\{\eta_{\alpha\beta}\}$ give no indication of how the deformed medium is oriented with respect to the field.[9] Thus, instead of $\mathbf{E}$, we use its contravariant components in the deformed medium: The potential energy must be the same for two similarly deformed specimens (i.e., described by the same parameters $\eta_{\alpha\beta}$), each of which is subjected to an electric field whose contravariant components are the same in both cases.

If we denote the α Cartesian component of the polarization in the medium by P_α, the dielectric susceptibility tensor $\chi_{\alpha\beta}$ is defined by

$$\chi_{\alpha\beta}(\mathbf{F},\mathbf{E}) = \partial P_\alpha / \partial E_\beta. \tag{2.14}$$

The polarization is the dipole moment per unit volume of the deformed medium, and is given by

$$P_\alpha = -\frac{\partial \hat{w}}{\partial E_\alpha} = -J^{-1}\frac{\partial \hat{W}}{\partial E_\alpha}. \tag{2.15}$$

Therefore, the susceptibility of the deformed medium is

$$\begin{aligned} \chi_{\alpha\beta}(\mathbf{F},\mathbf{E}) &= -J^{-1}\frac{\partial^2 \hat{W}}{\partial E_\alpha E_\beta} \\ &= -J^{-1}\sum_{\rho\sigma} F_{\alpha\rho}F_{\beta\sigma}\frac{\partial^2 W}{\partial \mathcal{E}_\rho \mathcal{E}_\sigma} \\ &= \sum_{\mu\nu} R_{\alpha\mu}R_{\beta\nu}\chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}}), \end{aligned} \tag{2.16}$$

where

$$\begin{aligned} \chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}}) = -J^{-1}\sum_{\rho\sigma} & [\mathbf{I}+2\boldsymbol{\eta}]^{1/2}{}_{\mu\rho} \\ & \times [\mathbf{I}+2\boldsymbol{\eta}]^{1/2}{}_{\nu\sigma}\frac{\partial^2 \tilde{W}}{\partial \mathcal{E}_\rho \partial \mathcal{E}_\sigma}. \end{aligned} \tag{2.17}$$

In Eqs. (2.16) and (2.17) we have expressed the dielectric susceptibility of a homogeneously deformed crystal in an electric field in a form in which the effects of a pure strain and of a rigid body rotation of the medium are displayed separately and explicity. $\chi^s{}_{\mu\nu} \times(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})$ describes the response of the susceptibility of a pure strain of the medium. If the deformation of the medium described by the $\{\epsilon_{\alpha\beta}\}$ has a rigid body rotation of the medium in addition to a pure strain, Eq. (2.16) simply expresses the fact that the effect of the pure rotation on the susceptibility is to transform $\chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})$ according to the transformation law for a second-rank tensor under a pure rotation.

In studying the change in the susceptibility due to a homogeneous deformation of the medium it is clearly the change induced by a pure strain rather than a pure rotation which is of interest. In a measurement of the change of the susceptibility with deformation the effects of any pure rotation can be accounted for by the use of Eq. (2.16) or, alternatively, the experiment can be carried out in such a way that the deformation is a pure strain ($R_{\alpha\beta} = \delta_{\alpha\beta}$).

We can expand $\tilde{W}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})$ for a crystal of the diamond structure formally in powers of $\eta_{\alpha\beta}$ and $\mathcal{E}_\mu$ as

$$\begin{aligned} \tilde{W}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}}) = \tilde{W}_0 &+ \tfrac{1}{2}\sum_{\alpha\rho\beta\sigma} C_{\alpha\rho\beta\sigma}\eta_{\alpha\rho}\eta_{\beta\sigma} \\ &+ \tfrac{1}{6}\sum_{\alpha\rho\beta\sigma\gamma\tau} C_{\alpha\rho\beta\sigma\gamma\tau}\eta_{\alpha\rho}\eta_{\beta\sigma}\eta_{\gamma\tau} + \cdots \\ &+ \tfrac{1}{2}\sum_{\mu\nu} \mathcal{E}_\mu\mathcal{E}_\nu A_{\mu\nu} + \tfrac{1}{2}\sum_{\mu\nu\alpha\rho} \mathcal{E}_\mu\mathcal{E}_\nu A_{\mu\nu\alpha\rho}\eta_{\alpha\rho} \\ &+ \tfrac{1}{4}\sum_{\mu\nu\alpha\rho\beta\sigma} \mathcal{E}_\mu\mathcal{E}_\nu A_{\mu\nu\alpha\rho\beta\sigma}\eta_{\beta\sigma} + \cdots. \end{aligned} \tag{2.18}$$

The coefficients $\{C_{\alpha\rho\beta\sigma}\}$, $\{C_{\alpha\rho\beta\sigma\gamma\tau}\}$, $\cdots$ are the second-order, third-order, $\cdots$ elastic constants, respectively. $\tilde{W}_0$ is the potential-energy density of the undeformed crystal in the absence of the field. Terms containing odd powers of the field components are excluded by the presence of the inversion among the operations of the

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[9] Reference 1, p. 282.

point group of the space group $O_h{}^7$ of crystals of the diamond structure.

When Eq. (2.18) is substituted into Eq. (2.17), we can expand $\chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})$ to first order in the strain parameters with the result that

$$\chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})=-A_{\mu\nu}-\sum_{\rho\sigma}B_{\mu\nu\rho\sigma}\eta_{\rho\sigma}-\cdots, \qquad (2.19)$$

where

$$B_{\mu\nu\rho\sigma}=A_{\mu\nu\rho\sigma}+A_{\mu\sigma}\delta_{\nu\rho}+A_{\sigma\nu}\delta_{\mu\rho}-A_{\mu\nu}\delta_{\rho\sigma}. \qquad (2.20)$$

The dielectric tensor $\epsilon^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})$ is related to the dielectric susceptibility tensor by

$$\begin{aligned}\epsilon^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})&=\delta_{\mu\nu}+4\pi\chi^s{}_{\mu\nu}(\boldsymbol{\eta},\boldsymbol{\mathcal{E}})\\&=\delta_{\mu\nu}-4\pi A_{\mu\nu}-4\pi\sum_{\rho\sigma}B_{\mu\nu\rho\sigma}\eta_{\rho\sigma}-\cdots. \qquad (2.21)\end{aligned}$$

The Pockels' elasto-optic constants $\{p_{\mu\nu\rho\sigma}\}$ are defined by the relation[10]

$$(\boldsymbol{\epsilon}^{-1})_{\mu\nu}-(\epsilon_0{}^{-1})_{\mu\nu}=\sum_{\rho\sigma}p_{\mu\nu\rho\sigma}\eta_{\rho\sigma} \qquad (2.22)$$

to lowest order in the strain parameters, where $\boldsymbol{\epsilon}$ is the dielectric tensor for a strained medium, while $\boldsymbol{\epsilon}_0$ is the dielectric tensor for the unstrained medium. If we write $\boldsymbol{\epsilon}=\boldsymbol{\epsilon}_0+\delta\boldsymbol{\epsilon}$, then to first order in $\delta\boldsymbol{\epsilon}$

$$(\boldsymbol{\epsilon}^{-1})_{\mu\nu}-(\boldsymbol{\epsilon}_0{}^{-1})_{\mu\nu}=-\sum_{\rho\sigma}(\boldsymbol{\epsilon}_0{}^{-1})_{\mu\rho}\delta\epsilon_{\rho\sigma}(\boldsymbol{\epsilon}_0{}^{-1})_{\sigma\nu}. \qquad (2.23)$$

For cubic crystals $\boldsymbol{\epsilon}_0$ is isotropic,

$$(\boldsymbol{\epsilon}_0)_{\mu\nu}=\delta_{\mu\nu}\epsilon_0, \qquad (2.24)$$

and Eq. (2.23) takes the form

$$(\boldsymbol{\epsilon}^{-1})_{\mu\nu}-(\boldsymbol{\epsilon}_0{}^{-1})_{\mu\nu}=-(1/\epsilon_0{}^2)\delta\epsilon_{\mu\nu}. \qquad (2.25)$$

According to Eq. (2.21) $\delta\epsilon_{\mu\nu}$ is given by

$$\delta\epsilon_{\mu\nu}=-4\pi\sum_{\rho\sigma}B_{\mu\nu\rho\sigma}\eta_{\rho\sigma}, \qquad (2.26)$$

so that

$$(\boldsymbol{\epsilon}^{-1})_{\mu\nu}-(\boldsymbol{\epsilon}_0{}^{-1})_{\mu\nu}=(4\pi/\epsilon_0{}^2)\sum_{\rho\sigma}B_{\mu\nu\rho\sigma}\eta_{\rho\sigma}. \qquad (2.27)$$

Comparing Eqs. (2.22) and (2.27), we find that for cubic crystals Pockels' elasto-optic constants are given by

$$p_{\mu\nu\rho\sigma}=(4\pi/\epsilon_0{}^2)B_{\mu\nu\rho\sigma}. \qquad (2.28)$$

For cubic crystals the coefficient $A_{\mu\nu}$ is isotropic, and in view of Eq. (2.19) we write it as

$$A_{\mu\nu}=-\delta_{\mu\nu}\chi_0. \qquad (2.29)$$

On combining Eqs. (2.21) and (2.24) with Eq. (2.29), we find the expected result that χ_0 is given by

$$\chi_0=(\epsilon_0-1)/4\pi. \qquad (2.30)$$

Combining Eqs. (2.20), (2.28), and (2.29) we find that for cubic crystals

$$\begin{aligned}p_{\mu\nu\rho\sigma}=(4\pi/\epsilon_0{}^2)\{A_{\mu\nu\rho\sigma}&-\chi_0\\&\times[\delta_{\mu\sigma}\delta_{\nu\rho}+\delta_{\mu\rho}\delta_{\nu\sigma}-\delta_{\mu\nu}\delta_{\rho\sigma}]\}. \qquad (2.31)\end{aligned}$$

The fourth-rank tensors $p_{\mu\nu\rho\sigma}$ and $A_{\mu\nu\rho\sigma}$ have only three independent elements for cubic crystals. These are p_{1111}, p_{1122}, p_{1212}, and A_{1111}, A_{1122}, A_{1212}, respectively. The relations between these coefficients according to Eq. (2.31) are

$$\begin{aligned}p_{1111}&=(4\pi/\epsilon_0{}^2)[A_{1111}-\chi_0],\\p_{1122}&=(4\pi/\epsilon_0{}^2)[A_{1122}+\chi_0], \qquad (2.32)\\p_{1212}&=(4\pi/\epsilon_0{}^2)[A_{1212}-\chi_0].\end{aligned}$$

The inverse relations are

$$\begin{aligned}A_{1111}&=(\epsilon_0{}^2/4\pi)p_{1111}+\chi_0,\\A_{1122}&=(\epsilon_0{}^2/4\pi)p_{1122}-\chi_0, \qquad (2.33)\\A_{1212}&=(\epsilon_0{}^2/4\pi)p_{1212}+\chi_0.\end{aligned}$$

To obtain the electrostriction constants we proceed in a somewhat similar fashion. The general expression for the stress components in an arbitrarily deformed specimen in the presence of an electric field is[11]

$$\begin{aligned}T_{\alpha\gamma}=\frac{1}{2J}\bigg\{\sum_{\mu\nu}F_{\alpha\mu}F_{\gamma\nu}\bigg[\frac{\partial\tilde{W}}{\partial\eta_{\mu\nu}}+\frac{\partial\tilde{W}}{\partial\eta_{\nu\mu}}\bigg]&\\+E_\alpha\sum_\mu F_{\gamma\mu}\frac{\partial\tilde{W}}{\partial\mathcal{E}_\mu}+E_\gamma\sum_\mu F_{\alpha\mu}\frac{\partial\tilde{W}}{\partial\mathcal{E}_\mu}\bigg\}&. \qquad (2.34)\end{aligned}$$

When Eq. (2.18) for $\tilde{W}$ is substituted into Eq. (2.34), the expression for $T_{\alpha\gamma}$ becomes

$$\begin{aligned}T_{\alpha\gamma}=\frac{1}{J}\sum_{\mu\nu}F_{\alpha\mu}F_{\gamma\nu}\{\sum_{\beta\sigma}C_{\mu\nu\beta\sigma}\eta_{\beta\sigma}+\tfrac{1}{2}\sum_{\beta\sigma\delta\tau}C_{\mu\nu\beta\sigma\gamma\tau}\eta_{\beta\sigma}\eta_{\gamma\tau}+\tfrac{1}{2}\sum_{\beta\sigma}\mathcal{E}_\beta\mathcal{E}_\sigma A_{\beta\sigma\mu\nu}+\tfrac{1}{2}\sum_{\beta\sigma\delta\tau}\mathcal{E}_\beta\mathcal{E}_\sigma A_{\beta\sigma\mu\nu\delta\tau}\eta_{\delta\tau}+\cdots\}&\\+\frac{1}{2J}E_\alpha\sum_\mu F_{\gamma\mu}\{\sum_\nu\mathcal{E}_\nu A_{\mu\nu}+\sum_{\nu\beta\sigma}\mathcal{E}_\nu A_{\mu\nu\beta\sigma}\eta_{\beta\sigma}+\cdots\}+\frac{1}{2J}E_\gamma\sum_\mu F_{\alpha\mu}\{\sum_\nu\mathcal{E}_\nu A_{\mu\nu}+\sum_{\nu\beta\sigma}\mathcal{E}_\nu A_{\mu\nu\beta\sigma}\eta_{\beta\sigma}+\cdots\}&. \qquad (2.35)\end{aligned}$$

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[10] Reference 1, p. 376.
[11] Reference 1, p. 286.

