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A General Matrix Method for Treating Elastic Constants of Molecular Crystals; Application to Orthorhombic Polyethylene

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A general method is developed for treating elastic constants of molecular crystals, with the $\boldsymbol{B}$ matrices as commonly used in normal-coordinate treatments. Equations are written in matrix forms, convenient for calculating elastic constants from intramolecular and intermolecular force field and are readily programed for electronic computations. Partial derivatives of elastic constants with respect to force constants are also derived, for least-square adjustments of force fields with reference to experimental elastic constants as well as vibrational frequencies. Matrix treatments of elastic constants are much simplified by the use of crystal symmetry, just as are treatments of normal vibrations. The matrix methods are explained for the example of orthorhombic polyethylene.

Normal coordinate treatments of molecular vibrations are useful for vibrational assignments of infrared and Raman spectra of polyatomic molecules. The $\boldsymbol{GF}$ matrix method derived by Wilson[1] is commonly used in treating molecular vibrations. Inverse-kinetic energy matrices ($\boldsymbol{G}$) are constructed from $\boldsymbol{B}$ matrices, transformation matrices from Cartesian coordinates to intramolecular coordinates including bond-stretching, angle-bending[2] and internal-rotation coordinates.[3]

$\boldsymbol{B}$ matrices are also useful for treating normal vibrations of molecular crystals, where intermolecular coordinates are used together with intramolecular coordinates. In a previous paper,[4] applications of the $\boldsymbol{GF}$ matrix method were explained for factor-group vibrations of crystal lattices. Intermolecular and intramolecular force constants may be adjusted with reference to infrared and Raman frequencies observed for molecular crystals. However, too often, a unique set of force constants can not be obtained, because the number of observed frequencies is smaller than the number of force constants. In these cases, it is a common practice to assume certain type of potential functions.[2] Never-

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[1] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

[2] T. Shimanouchi, *Nippon Kagaku Zasshi*, **86**, 261 (1965); "Physical Chemistry," Vol. 4, ed. by H. Eyring, Academic Press, New York, N. Y. (1970), p. 233.

[3] T. Miyazawa and K. Fukushima, *J. Mol. Spectrosc.*, **15**, 308 (1965).

[4] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

theless, it is desirable to refer to additional experimental data that depend on force constants of crystals. For many inorganic crystals and some organic molecular crystals,⁵⁾ elastic constants have been measured and serve as useful data for studying force fields of crystals.

A general relation between force constants and elastic constants was discussed by Born and Huang.⁶⁾ However, in practical numerical treatments of elastic constants of molecular crystals together with their vibrational frequencies, it is important to formulate the transformation from the potential energy matrix ($\boldsymbol{F}$) to the elastic constant matrix ($\boldsymbol{C}$). This transformation may be derived with the $\boldsymbol{B}$ matrices as used in normal-coordinate treatments. Accordingly, in the present study, a general matrix method was developed for treating elastic constants from force fields of molecular crystals. Furthermore, partial derivatives of elastic constants with respect to force constants were derived and were formulated in matrix equations.

Energy Density due to Homogeneous Deformation

The potential energy (V) of a crystal lattice may be expressed in terms of an appropriate internal-coordinate vector ($\boldsymbol{R}$),

$$V = \frac{1}{2}\tilde{\boldsymbol{R}}\boldsymbol{F}_{\mathrm{R}}\boldsymbol{R} \tag{1}$$

where a tilde denotes transposed matrix or vector and $\boldsymbol{F}_{\mathrm{R}}$ is the potential energy matrix associated with the $\boldsymbol{R}$ vector.¹⁾ For a crystal of N unit cells, the energy density (ε) is given as,

$$\varepsilon = \frac{1}{2}\tilde{\boldsymbol{R}}\boldsymbol{F}_{\mathrm{R}}\boldsymbol{R}/Nv \tag{2}$$

where v is the volume per unit cell.

A unit cell of a crystal lattice may be denoted with an index vector $\boldsymbol{L}$ with integral components (h,k,l), so that the internal-coordinate vector ($\boldsymbol{R}$) is expressed as

$$\boldsymbol{R} = \begin{bmatrix} \vdots \\ \boldsymbol{R}(\boldsymbol{L}) \\ \vdots \end{bmatrix} \tag{3}$$

where $\boldsymbol{R}(\boldsymbol{L})$ is the internal-coordinate subvector for the unit cell $\boldsymbol{L}$. If such a crystal is subjected to a homogeneous deformation, the resulting structure remains a perfect lattice and $\boldsymbol{R}(\boldsymbol{L})$ is actually independent of $\boldsymbol{L}$. Accordingly, the internal-coordinate vector ($\boldsymbol{R}$) may be transformed into the internal symmetry-coordinate vector ($\boldsymbol{R}^0$),

$$\boldsymbol{R}^0 = N^{-1}\sum_{\boldsymbol{L}}\boldsymbol{R}(\boldsymbol{L}) \tag{4}$$

The $\boldsymbol{R}^0$ coordinates are symmetric with respect to translational symmetry operations. A corresponding transformation need be carried out on the potential energy matrix ($\boldsymbol{F}_{\mathrm{R}}$), yielding

$$\boldsymbol{F}_{\mathrm{R}}{}^0 = \sum_{\boldsymbol{\lambda}}\boldsymbol{F}_{\mathrm{R}}(\boldsymbol{\lambda}) \tag{5}$$

where $\boldsymbol{F}_{\mathrm{R}}(\boldsymbol{\lambda})$ is the potential-energy submatrix, associated with the $\boldsymbol{R}(\boldsymbol{L})$ vector and the $\boldsymbol{R}(\boldsymbol{L}+\boldsymbol{\lambda})$ vector. Equation (2) is written as

$$\varepsilon = \frac{1}{2}\sum_{\boldsymbol{L}}\tilde{\boldsymbol{R}}^0\sum_{\boldsymbol{\lambda}}\boldsymbol{F}_{\mathrm{R}}(\boldsymbol{\lambda})\boldsymbol{R}^0/Nv = \frac{1}{2}[\tilde{\boldsymbol{R}}^0\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{R}^0]/v \tag{6}$$

and the energy density is now expressed with a finite number of internal symmetry-coordinates ($\boldsymbol{R}^0$). The $\boldsymbol{F}_{\mathrm{R}}{}^0$ matrix may also be used for treating infrared and Raman-active normal vibrations of molecular crystals.

Elastic Strain

In a homogeneous deformation of a crystal lattice, the displacement of the mth atom in the cell ($\boldsymbol{L}$) is given⁷⁾ as

$$\xi_\alpha(\boldsymbol{L}, m) = \sum_{\beta}U_{\alpha\beta}X_\beta(\boldsymbol{L}, m) + \rho_\alpha(m) \qquad (\alpha, \beta = x, y, \text{ or } z) \tag{7}$$

where $U_{\alpha\beta}$ is external deformation parameter, $\boldsymbol{X}(\boldsymbol{L},m)$ is the position vector (column) of the mth atom of the cell ($\boldsymbol{L}$). The first term of the right side of Eq. (7) is due to the external deformation that is uniform throughout the crystal (even within a unit cell). The second term, $\boldsymbol{\rho}(m)$, is the internal strain vector of the mth atom that is common to every unit cell.