If we rewrite Eq. (2.35) as

$$T_{\alpha\gamma}=\sum_{\beta\delta} C_{\alpha\gamma\beta\delta}\eta_{\beta\delta}+\cdots-\sum_{\beta} E_{\beta}e_{\beta\alpha\gamma} -\tfrac{1}{2}\sum_{\beta\delta} E_{\beta}E_{\delta}\gamma_{\beta\delta\alpha\gamma}-\cdots, \quad (2.36)$$

the coefficients $\{e_{\beta\alpha\gamma}\}$ are piezoelectric constants, and vanish for crystal of the diamond structure; the coefficients $\{\gamma_{\beta\delta\alpha\gamma}\}$ are electrostriction constants. Comparing Eqs. (2.35) and (2.36), we see that the coefficient $\gamma_{\beta\delta\alpha\gamma}$ is given explicitly by

$$\gamma_{\beta\delta\alpha\gamma}=-\frac{1}{J}\{\sum_{\rho\sigma\mu\nu} F_{\beta\rho}F_{\delta\sigma}F_{\alpha\mu}F_{\gamma\nu}A_{\rho\sigma\mu\nu} +\tfrac{1}{2}\delta_{\alpha\beta}\sum_{\mu\nu} F_{\gamma\mu}F_{\delta\nu}A_{\mu\nu}+\tfrac{1}{2}\delta_{\alpha\delta}\sum_{\mu\nu} F_{\gamma\mu}F_{\beta\nu}A_{\mu\nu} +\tfrac{1}{2}\delta_{\gamma\beta}\sum_{\mu\nu} F_{\alpha\mu}F_{\delta\nu}A_{\mu\nu}+\tfrac{1}{2}\delta_{\gamma\delta}\sum_{\mu\nu} F_{\alpha\mu}F_{\beta\nu}A_{\mu\nu}\}, \quad (2.37)$$

to the lowest explicit order in the strain parameters. This expression can be rewritten in a form in which the effects of a rigid body rotation of the specimen and of a pure strain are explicitly separated. To do this we make use of Eq. (2.10) and the fact that the rotation matrix **R** is a real, orthogonal 3×3 matrix. We are then led to the result that

$$\gamma_{\beta\delta\alpha\gamma}=\sum_{\rho_1\sigma_1\mu_1\nu_1} R_{\beta\rho_1}R_{\delta\sigma_1}R_{\alpha\mu_1}R_{\gamma\nu_1}\gamma^{(T)}{}_{\rho_1\sigma_1\mu_1\nu_1}, \quad (2.38)$$

where

$$\gamma^{(T)}{}_{\rho_1\sigma_1\mu_1\nu_1}=-\frac{1}{J}\{\sum_{\rho\sigma\mu\nu} C_{\rho_1\rho}{}^{1/2}C_{\sigma_1\sigma}{}^{1/2}C_{\mu_1\mu}{}^{1/2}C_{\nu_1\nu}{}^{1/2}A_{\rho\sigma\mu\nu} +\tfrac{1}{2}\sum_{\mu\nu}[\delta_{\rho_1\mu_1}C_{\sigma_1\nu}{}^{1/2}C_{\nu_1\mu}{}^{1/2}+\delta_{\sigma_1\mu_1}C_{\rho_1\nu}{}^{1/2}C_{\nu_1\mu}{}^{1/2} +\delta_{\rho_1\nu}C_{\sigma_1\nu}{}^{1/2}C_{\mu_1\mu}{}^{1/2}+\delta_{\sigma_1\nu_1}C_{\beta_1\nu}{}^{1/2}C_{\mu_1\mu}{}^{1/2}]A_{\mu\nu}\}. \quad (2.39)$$

The superscript T denotes that these constants relate the electrostrictive stress to the applied electric field. Equation (2.38) is the transformation law for a fourth-rank tensor under a rigid body rotation of the specimen. The elements of the tensor $\gamma^{(T)}{}_{\rho_1\sigma_1\mu_1\nu_1}$ describe the response of the electrostriction constants to a pure strain applied to the specimen. Because we have neglected the contributions to $\gamma_{\beta\delta\alpha\gamma}$ which have an explicit dependence on the $\{\eta_{\rho\sigma}\}$ in writing Eq. (2.37), the dependence of the electrostriction constants on pure strains described by Eq. (2.39) is incomplete. However, we are interested in the electrostriction constants themselves, and not in their strain dependence, which is a higher-order physical effect than we consider here. Therefore, setting $J=1$, and $\mathbf{C}=\mathbf{I}$, we finally obtain for the electrostriction constants themselves

$$\gamma_{\beta\delta\alpha\gamma}{}^{(T)}=-\{A_{\beta\delta\alpha\gamma}+\tfrac{1}{2}[\delta_{\beta\alpha}A_{\gamma\delta}+\delta_{\delta\alpha}A_{\gamma\beta} +\delta_{\beta\gamma}A_{\alpha\delta}+\delta_{\delta\gamma}A_{\alpha\beta}]\}. \quad (2.40)$$

For cubic crystals, the tensor $\gamma_{\beta\delta\alpha\rho}{}^{(T)}$ has only three independent, nonzero elements, and these are

$$\begin{aligned}\gamma_{1111}{}^{(T)}&=-\{A_{1111}-2\chi_0\},\\ \gamma_{1122}{}^{(T)}&=-A_{1122},\\ \gamma_{1212}{}^{(T)}&=-\{A_{1212}-\chi_0\},\end{aligned} \quad (2.41)$$

where we have used Eq. (2.29).

For some purposes it is more convenient to consider the stress and field components as the independent variables determining the elastic strains. For this purpose we introduce the elastic compliances $\{S_{\alpha\beta\gamma\delta}\}$ which are defined by

$$\sum_{\beta\sigma} S_{\alpha\rho\beta\sigma}C_{\beta\sigma\gamma\tau}=\delta_{\alpha\gamma}\delta_{\rho\tau}=\sum_{\beta\sigma} C_{\alpha\rho\beta\sigma}S_{\beta\sigma\gamma\tau}. \quad (2.42)$$

We can, therefore, put Eq. (2.36) into the alternative form

$$\eta_{\alpha\gamma}=\sum_{\beta\delta} S_{\alpha\gamma\beta\delta}T_{\beta\delta}+\sum_{\mu\beta\delta} E_{\mu}S_{\alpha\gamma\beta\delta}e_{\mu\beta\delta} +\tfrac{1}{2}\sum_{\mu\nu\beta\delta} E_{\mu}E_{\nu}S_{\alpha\gamma\beta\delta}\gamma^{(T)}{}_{\mu\nu\beta\delta}+\cdots. \quad (2.43)$$

The electrostrictive strains induced in crystals of the diamond structure are obtained from this expression by setting $T_{\beta\delta}=0$. For crystals of the diamond structure the electrostrictive strain is given by

$$\eta_{\alpha\gamma}=\sum_{\mu\nu} E_{\mu}E_{\nu}\{\tfrac{1}{2}\sum_{\beta\delta} S_{\alpha\gamma\beta\delta}\gamma^{(T)}{}_{\mu\nu\beta\delta}\}. \quad (2.44)$$

The coefficients in curly brackets in this expression are called the electrostrictional moduli $\{\gamma^{(\eta)}{}_{\mu\nu\beta\delta}\}$:

$$\gamma^{(\eta)}{}_{\mu\nu\alpha\gamma}=\tfrac{1}{2}\sum_{\beta\delta} S^{(T)}{}_{\alpha\gamma\beta\delta}\gamma_{\mu\nu\beta\delta}. \quad (2.45)$$

Finally, on combining Eqs. (2.33) and (2.41), we obtain the relations between the elasto-optic constants and the electrostriction constants for crystals of the diamond structure:

$$-\gamma_{1111}{}^{(T)}=(\epsilon_0{}^2/4\pi)p_{1111}-\chi_0, \quad (2.46a)$$

$$-\gamma_{1122}{}^{(T)}=(\epsilon_0{}^2/4\pi)p_{1122}-\chi_0, \quad (2.46b)$$

$$-\gamma_{1212}{}^{(T)}=(\epsilon_0{}^2/4\pi)p_{1212}. \quad (2.46c)$$

III. LATTICE THEORY OF THE COEFFICIENTS $\{A_{\mu\nu\alpha\rho}\}$

The potential energy of an arbitrary nonprimitive crystal can be expanded in powers of the displacements of the atoms from their equilibrium positions as

$$\Phi_h=\Phi_0+\tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} \Phi_{\alpha\beta}(l\kappa;l'\kappa')u_{\alpha}(l\kappa)u_{\beta}(l'\kappa')+\cdots. \quad (3.1)$$

Here $u_{\alpha}(l\kappa)$ is the α Cartesian component of the displacement of the κth atom in the lth unit cell from its equilibrium position. The $\{\Phi_{\alpha\beta}(l\kappa;l'\kappa')\}$ are the atomic force constants. The harmonic approximation for the potential energy expressed by Eq. (3.1) suffices for our purposes. We subject the crystal to a deformation described by

$$u_\alpha(l\kappa)=\sum_\rho \epsilon_{\alpha\rho}x_\rho(l\kappa)=d_\alpha(l\kappa)\,. \tag{3.2}$$

The first term describes a homogeneous deformation of the crystal. $\mathbf{x}(l\kappa)$ is the position vector of the equilibrium position of the atom $(l\kappa)$ in the unstrained, field-free crystal. The deformation parameters $\{\epsilon_{\alpha\beta}\}$ are the elements of a real 3×3 matrix which is not necessarily symmetric. The displacements $\{d_\alpha(l\kappa)\}$ represent the relative displacements of the sublattices comprising the crystal in response to the macroscopic strain. They are nonzero for crystals every atom of which is not at a center of inversion symmetry. It will be seen that $d_\alpha(l\kappa)$ is independent of the cell index l. However, it is formally convenient to allow for a possible dependence on l until a later stage in our calculations. The values of the sublattice shifts $\{d_\alpha(l\kappa)\}$ will be obtained eventually by minimizing the potential energy of the strained crystal in the presence of the field. When we substitute Eq. (3.2) into Eq. (3.1) we obtain

$$\Phi_h=\Phi_0+\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}\{\sum_{l\kappa}\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')x_\rho(l\kappa)x_\sigma(l'\kappa'\})\}\epsilon_{\alpha\rho}\epsilon_{\beta\sigma}$$
$$+\sum_{l\kappa\alpha}\sum_{\beta\sigma}\{\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')x_\sigma(l'\kappa')\}d_\alpha(l\kappa)\epsilon_{\beta\sigma}+\tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')d_\alpha(l\kappa)d_\beta(l'\kappa')\,. \tag{3.3}$$

It is convenient at this point to eliminate the deformation parameters $\{\epsilon_{\alpha\rho}\}$ from this expression in favor of the Lagrangian finite strain parameters $\{\eta_{\alpha\rho}\}$, which are defined by

$$\eta_{\alpha\rho}=\tfrac{1}{2}\{\epsilon_{\alpha\rho}+\epsilon_{\rho\alpha}+\sum_\lambda \epsilon_{\lambda\alpha}\epsilon_{\lambda\rho}\}=\eta_{\rho\alpha}\,. \tag{3.4}$$

At the same time we must eliminate the components of the vector $\mathbf{d}(l\kappa)$ in favor of the contravariant components in the deformed crystal, $\{\bar{d}_\alpha(l\kappa)\}$, which are defined by[12]

$$\bar{d}_\alpha(l\kappa)=d_\alpha(l\kappa)+\sum_\rho \epsilon_{\rho\alpha}d_\rho(l\kappa)\,. \tag{3.5}$$

These displacement amplitudes, as well as the strain parameters $\{\eta_{\alpha\rho}\}$, make no reference to the absolute orientation of the crystal. Equation (3.5) can be easily inverted, with the result that

$$d_\alpha(l\kappa)=\bar{d}_\alpha(l\kappa)-\sum_\rho \epsilon_{\rho\alpha}\bar{d}_\rho(l\kappa)+O(\epsilon^2)\,. \tag{3.6}$$

To carry out these eliminations we make use of the result, which follows from the transformation properties of the atomic force constants under an infinitesimal rigid body rotation of the crystal, that the sum

$$\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')x_\sigma(l'\kappa')=G_{\alpha\beta\sigma}(l\kappa) \tag{3.7}$$

is symmetric in β and σ for every value of $(l\kappa\alpha)$. Consequently, the sum

$$\sum_{l\kappa}\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')x_\rho(l\kappa)x_\sigma(l'\kappa')=V_0G_{\alpha\rho\beta\sigma}\,, \tag{3.8}$$

where V_0 is the volume of the undeformed crystal, is symmetric in α and ρ and in β and σ, as well as in the interchange of $\alpha\rho$ with $\beta\sigma$. We therefore obtain the result that

$$W_h=V_0^{-1}\Phi_h=W_0+\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}G_{\alpha\rho\beta\sigma}\tfrac{1}{2}(\epsilon_{\alpha\rho}+\epsilon_{\rho\alpha})\tfrac{1}{2}(\epsilon_{\beta\sigma}+\epsilon_{\sigma\beta})+V_0^{-1}\sum_{l\kappa\alpha}\sum_{\beta\sigma}G_{\alpha\beta\sigma}(l\kappa)[\bar{d}_\alpha(l\kappa)-\sum_\rho \epsilon_{\rho\alpha}\bar{d}_\rho(l\kappa)+\cdots]\tfrac{1}{2}(\epsilon_{\beta\sigma}+\epsilon_{\sigma\beta})$$
$$+\tfrac{1}{2}V_0^{-1}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')[\bar{d}_\alpha(l\kappa)-\sum_\rho \epsilon_{\rho\alpha}\bar{d}_\rho(l\kappa)+\cdots][\bar{d}_\beta(l'\kappa')-\sum_\sigma \epsilon_{\sigma\beta}\bar{d}_\sigma(l'\kappa')+\cdots]$$
$$=W_0+\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}G_{\alpha\rho\beta\sigma}\eta_{\alpha\rho}\eta_{\beta\sigma}+V_0^{-1}\sum_{l\kappa\alpha}\sum_{\beta\sigma}G_{\alpha\beta\sigma}(l\kappa)\bar{d}_\alpha(l\kappa)\eta_{\beta\sigma}+\tfrac{1}{2}V_0^{-1}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')\bar{d}_\alpha(l\kappa)\bar{d}_\beta(l'\kappa')+\cdots. \tag{3.9}$$

In writing this expression we have neglected terms of third order in $\epsilon_{\alpha\rho}$ and $d_\alpha(l\kappa)$. However, it will become clear from the succeeding analysis that none of the omitted terms contribute to the potential energy density a term of the form $\tfrac{1}{2}\sum_{\mu\nu\alpha\rho}\mathcal{E}_\mu\mathcal{E}_\nu A_{\mu\nu\alpha\rho}\eta_{\alpha\rho}$. In the context of the present problem their neglect is therefore justified.

If we minimize the potential energy density given by Eq. (3.9) with respect to the $\{\bar{d}_\alpha(l\kappa)\}$, we see that in the approximation which this equation represents $\bar{d}_\alpha(l\kappa)$ is a linear function of the $\{\eta_{\alpha\rho}\}$.

In the presence of an external electric field $\mathbf{E}$, additional terms must be added to the potential energy of the crystal. These terms in the adiabatic approximation are given by[13]

$$\Phi'=-\sum_\mu E_\mu M_\mu-\tfrac{1}{2}\sum_{\mu\nu}E_\mu E_\nu P_{\mu\nu}-\cdots \tag{3.10}$$

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[12] Reference 1, pp. 139 and 281.

[13] Reference 1, p. 310. Although the field $\mathbf{E}$ appearing in this equation is strictly the external field, we assume that this is also the macroscopic field in the crystal, i.e., that there is no depolarizing field. This can be achieved experimentally either by plating the electrodes which give rise to the field to the faces of the crystal, or by choosing the crystal to be a thin slab parallel to the external field.

to second order in the field. Here M_μ is the μ Cartesian component of the crystal dipole moment operator, and $P_{\mu\nu}$ is the $\mu\nu$ element of the static electronic polarizability of the crystal. Both M_μ and $P_{\mu\nu}$ possess expansions in powers of the nuclear displacements:

$$M_\mu = M_\mu{}^{(0)} + \sum_{l\kappa\alpha} M_{\mu,\alpha}(l\kappa)u_\alpha(l\kappa) + \tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')u_\alpha(l\kappa)u_\beta(l'\kappa') + \cdots, \tag{3.11}$$

$$P_{\mu\nu} = P_{\mu\nu}{}^{(0)} + \sum_{l\kappa\alpha} P_{\mu\nu,\alpha}(l\kappa)u_\alpha(l\kappa) + \tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} P_{\mu\nu,\alpha\beta}(l\kappa;\, l'\kappa')u_\alpha(l\kappa)u_\beta(l'\kappa') + \cdots. \tag{3.12}$$

The first two terms on the right-hand side of Eq. (3.11) are absent for crystals of the diamond structure.

When we substitute Eq. (3.2) into Eqs. (3.11) and (3.12), we obtain for crystals of the diamond structure

$$\begin{aligned}\Phi' = {} & -\tfrac{1}{2}\sum_\mu\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} E_\mu M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')\{\sum_{\rho\sigma} x_\rho(l\kappa)x_\sigma(l'\kappa')\epsilon_{\alpha\rho}\epsilon_{\beta\sigma} + 2\sum_\sigma x_\sigma(l'\kappa')\epsilon_{\beta\sigma}d_\alpha(l\kappa) + d_\alpha(l\kappa)d_\beta(l'\kappa')\} \\ & -\tfrac{1}{2}\sum_{\mu\nu} P_{\mu\nu}{}^{(0)}E_\mu E_\nu - \tfrac{1}{2}\sum_{\mu\nu}\sum_{l\kappa\alpha} E_\mu E_\nu P_{\mu\nu,\alpha}(l\kappa)\{\sum_\rho x_\rho(l\kappa)\epsilon_{\alpha\rho} + d_\alpha(l\kappa)\} - \tfrac{1}{4}\sum_{\mu\nu}\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} E_\mu E_\nu P_{\mu\nu,\alpha\beta}(l\kappa;\, l'\kappa') \\ & \times\{\sum_{\rho\sigma} x_\rho(l\kappa)x_\sigma(l'\kappa')\epsilon_{\alpha\rho}\epsilon_{\beta\sigma} + 2\sum_\sigma x_\sigma(l'\kappa')\epsilon_{\beta\sigma}d_\alpha(l\kappa) + d_\alpha(l\kappa)d_\beta(l'\kappa')\} - \cdots.\end{aligned} \tag{3.13}$$

We must now eliminate the deformation parameters $\{\epsilon_{\alpha\rho}\}$ and the components of the inner displacements $\{d_\alpha(l\kappa)\}$ from this expression in favor of the finite strains $\{\eta_{\alpha\rho}\}$ and the contravariant displacement components $\{\bar{d}_\alpha(l\kappa)\}$. However, as pointed out by Born and Huang,[14] we must also eliminate the field components $\{E_\mu\}$ in favor of the contravariant components $\{\mathcal{E}_\mu\}$ in the deformed crystal, which are defined by

$$\mathcal{E}_\mu = E_\mu + \sum_\lambda \epsilon_{\lambda\mu}E_\lambda. \tag{3.14}$$

These field components make no reference to the absolute orientation of the crystal.

We use the conditions imposed on the coefficients $\{M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')\}$, $\{P_{\mu\nu,\alpha}(l\kappa)\}$, and $\{P_{\mu\nu,\beta\alpha}(l\kappa;\, l'\kappa')\}$ by the transformation properties of M_μ and $P_{\mu\nu}$ under infinitesimal rigid body rotations of the crystal to eliminate the parameters $\{\epsilon_{\alpha\rho}\}$, $\{d_\alpha(l\kappa)\}$, and $\{E_\mu\}$ from Φ' in favor of the $\{\eta_{\alpha\rho}\}$, $\{\bar{d}_\alpha(l\kappa)\}$, and $\{\mathcal{E}_\mu\}$. The necessary results are that the sums

$$\sum_{l'\kappa'} M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')x_\sigma(l'\kappa'), \tag{3.15a}$$

$$\sum_{l\kappa} P_{\mu\nu,\alpha}(l\kappa)x_\rho(l\kappa) - \delta_{\mu\alpha}P_{\nu\rho}{}^{(0)} - \delta_{\nu\alpha}P_{\mu\rho}{}^{(0)}, \tag{3.15b}$$

$$\sum_{l'\kappa'} P_{\mu\nu,\alpha\beta}(l\kappa;\, l'\kappa')x_\sigma(l'\kappa') - \delta_{\alpha\beta}P_{\mu\nu,\sigma}(l\kappa) - \delta_{\mu\beta}P_{\sigma\nu,\alpha}(l\kappa) - \delta_{\nu\beta}P_{\mu\sigma,\alpha}(l\kappa), \tag{3.15c}$$

are symmetric in β and σ, in α and ρ, and again in β and σ, respectively.

If we retain terms in Φ' of no higher order than third in $\eta_{\alpha\rho}$, $\mathcal{E}_\mu$, and $\bar{d}_\alpha(l\kappa)$, we can neglect the last three terms on the right-hand side of Eq. (3.13), with the consequence that

$$\begin{aligned}W' = V_0{}^{-1}\Phi' = {} & -\tfrac{1}{2}\sum_\mu\sum_{\alpha\rho\beta\sigma} \mathcal{E}_\mu M_{\mu\alpha\rho\beta\sigma}\eta_{\alpha\rho}\eta_{\beta\sigma} \\ & - V_0{}^{-1}\sum_\mu\sum_{l\kappa\alpha}\sum_{\beta\sigma} \mathcal{E}_\mu M_{\mu\alpha\beta\sigma}(l\kappa)\bar{d}_\alpha(l\kappa)\eta_{\beta\sigma} \\ & -\tfrac{1}{2}V_0{}^{-1}\sum_\mu\sum_{l\kappa\alpha}\sum_{l'\kappa'\beta} \mathcal{E}_\mu M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa') \\ & \qquad \times\bar{d}_\alpha(l\kappa)\bar{d}_\beta(l'\kappa') - \cdots, \\ & -\tfrac{1}{2}V_0{}^{-1}\sum_{\mu\nu} P_{\mu\nu}{}^{(0)}\mathcal{E}_\mu\mathcal{E}_\nu \\ & -\tfrac{1}{2}V_0{}^{-1}\sum_{\mu\nu}\sum_{\alpha\rho} \mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu\alpha\rho}\eta_{\alpha\rho} \\ & -\tfrac{1}{2}V_0{}^{-1}\sum_{\mu\nu}\sum_{l\kappa\alpha} \mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu,\alpha}(l\kappa)\bar{d}_\alpha(l\kappa) - \cdots,\end{aligned} \tag{3.16}$$

where

$$V_0M_{\mu\alpha\rho\beta\sigma} = \sum_{l\kappa}\sum_{l'\kappa'} M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')x_\rho(l\kappa)x_\sigma(l'\kappa'), \tag{3.17a}$$

$$M_{\mu\alpha\beta\sigma}(l\kappa) = \sum_{l'\kappa'} M_{\mu,\alpha\beta}(l\kappa;\, l'\kappa')x_\sigma(l'\kappa'), \tag{3.17b}$$

$$P_{\mu\nu\alpha\rho} = \sum_{l\kappa} P_{\mu\nu,\alpha}(l\kappa)x_\rho(l\kappa) - \delta_{\mu\alpha}P_{\nu\rho}{}^{(0)} - \delta_{\nu\alpha}P_{\mu\rho}{}^{(0)}. \tag{3.17c}$$

The coefficients $\{M_{\mu\alpha\rho\beta\sigma}\}$ vanish for crystals possessing a center of inversion. The first term on the right-hand side of Eq. (3.16) will therefore be omitted in all that follows.

The equation for $\bar{d}_\alpha(l\kappa)$ is obtained by minimizing the

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[14] Reference 1, pp. 282–283.

sum of W_h and W' with respect to $\bar{d}_\alpha(l\kappa)$:

$$\frac{\partial}{\partial\bar{d}_\alpha(l\kappa)}(W_h+W')=V_0^{-1}\sum_{\beta\sigma}G_{\alpha\beta\sigma}(l\kappa)\eta_{\beta\sigma}+V_0^{-1}\sum_{l'\kappa'\beta}\Phi_{\alpha\beta}(l\kappa;l'\kappa')\bar{d}_\beta(l'\kappa')+\cdots$$
$$-V_0^{-1}\sum_{\mu}\sum_{\beta\sigma}\mathcal{E}_\mu M_{\mu\alpha\beta\sigma}(l\kappa)\eta_{\beta\sigma}-V_0^{-1}\sum_{\mu}\sum_{l'\kappa'\beta}\mathcal{E}_\mu M_{\mu,\alpha\beta}(l\kappa;l'\kappa')\bar{d}_\beta(l'\kappa')-\tfrac{1}{2}V_0^{-1}\sum_{\mu\nu}\mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu,\alpha}(l\kappa)-\cdots=0. \quad (3.18)$$

It is shown in Appendix A that the solution of this equation can be written formally as

$$\bar{d}_\alpha{}^{(0)}(l\kappa)=-\sum_{l'\kappa'\beta}\Gamma_{\alpha\beta}(l\kappa;l'\kappa')\sum_{\gamma\tau}G_{\beta\gamma\tau}(l'\kappa')\eta_{\gamma\tau}+\tfrac{1}{2}\sum_{l'\kappa'\beta}\Gamma_{\alpha\beta}(l\kappa;l'\kappa')\sum_{\mu\nu}\mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu,\beta}(l'\kappa')+0(\eta^2,\eta\mathcal{E}), \quad (3.19)$$

where $\mathbf{\Gamma}$ is a suitably truncated form of the matrix $\mathbf{\Phi}^{-1}$. With the aid of the equilibrium condition (3.18) we can rewrite the potential energy density as

$$\tilde{W}=W_0+\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}G_{\alpha\rho\beta\sigma}\eta_{\alpha\rho}\eta_{\beta\sigma}+\tfrac{1}{2}V_0^{-1}\sum_{l\kappa\alpha}\sum_{\beta\sigma}G_{\alpha\beta\sigma}(l\kappa)\bar{d}_\alpha{}^{(0)}(l\kappa)\eta_{\beta\sigma}-\tfrac{1}{2}V_0^{-1}\sum_{\mu}\sum_{l\kappa\alpha}\sum_{\beta\sigma}\mathcal{E}_\mu M_{\mu\alpha\beta\sigma}(l\kappa)\bar{d}_\alpha{}^{(0)}(l\kappa)\eta_{\beta\sigma}$$
$$-\tfrac{1}{2}V_0^{-1}\sum_{\mu\nu}P_{\mu\nu}{}^{(0)}\mathcal{E}_\mu\mathcal{E}_\nu-\tfrac{1}{2}V_0^{-1}\sum_{\mu\nu}\sum_{\alpha\rho}\mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu\alpha\rho}\eta_{\alpha\rho}-\tfrac{1}{4}V_0^{-1}\sum_{\mu\nu}\sum_{l\kappa\alpha}\mathcal{E}_\mu\mathcal{E}_\nu P_{\mu\nu,\alpha}(l\kappa)d_\alpha{}^{(0)}(l\kappa)+\cdots. \quad (3.20)$$

When we substitute into Eq. (3.20) the explicit expression for $\bar{d}_\alpha{}^{(0)}(l\kappa)$ given by Eq. (3.19), and collect the terms of $O(\eta^2)$ and of $O(\eta E^2)$, we obtain

$$\tilde{W}=W_0+\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}G_{\alpha\rho\beta\sigma}\eta_{\alpha\rho}\eta_{\beta\sigma}-\tfrac{1}{2}\sum_{\alpha\rho\beta\sigma}\{V_0^{-1}\sum_{\mu\nu}\sum_{l\kappa}\sum_{l'\kappa'}\Gamma_{\mu\nu}(l\kappa;l'\kappa')G_{\mu\alpha\rho}(l\kappa)G_{\nu\beta\sigma}(l'\kappa')\}\eta_{\alpha\rho}\eta_{\beta\sigma}$$
$$-\tfrac{1}{2}\sum_{\mu\nu}\sum_{\alpha\rho}\mathcal{E}_\mu\mathcal{E}_\nu\{V_0^{-1}P_{\mu\nu\alpha\rho}\}\eta_{\alpha\rho}+\tfrac{1}{2}\sum_{\mu\nu}\sum_{\alpha\rho}\mathcal{E}_\mu\mathcal{E}_\nu\{V_0^{-1}\sum_{l\kappa\gamma}\sum_{l'\kappa'\delta}P_{\mu\nu,\gamma}(l\kappa)\Gamma_{\gamma\delta}(l\kappa;l'\kappa')G_{\delta\alpha\rho}(l'\kappa')\}\eta_{\alpha\rho}+\cdots. \quad (3.21)$$

If we compare this expression with Eq. (2.18), we can make the identifications

$$C_{\alpha\rho\beta\sigma}=G_{\alpha\rho\beta\sigma}-V_0^{-1}\sum_{l\kappa\mu}\sum_{l'\kappa'\nu}\Gamma_{\mu\nu}(l\kappa;l'\kappa')\times G_{\mu\alpha\rho}(l\kappa)G_{\nu\beta\sigma}(l'\kappa'), \quad (3.22)$$

$$A_{\mu\nu\alpha\rho}=-V_0^{-1}P_{\mu\nu\alpha\rho}+V_0^{-1}\sum_{l\kappa\gamma}\sum_{l'\kappa'\delta}P_{\mu\nu,\gamma}(l\kappa)\times\Gamma_{\gamma\delta}(l\kappa;l'\kappa')G_{\delta\alpha\rho}(l'\kappa'). \quad (3.23)$$

The identification of the coefficients $\{C_{\alpha\rho\beta\sigma}\}$ given by Eq. (3.22) as the ordinary elastic constants follows from results of Huang,[15] Leibfried and Ludwig,[16] and Lax.[17] The first term on the right-hand side of Eq. (3.22) gives the contribution to the elastic constants associated with the homogeneous deformation of each of the two sublattices comprising crystals of the diamond structure; the second term gives the contribution associated with the relative rigid body displacement of the two sublattices in response to the homogeneous deformation of the crystal. It should be noted that the coefficients $G_{\alpha\rho\beta\sigma}$ are defined by an expression, Eq. (3.8), which is a function of the equilibrium positions $\mathbf{x}(l\kappa)$ and $\mathbf{x}(l'\kappa')$ of the atoms $(l\kappa)$ and $(l'\kappa')$, rather than of the relative separation of these two atoms, $\mathbf{x}(l\kappa)-\mathbf{x}(l'\kappa')$. It follows, therefore, that the contribution to the sum in Eq. (3.8) from lattice sites in the surface of the crystal is of the same order of magnitude as the contribution from the lattice sites in the interior of the crystal: such a sum is said to be boundary sensitive.[16,17] Consequently, Eq. (3.8) does not provide a convenient starting point for the calculation of the elastic constants and must be transformed into a boundary insensitive form for this purpose. The way in which this is done is described in Refs. 16 and 17, and we will not go into it here, as it is not with the elastic constants that we are primarily concerned. In what follows we therefore focus our attention on the coefficients $\{A_{\mu\nu\alpha\rho}\}$.

We can simplify the expression for $A_{\mu\nu\alpha\rho}$ given by Eq. (3.23) and at the same time compare our results with those of Theimer.[2] Comparing Eq. (3.20) with Eq. (2.18), we can make the identification

$$A_{\mu\nu}=-V_0^{-1}P_{\mu\nu}{}^{(0)}=-\delta_{\mu\nu}\chi_0, \quad (3.24)$$

where the second equality is a consequence of Eq. (2.29), and is valid only for cubic crystals. Equation (3.24), together with Eqs. (3.17c) and (3.23), yields the result that for cubic crystals

$$A_{\mu\nu\alpha\rho}=B_{\mu\nu\alpha\rho}{}^{(1)}+B_{\mu\nu\alpha\rho}{}^{(2)}+\chi_0[\delta_{\mu\alpha}\delta_{\nu\rho}+\delta_{\nu\alpha}\delta_{\mu\rho}], \quad (3.25)$$

where

$$B_{\mu\nu\alpha\rho}{}^{(1)}=-V_0^{-1}\sum_{l\kappa}P_{\mu\nu,\alpha}(l\kappa)x_\rho(l\kappa), \quad (3.26a)$$

$$B_{\mu\nu\alpha\rho}{}^{(2)}=V_0^{-1}\sum_{l\kappa\gamma}\sum_{l'\kappa'\delta}P_{\mu\nu,\gamma}(l\kappa)\times\Gamma_{\gamma\delta}(l\kappa;l'\kappa')G_{\delta\alpha\rho}(l'\kappa'). \quad \mathbf{(3.26b)}$$

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[15] K. Huang, Proc. Roy. Soc. (London) **A203**, 178 (1950).