Now, for a crystal containing n atoms per unit cell, Eq. (7) may be reduced into a matrix form,

$$\boldsymbol{\xi}(\boldsymbol{L}) = \boldsymbol{P}(\boldsymbol{L})\boldsymbol{U} + \boldsymbol{\rho} \tag{8}$$

where

$$\tilde{\boldsymbol{\xi}}(\boldsymbol{L}) = [\xi_{\mathrm{x}}(\boldsymbol{L}, 1)\ \xi_{\mathrm{x}}(\boldsymbol{L}, 2) \cdots \xi_{\mathrm{x}}(\boldsymbol{L}, n)\ \xi_{\mathrm{y}}(\boldsymbol{L}, 1)\ \xi_{\mathrm{y}}(\boldsymbol{L}, 2) \cdots \xi_{\mathrm{y}}(\boldsymbol{L}, n)\ \xi_{\mathrm{z}}(\boldsymbol{L}, 1)\ \xi_{\mathrm{z}}(\boldsymbol{L}, 2) \cdots \xi_{\mathrm{z}}(\boldsymbol{L}, n)] \tag{9}$$

$$\tilde{\boldsymbol{P}}(\boldsymbol{L}) = \begin{bmatrix} \boldsymbol{X}(\boldsymbol{L},1) & \boldsymbol{X}(\boldsymbol{L},2) & \cdots & \boldsymbol{X}(\boldsymbol{L},n) & 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 & \boldsymbol{X}(\boldsymbol{L},1) & \boldsymbol{X}(\boldsymbol{L},2) & \cdots & \boldsymbol{X}(\boldsymbol{L},n) & 0 & 0 & \cdots & 0 \\ 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 & \boldsymbol{X}(\boldsymbol{L},1) & \boldsymbol{X}(\boldsymbol{L},2) & \cdots & \boldsymbol{X}(\boldsymbol{L},n) \end{bmatrix} \tag{10}$$

$$\tilde{\boldsymbol{U}} = [U_{\mathrm{xx}}\ U_{\mathrm{xy}}\ U_{\mathrm{xz}}\ U_{\mathrm{yx}}\ U_{\mathrm{yy}}\ U_{\mathrm{yz}}\ U_{\mathrm{zx}}\ U_{\mathrm{zy}}\ U_{\mathrm{zz}}] \tag{11}$$

$$\tilde{\boldsymbol{\rho}} = [\rho_{\mathrm{x}}(1)\ \rho_{\mathrm{x}}(2) \cdots \rho_{\mathrm{x}}(n)\ \rho_{\mathrm{y}}(1)\ \rho_{\mathrm{y}}(2) \cdots \rho_{\mathrm{y}}(n)\ \rho_{\mathrm{z}}(1)\ \rho_{\mathrm{z}}(2) \cdots \rho_{\mathrm{z}}(n)] \tag{12}$$

From the displacement vector ($\boldsymbol{\xi}$), the internal coordinate vector ($\boldsymbol{R}$) may be written as shown below, with the transformation matrix ($\boldsymbol{B}$)¹⁾.

$$\boldsymbol{R} = \boldsymbol{B}\boldsymbol{\xi} \tag{13}$$

For a crystal under a homogeneous deformation, unit cells are all equivalent with one another and accordingly, the internal coordinate vector $\boldsymbol{R}(\boldsymbol{L})$ of the cell ($\boldsymbol{L}$) is given as

$$\boldsymbol{R}(\boldsymbol{L}) = \sum_{\boldsymbol{\lambda}}\boldsymbol{B}(\boldsymbol{\lambda})\boldsymbol{\xi}(\boldsymbol{L}+\boldsymbol{\lambda}) \tag{14}$$

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5) K. H. Hellwedge, in Landolt-Boernstein Phys. Chem. Tables, new series, Group III-Vol. 1, Springer-Verlag, Berlin (1966), p. 1—39.

6) M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," Oxford University Press, London (1954), Chapter III.

7) A. E. H. Love, "Mathematical Theory of Elasticity," Cambridge University Press, Cambridge (1934).

where $\boldsymbol{\lambda}$ is a difference-index vector and the $\boldsymbol{B}(\boldsymbol{\lambda})$ submatrix is independent of $\boldsymbol{L}$. On substituting Eq. (8) into Eq. (14), the $\boldsymbol{R}^0$ vector is now written as a sum of the terms due to external deformation ($\boldsymbol{U}$) and internal strain vector ($\boldsymbol{\rho}$),

$$\boldsymbol{R}^0 = \boldsymbol{R}(\boldsymbol{L}) = \boldsymbol{D}_{\mathrm{U}}\boldsymbol{U} + \boldsymbol{B}_\rho\boldsymbol{\rho} \tag{15}$$

$$\boldsymbol{B}_\rho = \sum_{\boldsymbol{\lambda}}\boldsymbol{B}(\boldsymbol{\lambda}) \tag{16}$$

$$\boldsymbol{D}_{\mathrm{U}} = \sum_{\boldsymbol{\lambda}}\boldsymbol{B}(\boldsymbol{\lambda})\boldsymbol{P}(\boldsymbol{L}+\boldsymbol{\lambda}) \tag{17}$$

It may be remarked that, under a homogeneous deformation, the transformation matrix ($\boldsymbol{D}_{\mathrm{U}}$) for deformation parameters, is independent of the choice of cell ($\boldsymbol{L}$). A general method for calculating $\boldsymbol{D}_{\mathrm{U}}$ matrix elements for bond-stretching, angle-bending and torsional coordinates is described in Appendix I.

Internal displacement coordinates, $\rho_\alpha(m)$, of Eq. (15) are not all independent, since the mass-weighted linear combinations, $\sum_m M(m)\rho_\alpha(m)/\sum_m M(m)$, give overall-translation coordinates ($\alpha = x, y$, and z) of the crystal. Accordingly, after an appropriate orthogonal transformation, the columns of the $\boldsymbol{B}_\rho$ matrix associated with these three redundant coordinates may be reduced to zero. In treating elastic constants, these redundant coordinates are deleted and remaining $3n-3$ internal displacements are used. However, the generality of the treatment of elastic constants may well be retained by deleting internal displacement coordinates [$\rho_x(m)$, $\rho_y(m)$, and $\rho_z(m)$] of any single atom (m), in place of the actual "overall-translation" coordinates.

Elastic Constant Matrix

The deformation parameters (U) of Eq. (7) actually are not independent of "overall-rotation" modes of the crystal lattice. Accordingly, for deriving the elastic constant matrix ($\boldsymbol{C}$), it is necessary to introduce σ parameters as follows,

$$\begin{array}{lll} \sigma_1 = U_{xx} & \sigma_4 = U_{yz} + U_{zy} & \sigma_7 = U_{yz} - U_{zy} \\ \sigma_2 = U_{yy} & \sigma_5 = U_{zx} + U_{xz} & \sigma_8 = U_{zx} - U_{xz} \\ \sigma_3 = U_{zz} & \sigma_6 = U_{xy} + U_{yx} & \sigma_9 = U_{xy} - U_{yx} \end{array} \tag{18}$$

For a homogeneous deformation, σ_1—σ_6 are external strain parameters whereas σ_7—σ_9 are "overall-rotation" parameters for the x, y, and z axes.[7]

The energy density (ε) may be expressed in terms of σ parameters, after the reverse transformation,

$$\boldsymbol{U} = \boldsymbol{T}_\sigma\boldsymbol{\sigma} \tag{19}$$

However, since the energy density (ε) is independent of "overall-rotation" parameters σ_7—σ_9, the last three columns of the transformation matrix ($\boldsymbol{T}_\sigma$) are redundant and accordingly σ_7—σ_9 will be left out of the external strain-parameter vector ($\boldsymbol{\sigma}$),

$$\tilde{\boldsymbol{\sigma}} = [\sigma_1\ \sigma_2\ \sigma_3\ \sigma_4\ \sigma_5\ \sigma_6] \tag{20}$$

$$\boldsymbol{T}_\sigma = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \tag{21}$$