[16] G. Leibfried and W. Ludwig, Z. Physik **160**, 80 (1960); L. T. Hedin, Arkiv Fysik **18**, 369 (1960).

[17] M. Lax, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 583.

If we combine Eq. (3.25) with Eq. (2.31) we obtain for the elasto-optic constants

$$p_{\mu\nu\alpha\rho}=(4\pi/\epsilon_0{}^2)\{B_{\mu\nu\alpha\rho}{}^{(1)}+B_{\mu\nu\alpha\rho}{}^{(2)}+\chi_0\delta_{\mu\nu}\delta_{\alpha\rho}\}\,, \quad (3.27)$$

or alternatively

$$B_{\mu\nu\alpha\rho}{}^{(1)}+B_{\mu\nu\alpha\rho}{}^{(2)}=(\epsilon_0{}^2/4\pi)p_{\mu\nu\alpha\rho}-\chi_0\delta_{\mu\nu}\delta_{\alpha\rho}. \quad (3.28)$$

The physical interpretation of the coefficients $\{B_{\mu\nu\alpha\rho}{}^{(1)}\}$ is readily seen. The atoms comprising a crystal possess electronic charge distributions of finite spatial extent surrounding their nuclei. As two atoms are brought closer together than their equilibrium separation in the crystal the overlap of their electron clouds increases. However, because of the exclusion principle, the electrons try to avoid the region of maximum overlap, and the electronic charge distributions on the two atoms accordingly distort. The degree and nature of this distortion is a function of the relative separation and orientation of the two atoms. The distorted charge distributions respond differently to an external electric field than do the undistorted charge distributions, so that the electronic polarizability of the crystal is a function of the displacements of the atoms from their equilibrium positions. The coefficient $P_{\mu\nu,\alpha}(l\kappa)$ gives the first-order change in the $\mu\nu$ component of the electronic polarizability of the crystal when the atom $(l\kappa)$ is given a unit displacement in the x direction, all other atoms being kept fixed at their equilibrium position. The coefficients $\{B_{\mu\nu\alpha\rho}{}^{(1)}\}$ and $\{B_{\mu\nu\alpha\rho}{}^{(2)}\}$ therefore give the change in the polarizability of the crystal (strictly, the susceptibility) when the atoms comprising the crystal are displaced from their equilibrium positions in the pattern associated with a homogeneous deformation of the crystal. In particular, the coefficients $\{B_{\mu\nu\alpha\rho}{}^{(1)}\}$ give the change in the polarizability due to the atomic displacements associated with the homogeneous deformation of each of the sublattices comprising the crystal. However, in crystals of the diamond structure every atom is not at a center of inversion symmetry, so that a homogeneous deformation of each sublattice is accompanied by a relative displacement of the two sublattices. The change in the electronic polarizability of the crystal associated with the latter displacement is described by the coefficients $\{B_{\mu\nu\alpha\rho}{}^{(2)}\}$.

The relation between the polarizability derivatives and the elasto-optic constants obtained by Theimer [Eq. (3.24) of Ref. 2] differs from the result given by Eq. (3.28) only by the absence of the term in χ_0 from the right-hand side of the latter. The presence of this term on the right-hand side of Eq. (3.27) has its origin in the change in the volume of a crystal accompanying a homogeneous deformation. That is, even if the atoms comprising a crystal were not polarizable and deformable, and the constituent sublattices did not undergo any relative displacements on the application of a strain or electric field to the crystal so that $B_{\mu\nu\alpha\rho}{}^{(1)}=B_{\mu\nu\alpha\rho}{}^{(2)}=0$, the dielectric polarization, which is the dipole moment per unit true volume, would still be a function of the strain parameters simply because the crystal volume is a function of the strain parameters. On the basis of this argument the elasto-optic constants in this artificial case would clearly be given by

$$p_{\mu\nu\alpha\rho}=(4\pi/\epsilon_0{}^2)\chi_0\delta_{\mu\nu}\delta_{\alpha\rho} \quad (3.29)$$

for cubic crystals, and this is just the expression into which Eq. (3.27) degenerates for this case. Theimer's theory, on the other hand, predicts that the elasto-optic constants vanish in this case.

IV. DETERMINATION OF THE COEFFICIENTS $\{B_{\mu\nu\alpha\rho}{}^{(2)}\}$ FOR CRYSTALS OF THE DIAMOND STRUCTURE

The translation vectors for a crystal of the diamond structure are

$$\mathbf{x}(l)=l_1\mathbf{a}_1+l_2\mathbf{a}_2+l_3\mathbf{a}_3\,, \quad (4.1)$$

where l_1, l_2, l_3 are three integers which can be positive, negative, or zero, and to which we refer collectively as l. The three primitive translation vectors are given by

$$\mathbf{a}_1=\tfrac{1}{2}a_0(0,1,1),\quad \mathbf{a}_2=\tfrac{1}{2}a_0(1,0,1),\quad \mathbf{a}_3=\tfrac{1}{2}a_0(1,1,0)\,, \quad (4.2)$$

where a_0 is the lattice parameter. The basis vectors are

$$\mathbf{x}(1)=0,\quad \mathbf{x}(2)=\tfrac{1}{4}a_0(1,1,1). \quad (4.3)$$

In what follows we assume that the crystal which we study contains N primitive unit cells. Consequently the volume V_0 of the undeformed crystal is given by Nv_a, where v_a is the volume of an undeformed primitive unit cell, which for crystals of the diamond structure is $v_a=a_0{}^3/4$. This assumption means that the cell index l takes on only N values.

We consider first the coefficients $\{B_{\mu\nu\alpha\rho}{}^{(2)}\}$, which according to Eq. (3.26b) are given by

$$B_{\mu\nu\alpha\rho}{}^{(2)}=V_0{}^{-1}\sum_{l\kappa\gamma}\sum_{l'\kappa'\delta}P_{\mu\nu,\gamma}(l\kappa)\times\Gamma_{\gamma\delta}(l\kappa;l'\kappa')G_{\delta\alpha\rho}(l'\kappa'). \quad (4.4)$$

The coefficient $G_{\alpha\beta\sigma}(l\kappa)$ appearing in this expression is defined by Eq. (3.7) as

$$G_{\alpha\beta\sigma}(l\kappa)=\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;l'\kappa')x_\sigma(l'\kappa'). \quad (4.5)$$

It follows from Eq. (4.5) and from infinitesimal translation invariance, as expressed by Eq. (A6), that

$$\sum_{l\kappa}G_{\alpha\beta\sigma}(l\kappa)=0. \quad (4.6)$$

The evaluation of the expression (4.5) for $G_{\alpha\beta\sigma}(l\kappa)$ is greatly simplified if we use the condition of infinitesimal translation invariance, Eq. (A6), to rewrite Eq. (4.5) in the form

$$G_{\alpha\beta\sigma}(l\kappa)=-\sum_{l'\kappa'}\Phi_{\alpha\beta}(l\kappa;l'\kappa')x_\sigma(l\kappa;l'\kappa'). \quad (4.7)$$

With the expression for $G_{\alpha\beta\sigma}(l\kappa)$ written in this boundary-insensitive form we can take advantage of the fact that the atomic force constants depend on l and l' only through their difference. This fact enables us to change the summation variable from l' to a new variable $\bar{l}=l'-l$ to obtain

$$G_{\alpha\beta\sigma}(l\kappa)=-\sum_{\bar{l}\kappa'}\Phi_{\alpha\beta}(0\kappa;\bar{l}\kappa')x_\sigma(0\kappa;\bar{l}\kappa'). \tag{4.8}$$

The right-hand side of this equation is independent of l, so that the only coefficients we have to consider are $G_{\alpha\beta\sigma}(01)$ and $G_{\alpha\beta\sigma}(02)$. However, these coefficients are not independent, for in view of Eq. (4.7) the following relation must hold:

$$G_{\alpha\beta\sigma}(01)=-G_{\alpha\beta\sigma}(02). \tag{4.9}$$

Because $G_{\alpha\beta\sigma}(01)$ enters into the expression for the relative displacement of the two sublattices comprising the diamond structure when the crystal is homogeneously deformed, it might be thought that only the atomic force constants coupling atoms on different sublattices should contribute to the sum (4.8). That this conjecture is correct is shown by the following argument: In terms of the sums

$$\hat{G}_{\alpha\beta\sigma}(\kappa\kappa')=\sum_{l'}\Phi_{\alpha\beta}(l\kappa;l'\kappa')x_\sigma(l\kappa;l'\kappa'), \tag{4.10}$$

the expressions for $G_{\alpha\beta\sigma}(01)$ and $G_{\alpha\beta\sigma}(02)$ become

$$G_{\alpha\beta\sigma}(01)=-[\hat{G}_{\alpha\beta\sigma}(11)+\hat{G}_{\alpha\beta\sigma}(12)], \tag{4.11a}$$

$$G_{\alpha\beta\sigma}(02)=-[\hat{G}_{\alpha\beta\sigma}(21)+\hat{G}_{\alpha\beta\sigma}(22)]. \tag{4.11b}$$

From the symmetry of the atomic force constants,

$$\Phi_{\alpha\beta}(l\kappa;l'\kappa')=\Phi_{\alpha\beta}(l\kappa;l'\kappa'), \tag{4.12}$$

and the fact that $\Phi_{\alpha\beta}(l\kappa;l'\kappa')$ depends on l and l' only through their difference, it is straightforward to establish the general property

$$\hat{G}_{\alpha\beta\sigma}(\kappa\kappa')=-\hat{G}_{\beta\alpha\sigma}(\kappa'\kappa). \tag{4.13}$$

In particular, we have that

$$\hat{G}_{\alpha\beta\sigma}(\kappa\kappa)=-\hat{G}_{\beta\alpha\sigma}(\kappa\kappa). \tag{4.14}$$

To proceed farther we need to establish the transformation law for $\hat{G}_{\alpha\beta\sigma}(\kappa\kappa')$ under an operation of the space group of the crystal. In the Seitz[18] notation a space-group operation is written in the form $\{\mathbf{S}|\mathbf{v}(S)+\mathbf{x}(m)\}$, and is defined through its effect on the position vector $\mathbf{x}(l\kappa)$:

$$\begin{aligned}\{\mathbf{S}|\mathbf{v}(S)+\mathbf{x}(m)\}\mathbf{x}(l\kappa)\\ =\mathbf{S}\mathbf{x}(l\kappa)+\mathbf{v}(S)+\mathbf{x}(m)\equiv\mathbf{x}(LK).\end{aligned} \tag{4.15}$$

In this equation $\mathbf{S}$ is a real, orthogonal, 3×3 matrix representative of one of the proper or improper rotations of the point group of the space group, $\mathbf{v}(S)$ is a nonprimitive displacement associated with certain rotational elements of nonsymmorphic space groups, that is, space groups which contain screw axes and glide planes among their symmetry elements, and $\mathbf{x}(m)$ is a translation vector of the crystal. The second equation in Eq. (4.15) expresses the fact that inasmuch as $\{\mathbf{S}|\mathbf{v}(S)+\mathbf{x}(m)\}$ is a symmetry operation of the crystal, it must send the lattice site $(l\kappa)$ into an equivalent lattice site, which we denote by (LK). In what follows we will use the convention of labeling by capital letters the lattice site into which a given lattice site, labeled by lower case letters, is sent by a space-group operation.

Under a space-group operation the atomic force constants transform according to[19]

$$\Phi_{\alpha\beta}(LK;L'K')=\sum_{\mu\nu}S_{\alpha\mu}S_{\beta\nu}\Phi_{\mu\nu}(l\kappa;l'\kappa'). \tag{4.16}$$

Combining Eqs. (4.10) and (4.16), we find that

$$\begin{aligned}\hat{G}_{\alpha\beta\sigma}(KK')&=\sum_{L'K'}\Phi_{\alpha\beta}(LK;L'K')x_\sigma(LK;L'K')\\ &=\sum_{L'K'}\sum_{\mu\nu\tau}S_{\alpha\mu}S_{\beta\nu}\Phi_{\mu\nu}(l\kappa;l'\kappa')S_{\sigma\tau}x_\tau(l\kappa;l'\kappa')\\ &=\sum_{\mu\nu\tau}S_{\alpha\mu}S_{\beta\nu}\hat{G}_{\mu\nu\tau}(\kappa\kappa').\end{aligned} \tag{4.17}$$

In going from the second to the third line of this equation we made the change of summation variables $\mathbf{x}(l'\kappa')=\{\mathbf{S}|\mathbf{v}(S)+\mathbf{x}(m)\}^{-1}x(L'K')$.

The space group of diamond is $O_h{}^7$. If we ignore the invariant subgroup of translations through the lattice vectors $\{\mathbf{x}(m)\}$, this space group consists of 48 elements $\{\mathbf{S}|\mathbf{v}(S)\}$, in which the purely rotational elements $\{\mathbf{S}\}$ comprise the point group O_h. The 24 symmetry elements whose purely rotational parts comprise the point group T_d contain no nonprimitive translations and do not interchange the two sublattices of the diamond structure. The remaining 24 symmetry elements have a nonprimitive translation through the vector $\frac{1}{4}a_0(1,1,1)$ associated with them, and interchange the two sublattices. The use of the first group of 24 symmetry operations in Eq. (4.17) yields the result that the elements of the third-rank tensor $\hat{G}_{\alpha\beta\sigma}(\kappa\kappa')$ are given by

$$\hat{G}_{\alpha\beta\sigma}(\kappa\kappa')=\hat{G}(\kappa\kappa')|\epsilon_{\alpha\beta\sigma}|, \tag{4.18}$$

where $\hat{G}(\kappa\kappa')$ is a coefficient which is independent of α, β, σ. However, we see that the results expressed by Eqs. (4.14) and (4.18) are compatible only if $\hat{G}(\kappa\kappa)=0$. Moreover, the presence of a center of inversion in crystals of the diamond structure has the consequence that

$$\hat{G}(12)=-\hat{G}(21). \tag{4.19}$$

Using these results in Eqs. (4.11) we find that

$$\begin{aligned}G_{\alpha\beta\sigma}(01)&=-\hat{G}(12)|\epsilon_{\alpha\beta\sigma}|=-G_{\alpha\beta\sigma}(02)\\ &=-\sum_{l'}\Phi_{\alpha\beta}(01;l'2)x_\sigma(01;l'2).\end{aligned} \tag{4.20}$$

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[18] F. Seitz, Ann. Math. **37**, 17 (1936).

[19] G. H. Begbie and M. Born, Proc. Roy. Soc. (London) **A188**, 179 (1947).

In obtaining Eq. (4.20) we have established two results. We have shown that the coefficients $G_{\alpha\beta\sigma}(01) = -G_{\alpha\beta\sigma}(02)$ are expressible only in terms of atomic force constants coupling atoms on different sublattices of the diamond structure. At the same, time we have shown that $G_{\alpha\beta\sigma}(01)$. has the form

$$G_{\alpha\beta\sigma}(01)=G|\epsilon_{\alpha\beta\sigma}|\,, \qquad (4.21\text{a})$$

where

$$G\equiv-\hat{G}(12)=-\sum_{l'}\Phi_{12}(01;l'2)x_3(01;l'2)\,. \qquad (4.21\text{b})$$

The preceding results enable us to rewrite the expression for the coefficient $B_{\mu\nu\alpha\rho}{}^{(2)}$, Eq. (4.4), in the following form:

$$B_{\mu\nu\alpha\rho}{}^{(2)}=\frac{PG}{Mv_a}\sum_{\gamma\delta}|\epsilon_{\mu\nu\gamma}||\epsilon_{\delta\alpha\rho}| \times\{\Gamma_{\gamma\delta}(11)-\Gamma_{\gamma\delta}(12)-\Gamma_{\gamma\delta}(21)+\Gamma_{\gamma\delta}(22)\}\,, \qquad (4.22)$$

where $M(=M_1=M_2)$ is the mass of one of the atoms comprising the crystal. The elements of the 3×3 matrix $\mathbf{\Gamma}(\kappa\kappa')$ are defined by Eq. (A10) of Appendix A as

$$\sum_{ll'}\Gamma_{\alpha\beta}(l\kappa;l'\kappa')=\frac{N}{(M_\kappa M_{\kappa'})^{1/2}}\Gamma_{\alpha\beta}(\kappa\kappa')\,, \qquad (4.23)$$

so that according to Eq. (A19),

$$\Gamma_{\alpha\beta}(\kappa\kappa')={\sum_j}'\frac{e_\alpha(\kappa|\mathbf{0}j)e_\beta(\kappa'|\mathbf{0}j)}{\omega_j{}^2(\mathbf{0})}\,. \qquad (4.24)$$

In Eq. (4.24) $\omega_j(\mathbf{0})$ is the frequency of a normal mode of infinite wavelength ($\mathbf{k}=0$) labeled by the branch index j, and $\mathbf{e}(k|\mathbf{0}j)$ is the corresponding unit polarization vector. The prime on the sum means that it extends over the optical branches only. The form of $e_\alpha(\kappa|\mathbf{0}j)$ is determined by symmetry in crystals of the diamond structure, and is[20]

$$e_\alpha(1|\mathbf{0}j)=2^{-1/2}\delta_{\alpha j}=-e_\alpha(2|\mathbf{0}j)\,, \qquad (4.25)$$

where $j=1,2,3$ labels the three optical branches. The frequencies of the three optical vibration modes at $\mathbf{k}=0$ in crystals of the diamond structure are all equal, and equal ω_R, the Raman frequency. Putting these results together, we find that

$$\Gamma_{\alpha\beta}(11)=\Gamma_{\alpha\beta}(22)=-\Gamma_{\alpha\beta}(12) =-\Gamma_{\alpha\beta}(21)=\delta_{\alpha\beta}/2\omega_R{}^2. \qquad (4.26)$$

It follows, therefore, that the coefficient $B_{\mu\nu\alpha\rho}{}^{(2)}$ is given by

$$B_{\mu\nu\alpha\rho}{}^{(2)}=\frac{2}{v_a}\frac{G}{M\omega_R{}^2}P\sum_\gamma|\epsilon_{\mu\nu\gamma}||\epsilon_{\gamma\alpha\rho}|\,. \qquad (4.27)$$

The only nonzero elements of this tensor are

$$\begin{aligned}B_{1212}{}^{(2)}&=B_{2112}{}^{(2)}=B_{1221}{}^{(2)}=B_{2121}{}^{(2)}=B_{1313}{}^{(2)}\\&=B_{3113}{}^{(2)}=B_{1331}{}^{(2)}=B_{3131}{}^{(2)}=B_{2323}{}^{(2)}=B_{3223}{}^{(2)}\\&=B_{2332}{}^{(2)}=B_{3232}{}^{(2)}=(2/v_a)(G/M\omega_R{}^2)p\,. \qquad (4.28)\end{aligned}$$

Equations (3.28) consequently simplify to

$$B_{1111}{}^{(1)}=(\epsilon_0{}^2/4\pi)p_{1111}-\chi_0\,, \qquad (4.29\text{a})$$

$$B_{1122}{}^{(1)}=(\epsilon_0{}^2/4\pi)p_{1122}-\chi_0\,, \qquad (4.29\text{b})$$

$$B_{1212}{}^{(1)}+(2/v_a)(G/M\omega_R{}^2)P=(\epsilon_0{}^2/4\pi)p_{1212}\,. \qquad (4.29\text{c})$$

These equations are as far as we can go toward evaluating P without adopting some specific model for the lattice dynamical and optical properties of crystals of the diamond structure.

The vibrational properties of the crystal enter Eqs. (4.29) through the parameter G and through the Raman frequency in the combination $M\omega_R{}^2$. The expression for the former is given by Eq. (4.21b); the combination $M\omega_R{}^2$ can be expressed in terms of atomic force constants by[21]

$$M\omega_R{}^2=-2\sum_{l'}\Phi_{\alpha\alpha}(01;l'2)\,. \qquad (4.30)$$

That only force constants coupling atoms on different sublattices appear in this expression is a reflection of the fact that the Raman frequency is the frequency of a vibration mode in which the two sublattices beat rigidly against each other.

Sophisticated force-constant models for crystals of the diamond structure have been developed. Herman[22] has written down the force-constant matrices for interactions between atoms which are first, second, $\cdots$, fifth neighbors. Pope[23] has extended Herman's results to obtain the sixth-neighbor force-constant matrix. The force-constant matrices for first-, third-, and fifth-neighbor interactions have the forms

$$-\Phi_{\alpha\beta}(000;111)=\begin{pmatrix}\alpha_1&\rho_1&\rho_1\\\rho_1&\alpha_1&\rho_1\\\rho_1&\rho_1&\alpha_1\end{pmatrix}, \qquad (4.31\text{a})$$

$$-\Phi_{\alpha\beta}(000;\bar{3}11)=\begin{pmatrix}\alpha_3&\rho_3&\rho_3\\\rho_3&\beta_3&\tau_3\\\rho_3&\tau_3&\beta_3\end{pmatrix}, \qquad (4.31\text{b})$$

$$-\Phi_{\alpha\beta}(000;331)=\begin{pmatrix}\alpha_5&\rho_5&\sigma_5\\\rho_5&\alpha_5&\sigma_5\\\sigma_5&\sigma_5&\gamma_5\end{pmatrix}. \qquad (4.31\text{c})$$

On the right-hand side of each equation we have expressed the argument $(01;l'2)$ of each force-constant matrix in terms of the components of the vectors $\mathbf{x}(01)$ and $\mathbf{x}(l'2)$ in units of $a_0/4$. The remaining first-, third-, and fifth-neighbor force-constant matrices can be ob-

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[20] M. Lax, Symmetry Principles in Solid State Physics (to be published).

[21] S. Ganesan and A. A. Maradudin (to be published).

[22] F. Herman, J. Phys. Chem. Solids 8, 405 (1959).

[23] N. K. Pope, in *Proceedings of the International Conference on Lattice Dynamics, Copenhagen, 1963*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 147.

tained by applying Eq. (4.16) to the results given by Eqs. (4.31).

Substituting Eqs. (4.31) into Eqs. (4.21b) and (4.30) yields the expressions

$$G=-a_0[\rho_1+(2\rho_3-3\tau_3)+(\rho_5+6\sigma_5)], \tag{4.32a}$$

$$M\omega_R{}^2=8[\alpha_1+(\alpha_3+2\beta_3)+(\gamma_5+2\alpha_5)]. \tag{4.32b}$$

The coefficient $(2/v_a)(G/M\omega_R{}^2)$ appearing on the right-hand side of Eq. (4.29c) is therefore given by

$$\frac{2}{v_a}\frac{G}{M\omega_R{}^2}=-\frac{1}{a_0{}^2}\frac{\rho_1+(2\rho_3-3\tau_3)+(\rho_5+6\sigma_5)}{\alpha_1+(\alpha_3+2\beta_3)+(\gamma_5+2\alpha_5)}. \tag{4.33}$$

At the present time the only crystal of the diamond structure for which all of the force constants appearing in Eq. (4.31) are known is germanium.[23] The results (in units of 10^4 dyn/cm) are

$$\alpha_1=3.910,\quad \rho_1=3.044,\quad \alpha_3=-0.781,\quad \beta_3=0.733,$$
$$\rho_3=0.378,\quad \tau_3=-0.453,\quad \alpha_5=0.490,\quad \rho_5=0.514,$$

and

$$\sigma_5=\gamma_5=0. \tag{4.34}$$

The value of $(2/v_a)(G/M\omega_R{}^2)$ obtained by combining Eqs. (4.33) and (4.34) is given in Table I.

For silicon and diamond no such extensive force-constant data exist, and we are forced to use a much cruder force-constant model to evaluate G and $M\omega_R{}^2$. Because of its simplicity the model we chose to use is a nearest- and next-nearest-neighbor force-constant model in which the nearest-neighbor interactions are still described by the force-constant matrix (4.31a), while the next-nearest-neighbor interactions are assumed to be of the central-force type, and are described by the force-constant matrix

$$-\Phi_{\alpha\beta}(000;\,220)=\begin{bmatrix}\alpha_2 & \alpha_2 & 0\\ \alpha_2 & \alpha_2 & 0\\ 0 & 0 & 0\end{bmatrix}. \tag{4.35}$$

The three elastic constants of the crystal can be expressed in terms of the three force constants α_1, ρ_1, and α_2 by

$$\begin{aligned}a_0C_{11}&=\alpha_1+8\alpha_2,\\ a_0C_{12}&=2\rho_1-\alpha_1+4\alpha_2,\\ a_0C_{44}&=\alpha_1+4\alpha_2-(\rho_1{}^2/\alpha_1).\end{aligned} \tag{4.36}$$

From Eq. (4.33) we obtain the result that on the basis of the present simple model

$$\frac{2}{v_a}\frac{G}{M\omega_R{}^2}=-\frac{1}{a_0{}^2}\frac{\rho_1}{\alpha_1}. \tag{4.37}$$

Values of α_1, ρ_1, and α_2 obtained from experimental values of the elastic constants are given in Table I for diamond, silicon, and germanium, together with the values of $(2/v_a)(G/M\omega_R{}^2)$ obtained by substituting them into Eq. (4.37).

TABLE I. Values of physical constants and of derived quantities used in this paper.

	Diamond	Silicon	Germanium
a_0(Å)	3.567	5.430	5.657
C_{11}(10^{12} dyn/cm^2)	10.76[a]	1.66[a]	1.29[a]
C_{12}	1.25	0.64	0.48
C_{44}	5.76	0.80	0.68
S_{11}(10^{-14} cm^2/dyn)	9.55	76.8	96.4
S_{12}	−0.99	−21.4	−26.0
S_{44}	17.35	126	149
ϵ_0	5.86	11.6	16.0
χ_0	0.386	0.854	1.193
$q_{11}-q_{12}$(10^{-12} cm^2/dyn)		21[b]	3[c]
q_{44}		7	14
$\frac{1}{n}\frac{dn}{dT}$(10^{-7} cm^2/Kg)		3[d]	7[d]
q_{11}(10^{-12} cm^2/dyn)	+1.71[e]	+25	+10
q_{12}	−0.74	−4	+7
q_{44}	+0.95	+7	+14
π_{11}(10^{-13} cm^2/dyn)	−0.51	−1	−0.4
π_{12}	+0.22	+0.3	−0.25
π_{44}	−0.28	−0.5	−0.55
p_{1111}	−0.49	−0.2	−0.07
p_{1122}	+0.20	−0.003	−0.06
p_{1212}	−0.16	−0.04	−0.04
$p_{1111}-p_{1122}-2p_{1212}$	−0.37	-0.07_5	+0.06
$\gamma_{1111}{}^{(T)}$	1.72	3	3
$\gamma_{1122}{}^{(T)}$	−0.16	0.9	2
$\gamma_{1212}{}^{(T)}$	0.44	0.4	0.7_5
$\gamma_{1111}{}^{(\eta)}[10^{-17}(\mathrm{cm}/V)^2]$	0.093	0.3	0.7
$\gamma_{1122}{}^{(\eta)}$	−0.017	−0.03	0.6
$\gamma_{1212}{}^{(\eta)}$	0.021	0.15	0.3
P (Å^2)[f]			10
P (Å^2)[g]	−3.8	−7	12
α_1(10^4 dyn/cm)	149.4	14.9	8.16
ρ_1(10^4 dyn/cm)	104.7	10.7	5.66
α_2(10^4 dyn/cm)	−13.9	−0.736	−0.108
$-(8G/a_0M\omega_R{}^2)$[f]			1.17
$-(8G/a_0M\omega_R{}^2)$[g]	0.701	0.715	0.694
$L(r_0)$ (Å^3)	6.448	25.5	15.8
$T(r_0)$ (Å^3)	−1.57	0.674	12.4
$r_0L'(r_0)$ (Å^3)	9.62	63.6	116.5
$r_0T'(r_0)$ (Å^3)	1.17	34.1	70.3

[a] H. B. Huntington, Solid State Phys. **7**, 213 (1958), Table 4.1, p. 93.

[b] K. J. Schmidt-Tiedmann, J. Appl. Phys. **32**, 2058 (1961); Phys. Rev. Letters **7**, 372 (1961).

[c] V. I. Nikitenko and G. P. Martynenko, Fiz. Tverd. Tela **7**, 622 (1965) [English transl.: Soviet Phys.—Solid State **7**, 494 (1965)].

[d] M. Cardona, W. Paul and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1961).

[e] G. M. Ramachandran, Proc. Ind. Acad. Sci. **A25**, 171 (1950).

[f] Equation (4.33).

[g] Equation (4.37).

We now turn to a discussion of the tensor $B_{\mu\nu\alpha\rho}{}^{(1)}$.

V. DETERMINATION OF THE COEFFICIENTS $\{B_{\mu\nu\alpha\rho}{}^{(1)}\}$ FOR CRYSTALS OF THE DIAMOND STRUCTURE

We have seen in the preceding section that the only nonzero components of the tensor $B_{\mu\nu\alpha\rho}{}^{(2)}$ are proportional to the parameter P which is being sought. However, from Eq. (4.29) we see that in order to obtain P

from experimental data we need to know the components of the tensor $B_{\mu\nu\alpha\rho}^{(1)}$, in particular the component $B_{1212}^{(1)}$, since $B_{1111}^{(1)}$ and $B_{1122}^{(1)}$ can be obtained from experimental data. In obtaining these values we are faced with the following problem. We see from Eq. (3.26a) that the first-order electronic polarizability coefficients $\{P_{\mu\nu,\alpha}(l\kappa)\}$ enter into the expression for $B_{\mu\nu\alpha\rho}^{(1)}$, just as they also enter into the expression for $B_{\mu\nu\alpha\rho}^{(2)}$. However, in the case of $B_{\mu\nu\alpha\rho}^{(1)}$ they do so in a boundary-sensitive manner, unlike the boundary-insensitive manner in which they enter into $B_{\mu\nu\alpha\rho}^{(2)}$. The expression (3.26a) for $B_{\mu\nu\alpha\rho}^{(1)}$ must therefore be rewritten in a boundary-insensitive form, and this requires a microscopic model for the electronic polarizability of the crystal. A consequence of this is that $B_{\mu\nu\alpha\rho}^{(1)}$ is not simply proportional to P, but instead is a combination of the microscopic parameters in terms of which $P_{\mu\nu,\alpha}(l\kappa)$ or P is expressible. The equation (4.29) must therefore be regarded not as an equation for P itself but for the parameters in the microscopic model of P. It is to the establishment of a microscopic model for the electronic polarizability of crystals of the diamond structure that we now turn.