On substituting Eq. (19) into Eq. (15), the $\boldsymbol{R}^0$ vector is rewitten as,

$$\boldsymbol{R}^0 = \boldsymbol{D}_\sigma\boldsymbol{\sigma} + \boldsymbol{B}_\rho\boldsymbol{\rho} \tag{22}$$

where

$$\boldsymbol{D}_\sigma = \boldsymbol{D}_{\mathrm{U}}\boldsymbol{T}_\sigma = [\sum_{\boldsymbol{\lambda}}\boldsymbol{B}(\boldsymbol{\lambda})\boldsymbol{P}(\boldsymbol{L}+\boldsymbol{\lambda})]\boldsymbol{T}_\sigma \tag{23}$$

From Eqs. (6) and (22), the energy density(ε) is derived as,

$$\varepsilon = \frac{1}{2}[\tilde{\boldsymbol{\sigma}}\tilde{\boldsymbol{D}}_\sigma + \tilde{\boldsymbol{\rho}}\boldsymbol{B}_\rho]\boldsymbol{F}_{\mathrm{R}}{}^0[\boldsymbol{D}_\sigma\boldsymbol{\sigma} + \boldsymbol{B}_\rho\boldsymbol{\rho}]/v \tag{24}$$

However, the internal strain vector ($\boldsymbol{\rho}$) is related to the external strain parameters (σ),

$$\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho\boldsymbol{\rho} + \tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{D}_\sigma\boldsymbol{\sigma} = 0 \tag{25}$$

so that the energy density (ε) is minimized with respect to internal strains ($\boldsymbol{\rho}$). Accordingly, the $\boldsymbol{\rho}$ vector given in Eq. (25) is put into Eq. (22) and the internal symmetry coordinates are now expressed in terms of the external strain parameters,

$$\boldsymbol{R}^0 = \boldsymbol{H}_\sigma\boldsymbol{\sigma} \tag{26}$$

where

$$\boldsymbol{H}_\sigma = \{\boldsymbol{E} - \boldsymbol{B}_\rho[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\}\boldsymbol{D}_\sigma \tag{27}$$

The energy density is now derived as

$$\varepsilon = \frac{1}{2}\tilde{\boldsymbol{\sigma}}\tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{H}_\sigma\boldsymbol{\sigma}/v = \frac{1}{2}\tilde{\boldsymbol{\sigma}}\boldsymbol{C}\boldsymbol{\sigma} \tag{28}$$

and the elastic constant matrix is thus derived as

$$\boldsymbol{C} = \tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{H}_\sigma/v \tag{29}$$

On substituting Eq. (27) into Eq. (29), the elastic constant matrix is also written as,

$$\boldsymbol{C} = \{\tilde{\boldsymbol{D}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{D}_\sigma - \tilde{\boldsymbol{D}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{D}_\sigma\}/v \tag{30}$$

The elastic stress vector ($\boldsymbol{S}_\sigma$) is now given as

$$\boldsymbol{S}_\sigma = \boldsymbol{C}_\sigma \tag{31}$$

and, therefore, when an elastic stress is applied to a crystalline lattice, the internal coordinate vector $\boldsymbol{R}^0$ is derived as

$$\boldsymbol{R}^0 = \boldsymbol{H}_\sigma\boldsymbol{\sigma} = \boldsymbol{H}_\sigma\boldsymbol{C}^{-1}\boldsymbol{S}_\sigma \tag{32}$$

Partial Derivatives of Elastic Constants

The potential energy submatrices, $\boldsymbol{F}_{\mathrm{R}}(\boldsymbol{\lambda})$, have been shown to be useful for calculating elastic constants of molecular crystals. Accordingly, experimental elastic constants as well as vibrational frequencies may be referred to in adjusting force fields or force constants of crystals. For least-square adjustments,[8] however, it is necessary to formulate partial derivatives of elastic constants with respect to force constants.

The potential-energy matrix ($\boldsymbol{F}_{\mathrm{R}}{}^{0}$) may be expressed as a sum of matrices associated with force constants, $K(h)$,

$$\boldsymbol{F}_{\mathrm{R}}{}^{0} = \sum_{h}\boldsymbol{A}(h)K(h) \tag{33}$$

and accordingly

$$\Delta\boldsymbol{F}_{\mathrm{R}}{}^{0} = \sum_{h}\boldsymbol{A}(h)\Delta K(h) \tag{34}$$

Then, as proved in Appendix II, the derivatives of elastic constants with respect to force constants are expressed as,

$$\partial C_{ij}/\partial K(h) = [\tilde{\boldsymbol{H}}_{\sigma}\boldsymbol{A}(h)\boldsymbol{H}_{\sigma}]_{ij}/v \tag{35}$$

It may be seen that an elastic constant (C_{ij}) is expressed as a linear combination of partial derivatives $\partial C_{ij}/\partial K(h)$. Thus, from Eqs. (29), (33), and (35),

$$\begin{aligned} C_{ij} &= \{\tilde{\boldsymbol{H}}_{\sigma}\boldsymbol{F}_{\mathrm{R}}{}^{0}\boldsymbol{H}_{\sigma}/v\}_{ij} \\ &= \sum_{h}\{[\tilde{\boldsymbol{H}}_{\sigma}\boldsymbol{A}(h)\boldsymbol{H}_{\sigma}]_{ij}/v\}K(h) \\ &= \sum_{h}\{\partial C_{ij}/\partial K(h)\}K(h) \end{aligned} \tag{36}$$

This equation may be rewritten as

$$\sum_{h}[\partial C_{ij}/\partial K(h)]K(h)/C_{ij} = 1 \tag{37}$$

so that each term represents the fractional contribution of the *h*th potential term to the elastic constant (C_{ij}).

The equations for elastic constants, Eqs. (26), (28), (29), (35), (36), and (37), correspond closely with the equations for normal vibrations,[1,9]

$$\boldsymbol{R} = \boldsymbol{L}\boldsymbol{Q} \tag{38}$$

$$V = \frac{1}{2}\tilde{\boldsymbol{Q}}\boldsymbol{\Lambda}\boldsymbol{Q} \tag{39}$$

$$\boldsymbol{\Lambda} = \tilde{\boldsymbol{L}}\boldsymbol{F}\boldsymbol{L} \tag{40}$$

$$\partial\lambda(a)/\partial K(h) = [\tilde{\boldsymbol{L}}\boldsymbol{A}(h)\boldsymbol{L}]_{aa} \tag{41}$$

$$\lambda(a) = \sum_{h}[\partial\lambda(a)/\partial K(h)]K(h) \tag{42}$$

$$\sum_{h}[\partial\lambda(a)/\partial K(h)]K(h)/\lambda(a) = 1 \tag{43}$$

where $\boldsymbol{L}$ is the eigenvector matrix, $\boldsymbol{Q}$ is normal-coordinate vector, $\boldsymbol{\Lambda}$ is diagonal frequency-parameter matrix, and $\lambda(a)$ is the *a*th frequency-parameter (squared angular frequency).