If we are to use experimental values of the elasto-optic constants and the static dielectric susceptibility to determine the value of the polarizability derivative P, the model of the electronic polarizability we choose must contain as many parameters as there are pieces of experimental information, no more, no less. The model we have chosen to use in our work has this property.

This model assumes that the electronic polarizability of a crystal of the diamond structure can be expressed as the sum of the electronic polarizabilities of the bonds between nearest-neighbor pairs of atoms in the crystal.

The motivation for our choice of this model is the fact that physical chemists have long described the polarizability of molecules in terms of the polarizabilities of the atomic bonds comprising the molecules.[24] In particular, the concept of the polarizability of a carbon bond is well established. We exploit this concept by regarding a diamond crystal as a very large molecule made up of carbon atoms, whose polarizability is therefore given by summing the polarizabilities of the bonds between all atom pairs. Because the atomic bonding in silicon and germanium is of the same type as in diamond, it is not unreasonable to expect that if our model has any validity for diamond, it will have the same validity for these two crystals.

As an atomic bond does not have spherical symmetry, but rather possesses cylindrical symmetry with respect to the line joining the atomic centers, we attribute to each bond a longitudinal polarizability and a transverse polarizability. Let us denote by $L_{\kappa\kappa'}(r)=L_{\kappa'\kappa}(r)$ and $T_{\kappa\kappa'}(r)=T_{\kappa'\kappa}(r)$, the longitudinal and transverse electronic polarizabilities, respectively, of the bond between two atoms of types κ and κ' separated by a distance r. The total electronic polarizability of the crystal can therefore be written as

$$P_{\mu\nu}=\tfrac{1}{2}\sum_{l\kappa}\sum_{l'\kappa'}{}' \frac{R_\mu(l\kappa;\,l'\kappa')R_\nu(l\kappa;\,l'\kappa')}{R^2(l\kappa;\,l'\kappa')}L_{\kappa\kappa'}(R(l\kappa;\,l'\kappa'))$$
$$+\tfrac{1}{2}\sum_{l\kappa}\sum_{l'\kappa'}{}'\left[\delta_{\mu\nu}-\frac{R_\mu(l\kappa;\,l'\kappa')R_\nu(l\kappa;\,l'\kappa')}{R^2(l\kappa;\,l'\kappa')}\right]$$
$$\times T_{\kappa\kappa'}(R(l\kappa;\,l'\kappa')),\quad (5.1)$$

where the factor of $\frac{1}{2}$ corrects for the double counting of bonds, and the primes on the sums denote that the terms with $(l\kappa)=(l'\kappa')$ are omitted. In writing Eq. (5.1) we have introduced the notation

$$R_\mu(l\kappa)=x_\mu(l\kappa)+u_\mu(l\kappa)\quad (5.2a)$$

and

$$R_\mu(l\kappa;\,l'\kappa')=R_\mu(l\kappa)-R_\mu(l'\kappa').\quad (5.2b)$$

The functions $L_{\kappa\kappa'}(R(l\kappa;\,l'\kappa'))$ and $T_{\kappa\kappa'}(R(l\kappa;\,l'\kappa'))$ in Eq. (5.1) are nonzero only if the two atoms whose positions are given by $\mathbf{R}(l\kappa)$ and $\mathbf{R}(l'\kappa')$ are nearest neighbors.

Expanded to first order in the atomic displacements, the electronic polarizability takes the form

$$P_{\mu\nu}=P_{\mu\nu}^{(0)}+\tfrac{1}{2}\sum_{l\kappa\alpha}\sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa')$$
$$\times[u_\alpha(l\kappa)-u_\alpha(l'\kappa')]+\cdots,\quad (5.3)$$

where

$$P_{\mu\nu}^{(0)}=\tfrac{1}{2}\sum_{l\kappa}\sum_{l'\kappa'}{}' \frac{x_\mu(l\kappa;\,l'\kappa')x_\nu(l\kappa;\,l'\kappa')}{x^2(l\kappa;\,l'\kappa')}L_{\kappa\kappa'}(x(l\kappa;\,l'\kappa'))$$
$$+\tfrac{1}{2}\sum_{l\kappa}\sum_{l'\kappa'}{}'\left[\delta_{\mu\nu}-\frac{x_\mu(l\kappa;\,l'\kappa')x_\nu(l\kappa;\,l'\kappa')}{x^2(l\kappa;\,l'\kappa')}\right]$$
$$\times T_{\kappa\kappa'}(x(l\kappa;\,l'\kappa'))\quad (5.4)$$

and

$$f_{\mu\nu\alpha}(l\kappa;\,l'\kappa')=\left\{\delta_{\mu\nu}\frac{x_\alpha}{r}T'_{\kappa\kappa'}(r)+\frac{x_\mu x_\nu x_\alpha}{r^3}\right.$$
$$\times\left[L'_{\kappa\kappa'}(r)-\frac{2L_{\kappa\kappa'}(r)}{r}-T'_{\kappa\kappa'}(r)+2\frac{T_{\kappa\kappa'}(r)}{r}\right]$$
$$\left.\left.+\frac{x_\mu\delta_{\nu\alpha}+x_\nu\delta_{\mu\alpha}}{r^2}[L_{\kappa\kappa'}(r)-T_{\kappa\kappa'}(r)]\right\}\right|_{r=x(l\kappa;\,l'\kappa')},\quad (5.5)$$

where primes denote differentiation with respect to argument.

Equation (5.3) can be rewritten conveniently as

$$P_{\mu\nu}=P_{\mu\nu}^{(0)}+\sum_{l\kappa}\sum_{l'\kappa'\alpha}P_{\mu\nu,\alpha}^{(1)}(l\kappa;\,l'\kappa')u_\alpha(l'\kappa')+\cdots,\quad (5.6)$$

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[24] See, for example, S. Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1946), p. 537.

where

$$P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\,l'\kappa') = -\tfrac{1}{2} f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') \quad (l\kappa)\neq(l'\kappa'), \tag{5.7a}$$

$$P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\,l\kappa) = \tfrac{1}{2} \sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa'). \tag{5.7b}$$

It follows from Eq. (5.7) that the coefficients $\{P_{\mu\nu,\alpha}{}^{(1)} \times (l\kappa;\,l'\kappa')\}$ satisfy the condition

$$\sum_{l'\kappa'} P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\,l'\kappa') = 0, \tag{5.8}$$

which ensures that the electronic polarizability of the crystal does not change when the crystal is subjected to an arbitrary rigid body displacement.

For cubic crystals, which is all that we consider in this paper, the expression (5.4) for $P_{\mu\nu}{}^{(0)}$ can be simplified to

$$\begin{aligned}
P_{\mu\nu}{}^{(0)} &= \tfrac{1}{2}\delta_{\mu\nu} \sum_{l\kappa} \sum_{l'\kappa'}{}' \frac{x_\mu{}^2(l\kappa;\,l'\kappa')}{x^2(l\kappa;\,l'\kappa')} [L_{\kappa\kappa'}(x(l\kappa;\,l'\kappa')) - T_{\kappa\kappa'}(x(l\kappa;\,l'\kappa'))] \\
&\quad + \tfrac{1}{2}\delta_{\mu\nu} \sum_{l\kappa} \sum_{l'\kappa'}{}' T_{\kappa\kappa'}(x(l\kappa;\,l'\kappa')) = \tfrac{1}{6}\delta_{\mu\nu} \sum_{l\kappa} \sum_{l'\kappa'}{}' [L_{\kappa\kappa'}(x(l\kappa;\,l'\kappa')) + 2T_{\kappa\kappa'}(x(l\kappa;\,l'\kappa'))] \\
&= \tfrac{1}{3} N \delta_{\mu\nu} \sum_{l'\kappa'}{}' [L_{1\kappa'}(x(01;\,l'\kappa')) + 2T_{1\kappa'}(x(01;\,l'\kappa'))].
\end{aligned} \tag{5.9}$$

Comparing Eqs. (3.24) and (5.9) we find that for cubic crystals

$$\chi_0 = \tfrac{1}{3} v_a{}^{-1} \sum_{l'\kappa'}{}' [L_{1\kappa'}(x(01;\,l'\kappa')) + 2T_{1\kappa'}(x(01;\,l'\kappa'))]. \tag{5.10}$$

From Eq. (5.6) we see that the coefficients we have called $\{P_{\mu\nu,\alpha}(l\kappa)\}$ are given by

$$\begin{aligned}
P_{\mu\nu,\alpha}(l\kappa) &= \sum_{l'\kappa'} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\,l\kappa) \\
&= P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\,l\kappa) + \sum_{l'\kappa'}{}' P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\,l\kappa) \\
&= \tfrac{1}{2} \sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') - \tfrac{1}{2} \sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l'\kappa';\,l\kappa) \\
&= \sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa').
\end{aligned} \tag{5.11}$$

In writing the last line of this equation we have used the result, which follows directly from Eq. (5.5), that

$$f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') = -f_{\mu\nu\alpha}(l'\kappa';\,l\kappa). \tag{5.12}$$

The result given by Eq. (5.11) can be simplified if we note that

$$\begin{aligned}
\sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') &= -\sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l'\kappa';\,l\kappa) \\
&= -\sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,2l-l'\kappa') \\
&= -\sum_{l'\kappa'}{}' f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') = 0.
\end{aligned} \tag{5.13}$$

Combining Eqs. (5.11) and (5.13) we obtain

$$P_{\mu\nu,\alpha}(01) = \sum_{l'}{}' f_{\mu\nu\alpha}(01;\,l'2), \tag{5.14a}$$

$$P_{\mu\nu,\alpha}(02) = \sum_{l'}{}' f_{\mu\nu\alpha}(02;\,l'1) = -P_{\mu\nu,\alpha}(01). \tag{5.14b}$$

We are now in a position to calculate the coefficients $\{B_{\mu\nu\alpha\rho}{}^{(1)}\}$. Substituting Eq. (5.11) into Eq. (3.26a) we obtain the result that

$$\begin{aligned}
B_{\mu\nu\alpha\rho}{}^{(1)} &= -V_0{}^{-1} \sum_{l\kappa} P_{\mu\nu,\alpha}(l\kappa) x_\rho(l\kappa) \\
&= -V_0{}^{-1} \sum_{l'\kappa'} \sum_{l\kappa} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\,l\kappa) x_\rho(l\kappa) \\
&= V_0{}^{-1} \sum_{l'\kappa'} \sum_{l\kappa} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\,l\kappa) x_\rho(l'\kappa';\,l\kappa),
\end{aligned} \tag{5.15}$$

where we have used Eq. (5.8) in writing the last line of this equation. Finally, making use of Eqs. (5.7a) and (5.12) we find that

$$\begin{aligned}
B_{\mu\nu\alpha\rho}{}^{(1)} &= -\tfrac{1}{2} V_0{}^{-1} \sum_{l\kappa} \sum_{l'\kappa'} f_{\mu\nu\alpha}(l\kappa;\,l'\kappa') x_\rho(l\kappa;\,l'\kappa') = -v_a{}^{-1} \sum_{l'\kappa'} f_{\mu\nu\alpha}(01;\,l'\kappa') x_\rho(01;\,l'\kappa') \\
&= -v_a{}^{-1} \sum_{l'\kappa'} \Bigg\{ \delta_{\mu\nu} \frac{x_\alpha x_\rho}{r} T'_{1\kappa'}(r) + \frac{x_\mu x_\nu x_\alpha x_\rho}{r^3} \left[L'_{1\kappa'}(r) - \frac{2L_{1\kappa'}(r)}{r} + \frac{2T_{1\kappa'}(r)}{r} \right] \\
&\qquad + \frac{x_\mu x_\rho \delta_{\nu\alpha} + x_\nu x_\rho \delta_{\mu\alpha}}{r^2} [L_{1\kappa'}(r) - T_{1\kappa'}(r)] \Bigg\}_{r=x(01;\,l'\kappa')}.
\end{aligned} \tag{5.16}$$

For cubic crystals this expression simplifies to

$$\begin{aligned}
B_{\mu\nu\alpha\rho}{}^{(1)} &= -v_a{}^{-1} \sum_{l'\kappa'}{}' \Bigg\{ \tfrac{1}{3}\delta_{\mu\nu}\delta_{\alpha\rho} r T'_{1\kappa'}(r) + \tfrac{1}{3}(\delta_{\mu\rho}\delta_{\nu\alpha} + \delta_{\nu\rho}\delta_{\mu\rho}) [L_{1\kappa'}(r) - T_{1\kappa'}(r)] \\
&\qquad + \frac{x_\mu x_\nu x_\alpha x_\rho}{r^3} \left[L'_{1\kappa'}(r) - \frac{2L_{1\kappa'}(r)}{r} - T'_{1\kappa'}(r) + \frac{2T_{1\kappa'}(r)}{r} \right] \Bigg\}_{r=x(01;\,l'\kappa')}.
\end{aligned} \tag{5.17}$$

Our assumption of nearest-neighbor bond polarizabilities is computationally convenient because it leads to four independent microscopic parameters, which is the number of macroscopic parameters in this problem, viz., χ_0, p_{1111}, p_{1122}, p_{1212}. If we denote the nearest-neighbor separation in crystals of the diamond structure by $r_0=\frac{1}{4}3^{1/2}a_0$, the microscopic expressions for the quantities χ_0, P, $B_{1111}^{(1)}$, and $B_{1212}^{(1)}$ take the following forms:

$$\chi_0=(4/3v_a)[L_{12}(r_0)+2T_{12}(r_0)], \tag{5.18a}$$

$$P=(4/3^{3/2})[L_{12}'(r_0)-[2L_{12}(r_0)/r_0]-T_{12}'(r_0)+[2T_{12}(r_0)/r_0]], \tag{5.18b}$$

$$B_{1111}^{(1)}=-(4/3v_a)\{r_0T_{12}'(r_0)+2[L_{12}(r_0)-T_{12}(r_0)]\}-a_0^{-2}P, \tag{5.18c}$$

$$B_{1122}^{(1)}=-(4/3v_a)r_0T_{12}'(r_0)-a_0^{-2}P, \tag{5.18d}$$

$$B_{1212}^{(1)}=-(4/3v_a)[L_{12}(r_0)-T_{12}(r_0)]-a_0^{-2}P. \tag{5.18e}$$

$L_{12}(r_0)$, $T_{12}(r_0)$, $L_{12}'(r_0)$, and $T_{12}'(r_0)$ are the values of the longitudinal and transverse bond polarizabilities and of their first derivatives evaluated at the equilibrium separation between nearest-neighbor atoms in crystals of the diamond structure. The subscripts 12 emphasize the fact that in each nearest-neighbor pair in such crystals one of the atoms is on sublattice 1 while the other is on sublattice 2.

If all that we wish to obtain is the coefficient P, we can bypass the calculation of the parameters $L_{12}(r_0)$, $L_{12}'(r_0)$, $T_{12}(r_0)$, and $T_{12}'(r_0)$, and can solve directly for P. Combining Eqs. (5.18c), (5.18d), and (5.18e) with Eq. (4.29c), we obtain the relation

$$P=a_0^2\frac{\epsilon_0^2}{8\pi}\frac{p_{1111}-p_{1122}-2p_{1212}}{1-(8G/a_0M\omega_R^2)}, \tag{5.19}$$

which expresses P entirely in terms of experimentally determinable quantities.

From the numerical values for the parameter G presented in Table I we see that it is negative for diamond, silicon, and germanium. It follows, therefore, that, on the basis of the present model, the sign of P is determined by the sign of the combination $p_{1111}-p_{1122}-2p_{1212}$.

VI. NUMERICAL RESULTS

In Table I we have listed the values of the primary physical constants which either enter directly into the expression (5.19) for the electronic polarizability derivative P, or determine the values of derived quantities which appear in this expression. Among these primary physical constants are the stress derivatives of the dielectric tensor, $q_{ij}=\partial\epsilon_i/\partial T_j$, and the pressure derivative of the refractive index, $n^{-1}dn/dT$, from which the values of the elasto-optic constants quoted in this Table were derived. We have also listed the stress derivatives of the dielectric permittivity tensor, $\pi_{ij}=\partial\beta_i/\partial T_j$, where the permittivity tensor is the inverse of the dielectric tensor. [In defining these constants we have used the contracted Voigt notation for the various tensors rather than the full tensor notation. The relations between the constants in the two sets of notations are given, for example, in the book by Nye.[25]]

From Table I we see that in the only case where a comparison can be made at the present time, viz., that of germanium, the value of the quantity $-(8G/a_0M\omega_R^2)$ computed on the basis of Eq. (4.37) with values of the atomic force constants α_1 and ρ_1 obtained from the elastic constants through Eq. (4.36) is 41% smaller than the value computed from the more elaborate (and presumably more accurate) expression given by Eq. (4.33). It is perhaps not unreasonable to think that the values of $-(8G/a_0M\omega_R^2)$ computed for diamond and silicon from Eq. (4.37) may be in error by corresponding amounts. This possibility should be kept in mind in assessing the reliability of the numerical results obtained in this section, and it points up the desirability of having the values of the atomic force constants for diamond and silicon obtained from the fit of at least a fifth-neighbor general tensor-force model of such crystals to experimentally determined phonon-dispersion curves.

The values of P for diamond, silicon, and germanium calculated from Eq. (5.19) are presented in Table I. Two values of P are quoted for germanium corresponding to the two different expressions, Eqs. (4.33) and (4.37), used in calculating the quantity $-(8G/a_0M\omega_R^2)$. The value of $P=-3.78$ Å^2 calculated for diamond compares very favorably with the experimental result of Anastassakis *et al.*[6] that $|P|\cong4$ Å^2. While the experimental results can tell us nothing about the sign of P, the theoretical results obtained in this paper predict that the sign of P is the sign of $p_{1111}-p_{1122}-2p_{1212}$, which is negative for diamond.

Although at the present time no experimental values are available for even the magnitude of P for silicon and germanium, experimental results are available which enable us to make an indirect assessment of the reliability of our theoretical results for these two crystals. From a comparison of the intensities of the first-order Raman scattering of light by silicon and diamond, Russell[7] has estimated that

$$|P_{\mathrm{Si}}|/|P_{\mathrm{C}}|\approx2.7 \text{ (expt.)}. \tag{6.1a}$$

From Table I the corresponding theoretical value is found to be

$$|P_{\mathrm{Si}}|/|P_{\mathrm{C}}|=1.84 \text{ (theor.)}. \tag{6.1b}$$

The theoretical value of this ratio is within 35% of the experimental value, and the agreement between theory and experiment in this case must be considered as satisfactory.

A second, indirect, check on our theoretical results is provided by the recent experimental result of Parker

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[25] J. F. Nye, *Physical Properties of Crystals* (Oxford University Press, New York, 1957).

et al.,[8] who found that

$$|P_{\mathrm{Si}}|/|P_{\mathrm{Ge}}|=0.5-0.8 \text{ (expt.)}. \tag{6.2a}$$

From Table I the corresponding theoretical value is found to be

$$|P_{\mathrm{Si}}|/|P_{\mathrm{Ge}}|=0.58,\ 0.70 \text{ (theor.)}, \tag{6.2b}$$

where the two values quoted are associated with the two values of $-(8G/a_0M\omega_R{}^2)$ calculated for germanium. Again, the agreement between theory and experiment for this ratio must be considered as satisfactory.

From the expressions given by Eqs. (5.18) and (4.29), and the values of the physical constants we can solve for the values of $L_{12}(r_0)$, $T_{12}(r_0)$, $r_0L'_{12}(r_0)$, and $r_0T'_{12}(r_0)$ for each of the three crystals considered in this paper. The values obtained for these parameters are given in Table I. From these values we see that although the values of P are negative for diamond and silicon, and positive for germanium, the values of $L'_{12}(r_0)$ and $T'_{12}(r_0)$ are positive for all three crystals. That is, for values of the nearest-neighbor separation close to the equilibrium value the longitudinal and transverse bond polarizabilities increase with increasing bond length.

Turning now to the relations between the elasto-optic constants and the electrostriction constants, we find on combining Eqs. (2.41) and (3.24) that

$$\begin{aligned}\gamma_{1111}{}^{(T)}&=-\{(\epsilon_0{}^2/4\pi)p_{1111}-\chi_0\},\\ \gamma_{1122}{}^{(T)}&=-\{(\epsilon_0{}^2/4\pi)p_{1122}-\chi_0\},\\ \gamma_{1212}{}^{(T)}&=-(\epsilon_0{}^2/4\pi)p_{1212}.\end{aligned} \tag{6.3}$$

Values of the electrostriction constants computed on the basis of Eq. (6.3) are given in Table I. From these values and Eq. (2.45) we have also computed the values of the electrostrictional moduli $\gamma_{\mu\nu\alpha\beta}{}^{(\eta)}$, and these are also given in Table I. In carrying out the latter calculations we have used the relations[26]

$$\begin{aligned}S_{1111}&=S_{11}=\frac{C_{11}+C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})},\\ S_{1122}&=S_{12}=\frac{-C_{12}}{(C_{11}-C_{12})(C_{11}+2C_{12})},\\ S_{1212}&=\tfrac{1}{4}S_{44}=1/4C_{44},\end{aligned} \tag{6.4}$$

between the elastic compliances regarded as the elements of a fourth-rank tensor and expressed in the two suffix Voigt notation.

An attempt to measure the electrostriction constants of germanium has been made recently by Gundjian.[27] His experimental results are seven orders of magnitude larger than the theoretical values reported here. This discrepancy strongly suggests that the effects measured by Gundjian do not have their origin in electrostriction but reflect some other physical process.

In summary, we have presented in this paper a microscopic theory of the elasto-optic constants of crystals of the diamond structure which corrects an earlier theory of Theimer,[2] which relates the elasto-optic constants to the electronic polarizability derivative P, and which yields values of P for diamond, silicon, and germanium which are in satisfactory agreement with such experimental results for these coefficients as are available at the present time. In addition, the relations between the elasto-optic constants and the electrostriction constants for crystals of the diamond structure are established, and experimental values of the former have been used to calculate values of the latter for diamond, silicon, and germanium.

APPENDIX A

It has been shown[28] that the solution of the equation

$$\sum_{l'\kappa'\beta}\Phi_{\alpha\beta}(l\kappa;\,l'\kappa')d_\beta(l'\kappa')=C_\alpha(l\kappa), \tag{A1}$$

when the coefficients $\{C_\alpha(l\kappa)\}$ satisfy the condition

$$\sum_{l\kappa}C_\alpha(l\kappa)=0, \tag{A2}$$

can be written in the form

$$d_\alpha(l\kappa)=\sum_{s=1}^{3}a_su_\alpha{}^{(s)}+\sum_{l'\kappa'\beta}\Gamma_{\alpha\beta}(l\kappa;\,l'\kappa')C_\beta(l'\kappa'). \tag{A3}$$

In Eq. (A3) the $\{a_s\}$ are three arbitrary constants, while the vectors $\{\mathbf{u}^{(s)}\}$ are given by

$$\mathbf{u}^{(s)}=\mathbf{e}^{(s)}/(M_T)^{1/2}, \tag{A4}$$

where $\mathbf{e}^{(1)}$, $\mathbf{e}^{(2)}$, $\mathbf{e}^{(3)}$ are any three mutually perpendicular unit vectors and M_T is the total mass of the crystal. The elements of the matrix $\mathbf{\Gamma}$ are given by

$$\mathbf{\Gamma}_{\alpha\beta}(l\kappa;\,l'\kappa')=\frac{1}{(M_{l\kappa}M_{l'\kappa'})^{1/2}}\sum_s{}'\frac{B_\alpha{}^{(s)}(l\kappa)B_\beta{}^{(s)}(l'\kappa')}{\omega_s{}^2}, \tag{A5}$$

where $M_{l\kappa}$ is the mass of the atom $(l\kappa)$ and the sum over s is a sum over all the normal vibration modes of the crystal except for the three zero-frequency modes which describe pure rigid body translations of the crystal. ω_s is the frequency of the sth normal mode and $B_\alpha{}^{(s)}(l\kappa)$ is an element of the corresponding unit polarization vector.

Because the solutions of Eq. (A1) appear in this paper

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[26] R. F. S. Hearmon, *An Introduction to Applied Anisotropic Elasticity* (Clarendon Press, Oxford, England, 1961), p. 25.

[27] A. Gundjian, Solid State Commun. 3, 279 (1965).

[28] S. Ganesan, A. A. Maradudin, and E. Burstein, Phys. Rev (to be published).

only in sums of the form

$$\sum_{l_n\kappa_n\alpha_n} \Phi_{\alpha_1\cdots\alpha_n}(l_1\kappa_1;\ \cdots;\ l_n\kappa_n)d_{\alpha_n}(l_n\kappa_n)\,,$$

$$\sum_{l_n\kappa_n\alpha_n} P_{\mu\nu,\alpha_1\cdots\alpha_n}(l_1\kappa_1;\ \cdots;\ l_n\kappa_n)d_{\alpha_n}(l_n\kappa_n)\,,$$

the conditions which follow from infinitesimal translation invariance

$$\begin{aligned}\sum_{l_n\kappa_n\alpha_n} \Phi_{\alpha_1\cdots\alpha_n}(l_1\kappa_1;\ \cdots;\ l_n\kappa_n)&=0\,,\\ \sum_{l_n\kappa_n\alpha_n} P_{\mu\nu,\alpha_1\cdots\alpha_n}(l_1\kappa_1;\ \cdots;\ l_n\kappa_n)&=0\,,\end{aligned}\tag{A6}$$

have the consequence that the part of $d_\alpha(l\kappa)$ associated with pure translations of the crystal makes no contribution to such sums. Therefore for the purposes of this paper we can set the coefficients $\{a_s\}$ in Eq. (A3) equal to zero, so that the solution of Eq. (A1) is effectively

$$d_\alpha(l\kappa)=\sum_{l'\kappa'\beta} \Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')C_\beta(l'\kappa')\,.\tag{A7}$$

The expression for $\Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')$ given by Eq. (A5) is valid for an arbitrary crystal, either perfect or imperfect. However, for perfect crystals, which are all that are considered in this paper, a convenient representation of $\Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')$ is provided by expanding it in terms of the eigenvectors $\{e_\alpha(\kappa|\mathbf{k}j)\}$ and eigenvalues of $\{\omega_j^2(\mathbf{k})\}$ of the $3r\times 3r$ Fourier transformed dynamical matrix:

$$D_{\alpha\beta}(\kappa\kappa'|\mathbf{k})=\frac{1}{(M_\kappa M_{\kappa'})^{1/2}}\sum_{l'} \Phi_{\alpha\beta}(l\kappa;\ l'\kappa')\times e^{-i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\,,\tag{A8a}$$

$$\sum_{\kappa'\beta} D_{\alpha\beta}(\kappa\kappa'|\mathbf{k})e_\beta(\kappa'|\mathbf{k}j)=\omega_j^2(\mathbf{k})e_\alpha(\kappa|\mathbf{k}j)\,,\tag{A8b}$$

$$\sum_{\kappa\alpha} e_\alpha^*(\kappa|\mathbf{k}j)e_\alpha(\kappa|\mathbf{k}j)=\delta_{jj'}\,,\tag{A8c}$$

$$\sum_{j} e_\alpha^*(\kappa|\mathbf{k}j)e_\beta(\kappa'|\mathbf{k}j)=\delta_{\kappa\kappa'}\delta_{\alpha\beta}\,.\tag{A8d}$$

The allowed values of $\mathbf{k}$ are uniformly and densely distributed throughout the first Brillouin zone for the crystal, and the index $j(=1,\ 2,\ \cdots 3r)$ labels the $3r$ solutions of Eq. (A8b) corresponding to each value of $\mathbf{k}$. In this representation $\Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')$ has the form

$$\Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')=\frac{1}{N(M_\kappa M_{\kappa'})^{1/2}}\sum_{\mathbf{k}j}{}' \frac{e_\alpha(\kappa|\mathbf{k}j)e_\beta^*(\kappa'|\mathbf{k}j)}{\omega_j^2(\mathbf{k})}\times e^{i\mathbf{k}\cdot[\mathbf{x}(l)-\mathbf{x}(l')]}\,,\tag{A9}$$

where the prime on the sum means that the three terms for which $\mathbf{k}=0$ and for which j refers to the three acoustic branches of the phonon spectrum are excluded. [For these terms, $\omega_j(\mathbf{0})=0$.]

In the text we require the $3r\times 3r$ matrix whose elements are given by

$$\sum_{ll'} \Gamma_{\alpha\beta}(l\kappa;\ l'\kappa')=\frac{N}{(M_\kappa M_{\kappa'})^{1/2}}\Gamma_{\alpha\beta}(\kappa\kappa')\,.\tag{A10}$$

An explicit representation for $\Gamma_{\alpha\beta}(\kappa\kappa')$ follows on inserting Eq. (A9) into the left-hand side of Eq. (A10):

$$\Gamma_{\alpha\beta}(\kappa\kappa')=\sum_j{}' \frac{e_\alpha(\kappa|\mathbf{0}j)e_\beta(\kappa'|\mathbf{0}j)}{\omega_j^2(\mathbf{0})}\tag{A11}$$

[recall that $e_\alpha^*(\kappa|\mathbf{0}j)=e_\alpha(\kappa|\mathbf{0}j)$]. The prime on the sum on the right-hand side of this equation means that it extends over the optical branches of the phonon spectrum only.

APPENDIX B

In the text we employed a "bond polarizability" model of the electronic polarizability as the basis for an evaluation of the polarizability derivative P for diamond, silicon, and germanium from experimental values of the elasto-optic constants of these crystals. While this model proved to be a successful one in that predictions based on it appear to be in satisfactory agreement with experimental results, it nevertheless is based on assumptions which, while seemingly reasonable, may in fact prove to be overly restrictive. In this Appendix we describe briefly an attempt to construct a model of the electronic polarizability of crystals of the diamond structure which is based on a minimum number of assumptions. The model we consider is the same one used by Theimer[2] in his work, except that it is presented here as a special case of a much more general model.