Partial derivatives of elastic constants [Eq. (35)] and frequency parameters [Eq. (41)] may now be used for least-square adjustments[8] of force constants of molecular crystals with reference to experimental elastic constants and vibrational frequencies.

Symmetry Treatments

Treatments of elastic constants may be simplified by the use of factor-group symmetry, just as are treatment of normal vibrations.[1] By an appropriate orthogonal transformation, new symmetry-coordinate vectors are set up,

$$\boldsymbol{R}_{\mathrm{s}}{}^{0} = \boldsymbol{T}_{\mathrm{R}}\boldsymbol{R}^{0} \tag{44}$$

$$\boldsymbol{\rho}_{\mathrm{s}} = \boldsymbol{T}_{\rho}\boldsymbol{\rho} \tag{45}$$

and the potential-energy matrix ($\boldsymbol{F}_{\mathrm{R}}{}^{0}$) is transformed accordingly,

$$\boldsymbol{F}_{\mathrm{Rs}}{}^{0} = \boldsymbol{T}_{\mathrm{R}}\boldsymbol{F}_{\mathrm{R}}{}^{0}\tilde{\boldsymbol{T}}_{\mathrm{R}} \tag{46}$$

$$\boldsymbol{A}_{\mathrm{s}}(h) = \boldsymbol{T}_{\mathrm{R}}\boldsymbol{A}(h)\tilde{\boldsymbol{T}}_{\mathrm{R}} \tag{47}$$

From Eqs. (22), (44), and (45),

$$\boldsymbol{R}_{\mathrm{s}}{}^{0} = \boldsymbol{D}_{\mathrm{s}\sigma}\boldsymbol{\sigma} + \boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{\rho}_{\mathrm{s}} \tag{48}$$

where

$$\boldsymbol{D}_{\mathrm{s}\sigma} = \boldsymbol{T}_{\mathrm{R}}\boldsymbol{D}_{\sigma} \tag{49}$$

$$\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}} = \boldsymbol{T}_{\mathrm{R}}\boldsymbol{B}_{\rho}\tilde{\boldsymbol{T}}_{\rho} \tag{50}$$

After defining

$$\begin{aligned} \boldsymbol{H}_{\mathrm{s}\sigma} &= \boldsymbol{T}_{\mathrm{R}}\boldsymbol{H}_{\sigma} \\ &= [\boldsymbol{E}-\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}[\tilde{\boldsymbol{B}}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}]^{-1}\tilde{\boldsymbol{B}}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}]\boldsymbol{D}_{\mathrm{s}\sigma} \end{aligned} \tag{51}$$

the internal symmetry coordinate vector ($\boldsymbol{R}_{\mathrm{S}}{}^{0}$) is expressed as,

$$\boldsymbol{R}_{\mathrm{s}}{}^{0} = \boldsymbol{H}_{\mathrm{s}\sigma}\boldsymbol{\sigma} \tag{52}$$

$$= \boldsymbol{H}_{\mathrm{s}\sigma}\boldsymbol{C}^{-1}\boldsymbol{S}_{\sigma} \tag{53}$$

and the elastic constant matrix ($\boldsymbol{C}$) is derived as

$$\boldsymbol{C} = \{\tilde{\boldsymbol{H}}_{\mathrm{s}\sigma}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{H}_{\mathrm{s}\sigma}\}/v \tag{54}$$

$$\begin{aligned} &= \{\tilde{\boldsymbol{D}}_{\mathrm{s}\sigma}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{D}_{\mathrm{s}\sigma} \\ &\quad - \tilde{\boldsymbol{D}}_{\mathrm{s}\sigma}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}[\tilde{\boldsymbol{B}}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}]^{-1}\tilde{\boldsymbol{B}}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{F}_{\mathrm{Rs}}{}^{0}\boldsymbol{D}_{\mathrm{s}\sigma}\}/v \end{aligned} \tag{55}$$

Partial derivatives of elastic constants with respect to a force constant are given as,

$$\partial C_{ij}/\partial K(h) = [\tilde{\boldsymbol{H}}_{\mathrm{s}\sigma}\boldsymbol{A}_{\mathrm{s}}(h)\boldsymbol{H}_{\mathrm{s}\sigma}]_{ij}/v \tag{56}$$

The elastic constants of a symmetry species may be treated by the use only of relevant strain parameters (σ). For the example of orthorhombic crystals with the factor-group $\mathrm{D}_{2\mathrm{h}}$, strain parameters σ_1, σ_2, and σ_3 belong to the $\mathrm{a_g}$ species, and σ_4, σ_5, and σ_6 belong to the $\mathrm{b_{1g}}$, $\mathrm{b_{2g}}$, and $\mathrm{b_{3g}}$ species, respectively. $\boldsymbol{F}_{\mathrm{Rs}}{}^{0}$, $\boldsymbol{A}_{\mathrm{s}}(h)$ and $\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}$ matrices are commonly used for treating normal vibrations and elastic constants belonging to the same symmetry species.

Finally it may be remarked that, before inverting the matrix of $[\tilde{\boldsymbol{B}}_{\mathrm{s}\rho\mathrm{s}}\boldsymbol{F}_{\mathrm{R}}{}^{0}\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}]$ in Eqs. (51) and (55), the columns of the $\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}$ matrices associated with "overall-translation" displacements, if any, need be deleted. Fortunately, however, for factor groups having the inversion operation, elastic strains belong to *gerade* species whereas "overall-translation" displacements belong to *ungerade* species. Accordingly, the $\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}$ matrices associated with "overall-translation" displacements are separated, because of the inversion symmetry, from the $\boldsymbol{B}_{\mathrm{s}\rho\mathrm{s}}$ matrices as used for elastic properties.

Application to Polyethylene Crystal

The crystal structure of the orthorhombic polyethylene (Pnam-$\mathrm{D}_{2\mathrm{h}}^{16}$) was analysed by Bunn.[10] Two molecular chains pass through a unit cell along the c axis and there are four methylene groups per unit cell, with the lattice constants of $a_0=7.40$, $b_0=4.93$, and $c_0=2.54$ Å. The position vectors (Å) of four carbon atoms are

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[8] D. E. Mann, T. Shimanouchi, J. H. Meal, and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957).

[9] T. Miyazawa, *Nippon Kagaku Zasshi*, **76**, 1132 (1955).

[10] C. W. Bunn, *Trans. Faraday Soc.*, **35**, 482 (1939).

$$\boldsymbol{X}(1) = \begin{bmatrix} -0.281 \\ -0.320 \\ -0.635 \end{bmatrix} \qquad \boldsymbol{X}(2) = \begin{bmatrix} 0.281 \\ 0.320 \\ 0.635 \end{bmatrix}$$

$$\boldsymbol{X}(3) = \begin{bmatrix} 3.419 \\ 2.785 \\ -0.635 \end{bmatrix} \qquad \boldsymbol{X}(4) = \begin{bmatrix} 3.981 \\ 2.145 \\ 0.635 \end{bmatrix}$$

In the previous study,[11] the frequency distribution and specific heat of the orthorhombic polyethylene crystal were treated with skeletal approximation; methylene groups were regarded as united atoms. The Urey-Bradley field[12] was used as the intramolecular force field, with the bond-stretching terms $[K_r(\Delta r)^2/2]$, angle-bending terms $[K_\phi(\Delta\phi)^2/2]$, repulsion terms $[K_q(\Delta q)^2/2]$ and internal-rotation terms $[K_t(\Delta t)^2/2]$ (see Fig. 1 for intramolecular coordinates). The intermolecular force field was expressed as a sum of three types of stretching terms, $P_1(\Delta p_1)^2/2$, $P_2(\Delta p_2)^2/2$, and $P_3(\Delta p_3)^2/2$, corresponding to intermethylene contacts of $p_1=4.12$, $p_2=4.18$, and $p_3=4.57$ Å, respectively. The intermethylene-stretching coordinates per unit cell are shown in Figs. 1 and 2 and are also listed below,

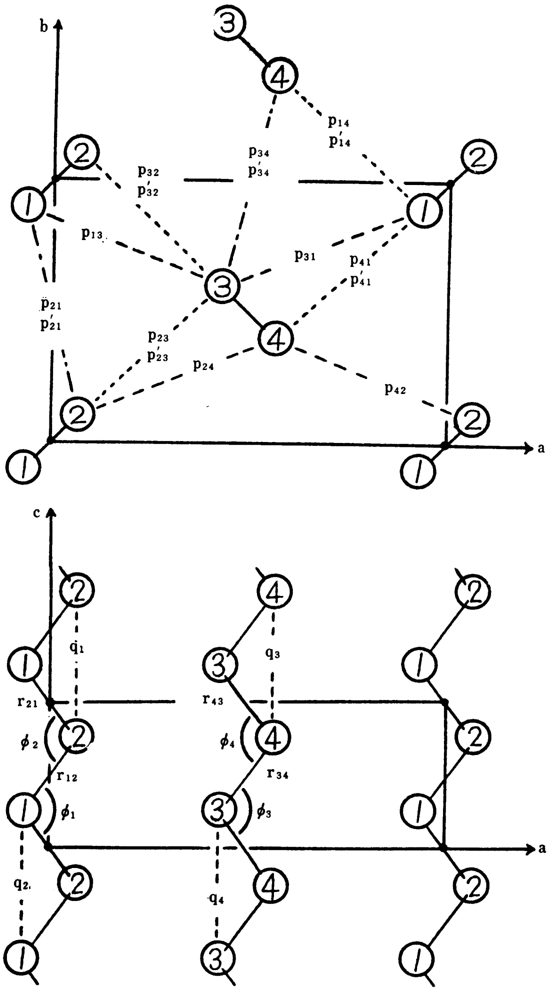

Fig. 1. Internal coordinates (*ab* and *ac* planes).

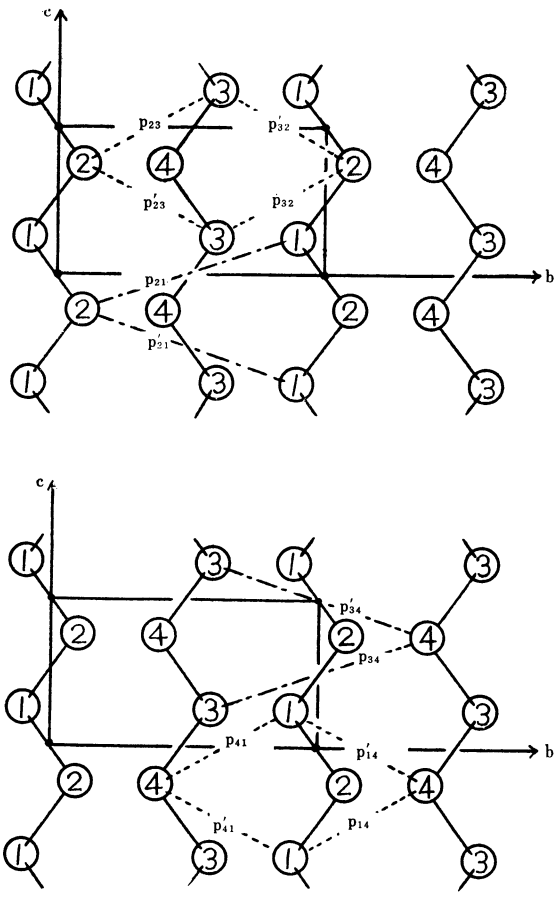

Fig. 2. Internal coordinates (*bc* plane).

Δp_1: Δp_{24}, Δp_{31}, Δp_{42}, and Δp_{13}

Δp_2: Δp_{23}, Δp_{41}, $\Delta p'_{23}$, $\Delta p'_{41}$, Δp_{32}, Δp_{14}, $\Delta p'_{32}$, and $\Delta p'_{14}$

Δp_3: Δp_{21}, $\Delta p'_{21}$, Δp_{34}, and $\Delta p'_{34}$

The intramolecular and intermolecular force constants were adjusted[11] as $K_r=4.0$ md/Å, $K_\phi=0.59$ md Å/rad², $K_q=0.35$ md/Å, $K_t=0.047$ md Å/rad², $P_1=P_2=0.025$, and $P_3=0.003$ md/Å. These force constants were used in the present study of the elastic constants of polyethylene.

The internal coordinate vector ($\boldsymbol{R}$) of the crystal lattice was transformed, with translational operations, into the $\boldsymbol{R}^0$ vector with twenty-eight components,

$$\tilde{\boldsymbol{R}}^0 = [\Delta r_{12}{}^0, \Delta r_{21}{}^0, \Delta r_{43}{}^0, \Delta r_{34}{}^0, \Delta\phi_1{}^0, \Delta\phi_2{}^0, \Delta\phi_3{}^0, \Delta\phi_4{}^0, \Delta q_1{}^0, \Delta q_2{}^0, \Delta q_3{}^0, \Delta q_4{}^0, \Delta p_{24}{}^0, \Delta p_{31}{}^0, \Delta p_{42}{}^0, \Delta p_{13}{}^0, \Delta p_{23}{}^0, \Delta p_{41}{}^0, \Delta p'_{23}{}^0, \Delta p'_{41}{}^0, \Delta p_{32}{}^0, \Delta p_{14}{}^0, \Delta p'_{32}{}^0, \Delta p'_{14}{}^0, \Delta p_{21}{}^0, \Delta p'_{21}{}^0, \Delta p_{34}{}^0, \Delta p'_{34}{}^0]$$

Internal-rotation coordinates (Δt) were deleted because they are antisymmetric with respect to the inversion symmetry and are redundant in treating elastic constants which belong to *gerade* species.

According to the factor-group symmetry of D_{2h}, the $\boldsymbol{R}^0$ vector was then transformed into symmetry-coordinate vectors ($\boldsymbol{R}_s{}^0$) for the symmetry species of elastic constants;

$$\tilde{\boldsymbol{R}}_s{}^0(\mathrm{a_g}) = [R_s{}^0(1), R_s{}^0(2), R_s{}^0(3), R_s{}^0(4), R_s{}^0(5), R_s{}^0(6)],$$
$$\tilde{\boldsymbol{R}}_s{}^0(\mathrm{b_{1g}}) = [R_s{}^0(7), R_s{}^0(8), R_s{}^0(9)],$$
$$\tilde{\boldsymbol{R}}_s{}^0(\mathrm{b_{2g}}) = [R_s{}^0(10), R_s{}^0(11), R_s{}^0(12)],$$
$$\tilde{\boldsymbol{R}}_s{}^0(\mathrm{b_{3g}}) = [R_s{}^0(13), R_s{}^0(14), R_s{}^0(15), R_s{}^0(16), R_s{}^0(17)].$$

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[11] T. Kitagawa and T. Miyazawa, This Bulletin, **43**, 372 (1970).

[12] T. Shimanouchi, *Pure Appl. Chem.*, **7**, 261 (1962).