Our starting assumption is that the static electronic polarizability of the crystal can be written as the sum of the atomic polarizabilities of all the atoms in the crystal:

$$P_{\mu\nu}=\sum_{l\kappa} P_{\mu\nu}(l\kappa)\,.\tag{B1}$$

The polarizability of each atom is assumed to be a function of the instantaneous positions of all the atoms in the crystal, and to admit of an expansion in powers of the displacements of the atoms from their equilibrium positions:

$$\begin{aligned}P_{\mu\nu}(l\kappa)=P_{\mu\nu}^{(0)}(l\kappa)&+\sum_{l'\kappa'\beta} P_{\mu\nu,\beta}^{(1)}(l\kappa;\ l'\kappa')u_\beta(l'\kappa')\\ &+\tfrac{1}{2}\sum_{l'\kappa'\beta}\sum_{l''\kappa''\gamma} P_{\mu\nu,\beta\gamma}^{(2)}(l\kappa;\ l'\kappa';\ l''\kappa'')\times u_\beta(l'\kappa')u_\gamma(l''\kappa'')+\cdots\,.\end{aligned}\tag{B2}$$

From a comparison of Eqs. (3.12) and (B2) we see that

$$P_{\mu\nu}^{(0)}=\sum_{l\kappa} P_{\mu\nu}^{(0)}(l\kappa)\,,\tag{B3a}$$

$$P_{\mu\nu,\alpha}(l\kappa)=\sum_{l'\kappa'} P_{\mu\nu,\alpha}^{(1)}(l'\kappa';\ l\kappa)\,,\tag{B3b}$$

$$P_{\mu\nu,\alpha\beta}(l\kappa;\ l'\kappa')=\sum_{l''\kappa''} P_{\mu\nu,\alpha\beta}^{(2)}(l''\kappa'';\ l\kappa;\ l'\kappa'),\ \text{etc.}\tag{B3c}$$

The coefficients $P_{\mu\nu}{}^{(0)}(l\kappa)$, $P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';l\kappa)$, $P_{\mu\nu,\alpha\beta}{}^{(2)} \times(l''\kappa'';l\kappa;l'\kappa')$, must satisfy certain general invariance conditions. From their definition as the partial derivatives of the atomic polarizability $P_{\mu\nu}(l\kappa)$ with respect to atomic displacements, it follows that $P_{\mu\nu,\alpha\beta}{}^{(2)}(l''\kappa'';l\kappa;l'\kappa'),\cdots$ are completely symmetric in the indices $(l\kappa\alpha)$, $(l'\kappa'\beta),\cdots$:

$$P_{\mu\nu,\alpha\beta}{}^{(2)}(l''\kappa'';l\kappa;l'\kappa')=P_{\mu\nu,\beta\alpha}{}^{(2)}(l''\kappa'';l'\kappa';l\kappa)\,, \tag{B4a}$$

$$\begin{aligned}P_{\mu\nu,\alpha\beta\gamma}{}^{(3)}&(l'''\kappa''';l\kappa;l'\kappa';l''\kappa'')\\ &=P_{\mu\nu,\alpha\gamma\beta}{}^{(3)}(l'''\kappa''';l\kappa;l''\kappa'';l'\kappa')\\ &=P_{\mu\nu,\beta\alpha\gamma}{}^{(3)}(l'''\kappa''';l'\kappa';l\kappa;l''\kappa'')=\cdots.\end{aligned} \tag{B4b}$$

From the fact that an arbitrary rigid body displacement of the crystal cannot change the atomic polarizability we obtain the conditions

$$\sum_{l\kappa} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';l\kappa)=0\,, \tag{B5a}$$

$$\begin{aligned}\sum_{l\kappa} &P_{\mu\nu,\alpha\beta}{}^{(2)}(l''\kappa'';l\kappa;l'\kappa')\\ &=\sum_{l'\kappa'} P_{\mu\nu,\alpha\beta}{}^{(2)}(l''\kappa'';l\kappa;l'\kappa')=0,\ \text{etc.}\end{aligned} \tag{B5b}$$

From the fact that $P_{\mu\nu}(l\kappa)$ must transform as a second-rank tensor under an infinitesimal rigid body rotation of the crystal, we obtain the following condition on the first-order coefficients:

$$\begin{aligned}\sum_{l'\kappa'} &P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')x_\beta(l'\kappa')-\delta_{\mu\alpha}P_{\beta\nu}{}^{(0)}(l\kappa)\\ &-\delta_{\nu\alpha}P_{\mu\beta}{}^{(0)}(l\kappa)=\sum_{l'\kappa'} P_{\mu\nu,\beta}{}^{(1)}(l\kappa;l'\kappa')x_\alpha(l'\kappa')\\ &\qquad-\delta_{\mu\beta}P_{\alpha\nu}{}^{(0)}(l\kappa)-\delta_{\nu\beta}P_{\mu\alpha}{}^{(0)}(l\kappa)\,.\end{aligned} \tag{B6}$$

In addition to these general conditions, which apply to a finite crystal as well as to an infinite one, there are others which have their origin in the structure and symmetry of a given crystal, and which presuppose an infinitely extended crystal. Under an operation of the space group of the crystal, the coefficients $\{P_{\mu\nu}{}^{(0)}(l\kappa)\}$ and $\{P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')\}$ transform according to

$$P_{\mu\nu}{}^{(0)}(LK)=\sum_{\rho\sigma} S_{\mu\rho}S_{\nu\sigma}P_{\rho\sigma}{}^{(0)}(l\kappa)\,, \tag{B7a}$$

$$P_{\mu\nu,\alpha}{}^{(1)}(LK;L'K')=\sum_{\rho\sigma\tau} S_{\mu\rho}S_{\nu\sigma}S_{\alpha\tau}P_{\rho\sigma\tau}{}^{(1)}(l\kappa;l'\kappa'). \tag{B7b}$$

If the space-group operation is a rigid body displacement of the crystal through one of its translation vectors, Eqs. (B7) yield the result that $P_{\mu\nu}{}^{(0)}(l\kappa)$ is independent of the cell index l, while $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')$ depends on l and l' only through their difference.

If in Eq. (B7a) we apply the 24 operations of the space group $O_h{}^7$ whose purely rotational elements comprise the point group T_d to the lattice site (01) we find that the coefficient $P_{\mu\nu}{}^{(0)}(01)$ has the form

$$P_{\mu\nu}{}^{(0)}(01)=\delta_{\mu\nu}P^{(0)}\,. \tag{B8a}$$

The remaining 24 operations of the space group yield the result

$$P_{\mu\nu}{}^{(0)}(02)=P_{\mu\nu}{}^{(0)}(01)\,. \tag{B8b}$$

Because $P_{\mu\nu}{}^{(0)}(l\kappa)$ is independent of the cell index l, the only nonzero, independent coefficients of this type are just those given by Eq. (B8). Combining Eqs. (B3a), (B8), and (3.24), we relate the coefficient $P^{(0)}$ in Eq. (B8a) to the measurable quantity χ_0 by

$$\chi_0=(2/v_a)P^{(0)}\,. \tag{B9}$$

So far in this discussion we have made no assumption regarding the interatomic separations $|\mathbf{x}(l\kappa)-\mathbf{x}(l'\kappa')|$ over which the coefficients $\{P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')\}$ are sensibly nonzero. In view of the origin of these coefficients in the distortion of the charge distributions of the atoms $(l\kappa)$ and $(l'\kappa')$ through the change in their overlap as their relative separation changes from its equilibrium value, we would expect $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')$ to decrease rapidly as $|\mathbf{x}(l\kappa)-\mathbf{x}(l'\kappa')|$ increases. In what follows, primarily to keep the number of independent parameters small, we assume that $P_{\mu\nu,\alpha}(l\kappa;l'\kappa')$ is nonzero only if $(l\kappa)=(l'\kappa')$, or if $(l\kappa)$ and $(l'\kappa')$ are nearest-neighbor sites.

The independent, nonzero elements of the tensor $P_{\mu\nu,\alpha}{}^{(1)}(01;02)$ are obtained from Eq. (B7b) if we restrict the operations of the space group $O_h{}^7$ to those which leave the lattice sites (01) and (02) fixed. If we display the elements of an arbitrary third-rank tensor according to the scheme

$$\left\{\begin{matrix} xxx\ xxy\ xxz & yxx\ yxy\ yxz & zxx\ zxy\ zxz\\ xyx\ xyy\ xyz & yyx\ yyy\ yyz & zyx\ zyy\ zyz\\ xzx\ xzy\ xzz & yzx\ yzy\ yzz & zzx\ zzy\ zzz\end{matrix}\right\}, \tag{B10}$$

the tensor $P_{\mu\nu,\alpha}{}^{(1)}(01;02)$ has the form

$$P_{\mu\nu,\alpha}{}^{(1)}(000;111)=\left\{\begin{matrix} a\ b\ b & d\ d\ f & d\ f\ d\\ d\ d\ f & b\ a\ b & f\ d\ d\\ d\ f\ d & f\ d\ d & b\ b\ a\end{matrix}\right\}. \tag{B11}$$

In writing the left-hand side of Eq. (B11) we have written out explicitly the Cartesian components of the position vectors $\mathbf{x}(01)$ and $\mathbf{x}(02)$ in units of $\frac{1}{4}a_0$. The elements of the tensors $P_{\mu\nu,\alpha}{}^{(1)}(000;\bar{1}\bar{1}1)$, $P_{\mu\nu,\alpha}{}^{(1)}(000;1\bar{1}\bar{1})$, and $P_{\mu\nu,\alpha}{}^{(1)}(000;\bar{1}1\bar{1})$ can be obtained from the result given by Eq. (B11) by the use of Eq. (B7b). The rotational invariance conditions, Eq. (B6), are satisfied by the form of the tensor $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')$ given by Eq. (B11).

According to Eq. (B3b) we have that

$$\begin{aligned}P_{\mu\nu,\alpha}(l\kappa)&=\sum_{l'\kappa'} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';l\kappa)\\ &=\sum_{l'} \{P_{\mu\nu,\alpha}{}^{(1)}(01;l-l'\kappa)+P_{\mu\nu,\alpha}{}^{(1)}(02;l-l'\kappa)\}\,,\end{aligned} \tag{B12}$$

because $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;l'\kappa')$ depends on l and l' only through their difference. In particular, we see that

$$
\begin{aligned}
P_{\mu\nu,\alpha}(01) &= \sum_{l} \{P_{\mu\nu,\alpha}{}^{(1)}(01;\, l1) + P_{\mu\nu,\alpha}{}^{(1)}(02;\, l1)\} \\
&= P_{\mu\nu,\alpha}{}^{(1)}(01;\, 01) + \sum_{l} P_{\mu\nu,\alpha}{}^{(1)}(02;\, l1) \\
&= -\sum_{l} P_{\mu\nu,\alpha}{}^{(1)}(01;\, l2) + \sum_{l} P_{\mu\nu,\alpha}{}^{(1)}(02;\, l1) \\
&= -2\sum_{l} P_{\mu\nu,\alpha}{}^{(1)}(01;\, l2)\,. \qquad \text{(B13)}
\end{aligned}
$$

The second line of this equation reflects our assumption that $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\, l'\kappa')$ vanishes if $(l\kappa)$ and $(l'\kappa')$ are more distant than nearest neighbors; the third line is a consequence of Eq. (B5a), and we have used Eq. (B7b) in writing the last line. Using Eq. (B11) in Eq. (B13) we obtain the result that

$$P_{\mu\nu,\alpha}{}^{(1)}(01) = -8f|\epsilon_{\mu\nu\alpha}|\,, \qquad \text{(B14)}$$

so that for this model

$$P = -8f. \qquad \text{(B15)}$$

The elements of the tensor $B_{\mu\nu\alpha\rho}{}^{(1)}$ take a simple form on the basis of the present model. We can use infinitesimal translation invariance as expressed by Eq. (B5a) to rewrite Eq. (3.26a) in the form

$$
\begin{aligned}
B_{\mu\nu\alpha\rho}{}^{(1)} &= -V_0^{-1}\sum_{l\kappa} P_{\mu\nu,\alpha}(l\kappa)x_\rho(l\kappa) \\
&= -V_0^{-1}\sum_{l'\kappa'}\sum_{l\kappa} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\, l\kappa)x_\rho(l\kappa) \\
&= -V_0^{-1}\sum_{l'\kappa'}\sum_{l\kappa} P_{\mu\nu,\alpha}{}^{(1)}(l'\kappa';\, l\kappa)x_\rho(l'\kappa';\, l\kappa). \qquad \text{(B16)}
\end{aligned}
$$

We now carry out the sums over l', κ, and κ', keeping in mind that $P_{\mu\nu,\alpha}{}^{(1)}(l\kappa;\, l'\kappa')$ depends on l and l' only through their difference, and that $(l\kappa)$ and $(l'\kappa')$ must be no farther apart than nearest neighbors:

$$
\begin{aligned}
B_{\mu\nu\alpha\rho}{}^{(1)} &= \frac{1}{v_a}\sum_{l} \{P_{\mu\nu,\alpha}{}^{(1)}(01;\, l2)x_\rho(01;\, l2) + P_{\mu\nu,\alpha}{}^{(1)}(02;\, l1)x_\rho(02;\, l1)\} \\
&= \frac{1}{v_a}\sum \{P_{\mu\nu,\alpha}{}^{(1)}(01;\, l2)x_\rho(01;\, l2) = P_{\mu\nu,\alpha}{}^{(1)}(01;\, -l2)x_\rho(01;\, -l2)\} \\
&= \frac{2}{v_a}\sum_{l} P_{\mu\nu,\alpha}{}^{(1)}(01;\, l2)x_\rho(01;\, l2)\,. \qquad \text{(B17)}
\end{aligned}
$$

The second equation follows from the fact that inversion is a symmetry operation which interchanges the two sublattices in crystals of the diamond structure.

According to symmetry arguments the tensor $B_{\mu\nu\alpha\rho}{}^{(1)}$ has only three independent elements, e.g., $B_{1111}{}^{(1)}$, $B_{1122}{}^{(1)}$, and $B_{1212}{}^{(1)}$, for crystals of the diamond structure. An explicit calculation based on Eqs. (B11) and (B17) confirms this and yields the results

$$B_{1111}{}^{(1)} = -(2/v_a)(a_0 a)\,, \qquad \text{(B18a)}$$

$$B_{1122}{}^{(1)} = -(2/v_a)(a_0 b)\,, \qquad \text{(B18b)}$$

$$B_{1212}{}^{(1)} = -(2/v_a)(a_0 d)\,. \qquad \text{(B18c)}$$

Combining Eqs. (3.28), (4.29), (B15), and (B18), we obtain finally the following relations between the microscopic parameters a, b, d, f and the macroscopic quantities $\{p_{\mu\nu\alpha\rho}\}$, ϵ_0, and $\chi_0 = (\epsilon_0 - 1)/4\pi$, for crystals of the diamond structure:

$$a = -(a_0{}^2/8)\{(\epsilon_0{}^2/4\pi)p_{1111} - \chi_0\}\,, \qquad \text{(B19a)}$$

$$b = -(a_0{}^2/8)\{(\epsilon_0{}^2/4\pi)p_{1122} - \chi_0\}\,, \qquad \text{(B19b)}$$

$$d + (G/a_0 M\omega_R{}^2)(8f) = -(a_0{}^2/8)(\epsilon_0{}^2/4\pi)p_{1212}\,. \qquad \text{(B19c)}$$

From the results given by Eqs. (B19) we see that the generality of the model on which they are based is at once its strength and its weakness. Other than the restriction to nearest-neighbor interactions, no assumptions have gone into determining the form of the tensor $P_{\mu\nu,\alpha}{}^{(1)}(000;\, 111)$. However, a consequence of this generality is that we have more microscopic parameters than there are relations between them and experimental quantities. As a result, we have no way of determining the parameter $f = -(P/8)$ uniquely. The value of the present model would seem to lie in the fact that when an accurate value of P is known, from some independent calculation or from experiment, so that all four parameters a, b, d, f are known, this model can serve as the basis for a less restrictive microscopic model of the electronic polarizability of crystals of the diamond structure than the one adopted in the test. Such a model could then be used in calculations of other properties of these crystals in which the electronic polarizability plays a central role, for example, in calculations of the second order Raman spectrum.