The transformation matrix elements are shown below, for each of bond-stretching (Δr), angle-bending ($\Delta\phi$), repulsion (Δq), and intermethylene-stretching coordinates (Δp_1, Δp_2, and Δp_3).

$$\begin{array}{c|cccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta r) & R^0(1) & R^0(2) & R^0(3) & R^0(4) \\
\hline
R_s{}^0(1) & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
R_s{}^0(7) & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\
R_s{}^0(10) & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\
R_s{}^0(13) & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2}
\end{array}$$

$$\begin{array}{c|cccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta\phi) & R^0(5) & R^0(6) & R^0(7) & R^0(8) \\
\hline
R_s{}^0(2) & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
R_s{}^0(14) & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2}
\end{array}$$

$$\begin{array}{c|cccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta q) & R^0(9) & R^0(10) & R^0(11) & R^0(12) \\
\hline
R_s{}^0(3) & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2}
\end{array}$$

$$\begin{array}{c|cccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta p_1) & R^0(13) & R^0(14) & R^0(15) & R^0(16) \\
\hline
R_s{}^0(4) & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
R_s{}^0(15) & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2}
\end{array}$$

$$\begin{array}{c|cccccccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta p_2) & R^0(17) & R^0(18) & R^0(19) & R^0(20) & R^0(21) & R^0(22) & R^0(23) & R^0(24) \\
\hline
R_s{}^0(5) & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} \\
R_s{}^0(8) & 8^{-1/2} & 8^{-1/2} & -8^{-1/2} & -8^{-1/2} & 8^{-1/2} & 8^{-1/2} & -8^{-1/2} & -8^{-1/2} \\
R_s{}^0(11) & 8^{-1/2} & 8^{-1/2} & -8^{-1/2} & -8^{-1/2} & -8^{-1/2} & -8^{-1/2} & 8^{-1/2} & 8^{-1/2} \\
R_s{}^0(16) & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & 8^{-1/2} & -8^{-1/2} & -8^{-1/2} & -8^{-1/2} & -8^{-1/2}
\end{array}$$

$$\begin{array}{c|cccc}
\boldsymbol{T}_{\mathrm{R}}(\Delta p_3) & R^0(25) & R^0(26) & R^0(27) & R^0(28) \\
\hline
R_s{}^0(6) & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\
R_s{}^0(9) & \frac{1}{2} & -\frac{1}{2} & \frac{1}{2} & -\frac{1}{2} \\
R_s{}^0(12) & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & \frac{1}{2} \\
R_s{}^0(17) & \frac{1}{2} & \frac{1}{2} & -\frac{1}{2} & -\frac{1}{2}
\end{array}$$

The potential-energy matrix ($\boldsymbol{F}$) was transformed accordingly as,

$$\boldsymbol{F}_{\mathrm{Rs}^0}(\mathrm{a_g}) = \begin{pmatrix} K_r & 0 & 0 & 0 & 0 & 0 \\ 0 & K_\phi & 0 & 0 & 0 & 0 \\ 0 & 0 & K_q & 0 & 0 & 0 \\ 0 & 0 & 0 & P_1 & 0 & 0 \\ 0 & 0 & 0 & 0 & P_2 & 0 \\ 0 & 0 & 0 & 0 & 0 & P_3 \end{pmatrix} \tag{57}$$

$$\boldsymbol{F}_{\mathrm{Rs}^0}(\mathrm{b_{1g}}) = \boldsymbol{F}_{\mathrm{Rs}^0}(\mathrm{b_{2g}}) = \begin{pmatrix} K_r & 0 & 0 \\ 0 & P_2 & 0 \\ 0 & 0 & P_3 \end{pmatrix} \tag{58}$$

$$\boldsymbol{F}_{\mathrm{Rs}^0}(\mathrm{b_{3g}}) = \begin{pmatrix} K_r & 0 & 0 & 0 & 0 \\ 0 & K_\phi & 0 & 0 & 0 \\ 0 & 0 & P_1 & 0 & 0 \\ 0 & 0 & 0 & P_2 & 0 \\ 0 & 0 & 0 & 0 & P_3 \end{pmatrix} \tag{59}$$

The internal strain vector $\boldsymbol{\rho}$ [Eq. (12)] of carbon atoms was also transformed into internal symmetry-strain vectors ($\boldsymbol{\rho}_s$) for the symmetry species of elastic constants,

$$\mathrm{a_g}\ \text{species}:\ \rho_s(1) = [\rho_x(1)-\rho_x(2)+\rho_x(3)-\rho_x(4)]/2$$

$$\rho_s(2) = [\rho_y(1)-\rho_y(2)-\rho_y(3)+\rho_y(4)]/2 \tag{60}$$

$$\mathrm{b_{1g}}\ \text{species}:\ \rho_s(3) = [\rho_z(1)-\rho_z(2)-\rho_z(3)+\rho_z(4)]/2 \tag{61}$$

$$\mathrm{b_{2g}}\ \text{species}:\ \rho_s(4) = [\rho_z(1)-\rho_z(2)+\rho_z(3)-\rho_z(4)]/2 \tag{62}$$

$$\mathrm{b_{3g}}\ \text{species}:\ \rho_s(5) = [\rho_x(1)-\rho_x(2)-\rho_x(3)+\rho_x(4)]/2 \tag{63}$$

$$\rho_s(6) = [\rho_y(1)-\rho_y(2)+\rho_y(3)-\rho_y(4)]/2 \tag{64}$$

The $\boldsymbol{B}_{s\rho s}$, $\boldsymbol{D}_{s\sigma}$, and $\boldsymbol{H}_{s\sigma}$ matrices were calculated, as shown in Tables 1—4, from $\boldsymbol{B}(\boldsymbol{\lambda})$ and $\boldsymbol{P}(\boldsymbol{L}+\boldsymbol{\lambda})$ submatrices, with Eqs. (16), (21), (23), (49), (50), and (51). Finally, with Eq. (54), the elastic constants were calculated as,

$\mathrm{a_g}$ species : $C_{11}=0.022_0$, $C_{22}=0.007_5$, $C_{33}=0.243$

$C_{23}=0.002_6$, $C_{31}=0.003_8$, $C_{12}=0.009_8$ md/Å^2

$\mathrm{b_{1g}}$ species: $C_{44}=0.001_5$ md/Å^2

$\mathrm{b_{2g}}$ species: $C_{55}=0.002_7$ md/Å^2

$\mathrm{b_{3g}}$ species: $C_{66}=0.012_6$ md/Å^2

Young's moduli of orthorhombic polyethylene were calculated as

$$E_a = 1/(C^{-1})_{11} = 0.009$$

$$E_b = 1/(C^{-1})_{22} = 0.003$$

$$E_c = 1/(C^{-1})_{33} = 0.243\ \text{md/Å}^2$$

In comparisn, Young's moduli measured at room temperature[13] are $E_a=0.005$, $E_b=0.004$, and $E_c=0.235$ md/Å^2. It may be remarked that the Young's modulus along the c axis (E_c) is due to the intramolecular force field and is much higher than the values of E_a or E_b which are due to intermolecular contacts. Finally, partial derivatives of elastic constants with respect to force constants were calculated with Eqs. (33), (47), and (56). The fractional distribution of potential terms is shown in Table 5.

The elastic constant along the c axis (C_{33}) is due to the intramolecular potential terms, K_r(22%), K_ϕ(38%), and K_q(40%), and the contributions of intermethylene terms (P_1, P_2, and P_3) are negligible. The elastic

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[13] I. Sakurada, T. Ito, and K. Nakamae, *J. Polym. Sci.*, Part C, **15**, 75 (1966); I. Sakurada, K. Kaji, K. Nakamae, and E. Shikata, Symposium on Macromolecules, 22F09, Matsuyama (1968).

TABLE 1. $\boldsymbol{D}_{s\sigma}$, $\boldsymbol{B}_{s\rho s}$, $\boldsymbol{H}_{s\sigma}$, AND $\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ MATRICES OF THE a_g SPECIES

		$\boldsymbol{D}_{s\sigma}$ (Å)			$\boldsymbol{B}_{s\rho_s}$	
		σ_1	σ_2	σ_3	$\rho_s(1)$	$\rho_s(2)$
$R_s^0(1)$	$[r]$	0.414	0.537	2.109	−0.735	−0.838
$R_s^0(2)$[a]	$[\phi]$	−0.805	−1.046	1.851	1.432	1.632
$R_s^0(3)$	$[q]$	0	0	5.080	0	0
$R_s^0(4)$	$[p_1]$	6.637	1.613	0	0	0.884
$R_s^0(5)$	$[p_2]$	6.650	4.104	1.089	2.119	0
$R_s^0(6)$	$[p_3]$	0.140	8.161	0.716	−0.249	1.902

a) $\boldsymbol{D}_{s\sigma}$ elements in rad and $\boldsymbol{B}_{s\rho s}$ elements in rad/Å unit.

		$\boldsymbol{H}_{s\sigma}$ (Å)			$\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ (Å^3/md)		
		σ_1	σ_2	σ_3	$S_{\sigma 1}$	$S_{\sigma 2}$	$S_{\sigma 3}$
$R_s^0(1)$	$[r]$	0.04	0.02	1.11	0.01	0.01	0.05
$R_s^0(2)$[a]	$[\phi]$	−0.08	−0.05	3.80	−0.03	−0.09	0.17
$R_s^0(3)$	$[q]$	0	0	5.08	−0.01	−0.06	0.23
$R_s^0(4)$	$[p_1]$	8.21	2.84	1.17	5.32	−2.89	−0.00
$R_s^0(5)$	$[p_2]$	3.43	2.24	0.79	0.59	2.44	0.00
$R_s^0(6)$	$[p_3]$	3.91	11.02	3.27	−12.48	32.22	−0.00

a) $\boldsymbol{H}_{s\sigma}$ elements in rad and $\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ elements in Å^{2}rad/md unit.

TABLE 2. $\boldsymbol{D}_{s\sigma}$, $\boldsymbol{B}_{s\rho s}$, $\boldsymbol{H}_{s\sigma}$, AND $\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ MATRICES[a] OF THE b_{1g} SPECIES

		$\boldsymbol{D}_{s\sigma}$	$\boldsymbol{B}_{s\rho s}$	$\boldsymbol{H}_{s\sigma}$	$\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$
		σ_4	$\rho_s(3)$	σ_4	$S_{\sigma 4}$
$R_s^0(7)$	$[r]$	1.064	−1.660	0.00	0.01
$R_s^0(8)$	$[p_2]$	2.115	0	2.11	15.67
$R_s^0(9)$	$[p_3]$	2.416	0.563	2.78	20.58

a) Units are given in Table 1.

TABLE 3. $\boldsymbol{D}_{s\sigma}$, $\boldsymbol{B}_{s\rho s}$, $\boldsymbol{H}_{s\sigma}$, AND $\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ MATRICES[a] OF THE b_{2g} SPECIES

		$\boldsymbol{D}_{s\sigma}$	$\boldsymbol{B}_{s\rho s}$	$\boldsymbol{H}_{s\sigma}$	$\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$
		σ_5	$\rho_s(4)$	σ_5	$S_{\sigma 5}$
$R_s^0(10)$	$[r]$	0.934	−1.660	0.01	0.04
$R_s^0(11)$	$[p_2]$	2.692	0.858	3.17	12.60
$R_s^0(12)$	$[p_3]$	−0.317	0.563	−0.00	−0.01

a) Units are given in Table 1.

TABLE 4. $\boldsymbol{D}_{s\sigma}$, $\boldsymbol{B}_{s\rho s}$, $\boldsymbol{H}_{s\sigma}$, AND $\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$ MATRICES[a] OF THE b_{3g} SPECIES

		$\boldsymbol{D}_{s\sigma}$	$\boldsymbol{B}_{s\rho_s}$		$\boldsymbol{H}_{s\sigma}$	$\boldsymbol{H}_{s\sigma}\boldsymbol{C}^{-1}$
		σ_6	$\rho_s(5)$	$\rho_s(6)$	σ_6	$S_{\sigma 6}$
$R_s^0(13)$	$[r]$	0.471	−0.735	−0.838	0.04	0.04
$R_s^0(14)$[b]	$[\phi]$	−0.918	1.432	1.632	−0.08	−0.07
$R_s^0(15)$	$[p_1]$	3.272	1.794	0	4.20	3.61
$R_s^0(16)$	$[p_2]$	5.224	0	1.665	5.32	4.58
$R_s^0(17)$	$[p_3]$	−1.070	−0.249	1.903	−1.08	−0.93

a) Units are given in Table 1.
b) See a) of Table 1.

TABLE 5. CONTRIBUTION (%) OF POTENTIAL TERMS

	K_r	K_ϕ	K_q	P_1	P_2	P_3
C_{11}	0	0	—	83	14	2
C_{22}	0	0	—	29	18	52
C_{33}	22	38	40	0	0	0
C_{23}	45	−44	—	35	18	46
C_{31}	50	−49	—	69	19	10
C_{12}	0	0	—	64	21	14
C_{44}	0	—	—	—	83	17
C_{55}	0	—	—	—	100	0
C_{66}	0	0	—	38	61	0

constant along the b axis (C_{22}) is largely due to the P_3 contacts (52%) which are nearly parallel to the b axis (see Figs. 1 and 2). The elastic constant along the a axis (C_{11}) is predominantly due to the P_1 contacts (83%) which are nearly parallel to the a axis (see Fig. 1). On the other hand, P_2 contacts are nearly parallel to body-diagonals of unit cells and, in fact, make greatest contributions to the elastic constants of C_{44}, C_{55}, and C_{66}.

Conclusion

In a previous paper by Walmsley,[14] a method for treating elastic constants of molecular crystals is presented, where molecules are regarded as rigid bodies and the potential energy is expressed as a sum of terms each due to the interaction of a different pair of molecules. However, a general method worked out in the present study for treating elastic constants is applicable to general force fields. For molecular crystals, molecules need not be regarded as rigid bodies and internal strains within molecules may also be taken into account.

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[14] S. H. Walmsley, *J. Chem. Phys.*, **48**, 1438 (1968).

The present equations for elastic constants are written in matrix form and are readily programed for electronic computation. Factor-group symmetry operations may be applied in refined treatments of elastic properties. Also, elastic constants and normal vibrations may be treated together, and derivatives for elastic constants and normal vibration frequencies may be used together for least-square adjustments of force constants with reference to experimental elastic constants and vibrational frequencies.

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Appendix I Transformation Matrix ($\boldsymbol{D}_{\mathrm{U}}$)

For the elastic constants of molecular crystals, it is necessary to derive $\boldsymbol{D}_{\mathrm{U}}$ matrix elements [Eq. (17)] associated with bond-stretching, angle-bending, and torsional coordinates. Explicit equations for each of these coordinates may be derived by the use of relevant $\boldsymbol{s}_i$ vectors[1] of the atoms (i) involved,

$$\boldsymbol{s}_i = [B_{xi}\ B_{yi}\ B_{zi}] \tag{A1}$$

After defining the position vector $\boldsymbol{X}(i)$ of the ith atom,

$$\boldsymbol{X}(i) = [X(i)\ Y(i)\ Z(i)] \tag{A2}$$

the row vector $\boldsymbol{D}_{\mathrm{U}}$ for an internal coordinate may be derived from Eqs. (10) and (17),

$$\begin{aligned}\boldsymbol{D}_{\mathrm{U}} &= \sum_i [B_{xi}X(i)\ B_{xi}Y(i)\ B_{xi}Z(i)\ B_{yi}X(i)\ B_{yi}Y(i)\\ &\qquad B_{yi}Z(i)\ B_{zi}X(i)\ B_{zi}Y(i)\ B_{zi}Z(i)]\\ &= \sum_i [\boldsymbol{s}_i \times \boldsymbol{X}(i)]\end{aligned} \tag{A3}$$

where × denotes a direct product.

For the stretching coordinate (Δr_{ij}) of the bond i—j, the $\boldsymbol{s}$ vectors are expressed by the unit vector from the atom j toward i,

$$\begin{aligned}\boldsymbol{s}_i &= \boldsymbol{e}_{ji}\\ \boldsymbol{s}_j &= -\boldsymbol{e}_{ji}\end{aligned} \tag{A4}$$

Accordingly, the $\boldsymbol{D}_{\mathrm{U}}$ vector is derived as

$$\boldsymbol{D}_{\mathrm{U}}(\Delta r_{ij}) = \boldsymbol{e}_{ji} \times \boldsymbol{X}(i) - \boldsymbol{e}_{ji} \times \boldsymbol{X}(j) = \boldsymbol{e}_{ji} \times \boldsymbol{r}_{ji} \tag{A5}$$

where $\boldsymbol{r}_{ji}$ is the vector from the atom j to i,

$$\boldsymbol{r}_{ji} = \boldsymbol{X}(i) - \boldsymbol{X}(j) \tag{A6}$$

For the bending coordinate ($\Delta\phi_{ijk}$) of the bond angle i–j–k, the $\boldsymbol{s}$ vectors may be expressed as,

$$\begin{aligned}\boldsymbol{s}_i &= \boldsymbol{p}_{ji}/r_{ji}\\ \boldsymbol{s}_j &= -\boldsymbol{s}_i - \boldsymbol{s}_k\\ \boldsymbol{s}_k &= \boldsymbol{p}_{jk}/r_{jk}\end{aligned} \tag{A7}$$

where the unit vectors $\boldsymbol{p}_{ji}$ and $\boldsymbol{p}_{jk}$ are perpendicular to $\boldsymbol{e}_{ji}$ and $\boldsymbol{e}_{jk}$, respectively, and point in the positive bending direction. Accordingly, the $\boldsymbol{D}_{\mathrm{U}}$ vector is derived as

$$\begin{aligned}\boldsymbol{D}_{\mathrm{U}}(\Delta\phi_{ijk}) &= \boldsymbol{s}_i \times \boldsymbol{r}_{ji} + \boldsymbol{s}_k \times \boldsymbol{r}_{jk}\\ &= \boldsymbol{p}_{ji} \times \boldsymbol{e}_{ji} + \boldsymbol{p}_{jk} \times \boldsymbol{e}_{jk}\end{aligned} \tag{A8}$$

For the torsional coordinate ($\Delta\tau_{ijkl}$) of the dihedral angle i–j–k–l, the $\boldsymbol{s}$ vectors may be expressed as

$$\begin{aligned}\boldsymbol{s}_i &= \boldsymbol{p}_{kji}/r_{ji}\sin\phi_{kji}\\ \boldsymbol{s}_j &= -\boldsymbol{s}_i + \boldsymbol{p}_{kji}\cos\phi_{kji}/r_{kj}\sin\phi_{kji} - \boldsymbol{p}_{jkl}\cos\phi_{jkl}/r_{jk}\sin\phi_{jkl}\\ \boldsymbol{s}_k &= -\boldsymbol{s}_l + \boldsymbol{p}_{jkl}\cos\phi_{jkl}/r_{jk}\sin\phi_{jkl} - \boldsymbol{p}_{kji}\cos\phi_{kji}/r_{kj}\sin\phi_{kji}\\ \boldsymbol{s}_l\,\boldsymbol{p} &= {}_{jkl}/r_{kl}\sin\phi_{jkl}\end{aligned} \tag{A9}$$

where the unit vectors $\boldsymbol{p}_{kji}$ and $\boldsymbol{p}_{jkl}$ are perpendicular to the planes of bond angles ϕ_{kji} and ϕ_{jkl}, respectively, and point in the positive torsional direction. Accordingly, the $\boldsymbol{D}_{\mathrm{U}}$ vector is derived as

$$\begin{aligned}\boldsymbol{D}_{\mathrm{U}}(\Delta\tau_{ijkl}) &= \boldsymbol{p}_{kji} \times (\boldsymbol{e}_{ji} + \boldsymbol{e}_{kj}\cos\phi_{kji})/\sin\phi_{kji}\\ &\quad + \boldsymbol{p}_{jkl} \times (\boldsymbol{e}_{kl} + \boldsymbol{e}_{jk}\cos\phi_{jkl})/\sin\phi_{jkl}\end{aligned} \tag{A10}$$

Appendix II Derivation of $\partial C_{ij}/\partial K(h)$

From Eqs. (29) and (34),

$$\Delta\boldsymbol{C} = [\tilde{\boldsymbol{H}}_\sigma \Delta\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{H}_\sigma + \Delta\tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{H}_\sigma + \tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\Delta\boldsymbol{H}_\sigma]/v \tag{A11}$$

Also from Eq. (27)

$$\Delta\boldsymbol{H}_\sigma = -\boldsymbol{B}_\rho\Delta\{[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\}\boldsymbol{D}_\sigma \tag{A12}$$

and

$$\begin{aligned}\tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\Delta\boldsymbol{H}_\sigma &= -\tilde{\boldsymbol{D}}_\sigma\{\boldsymbol{E} - \boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\}\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho\\ &\quad \times \Delta\{[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\}\boldsymbol{D}_\sigma\end{aligned} \tag{A13}$$

However, since

$$\{\boldsymbol{E} - \boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho[\tilde{\boldsymbol{B}}_\rho\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho]^{-1}\tilde{\boldsymbol{B}}_\rho\}\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{B}_\rho = 0 \tag{A14}$$

the matrix $\tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\Delta\boldsymbol{H}_\sigma$ and the transposed matrix $\Delta\tilde{\boldsymbol{H}}_\sigma\boldsymbol{F}_{\mathrm{R}}{}^0\boldsymbol{H}_\sigma$ in Eq. (A11) are both reduced to zero, leaving

$$\Delta\boldsymbol{C} = \{\sum_h [\tilde{\boldsymbol{H}}_\sigma\boldsymbol{A}(h)\boldsymbol{H}_\sigma]\Delta K(h)\}/v \tag{A15}$$

Accordingly, the partial derivative of the elastic constant (C_{ij}) with respect to the force constant $K(h)$ is given by Eq. (35) in the main text.