Ca^{2+} ions do not bind to heparin in a highly specific manner. The results of investigations of divalent counterion binding to heparin by equilibrium dialysis[23,24] and by circular dichroism[25] indicate a similar type of binding for Mg^{2+}, Ca^{2+}, and Ba^{2+} ions and a highly specific binding for Cu^{2+} ions.

Since the coions can interact with the polyion only by Debye–Hückel forces, the Manning theory for the coions gives

$$D_2/D_2^0 = 1 - z_2^2 A_2/3 \quad (7)$$

where the subscript 2 refers to the coions. The experimental $D_{Cl^-}/D_{Cl^-}^0$ points for NaH and NaDS are shown in Figures 5 and 6, respectively, along with the lines calculated using eq 6. For the NaH solutions, the $D_{Cl^-}/D_{Cl^-}^0$ experimental points appear to be fairly independent of X and of simple salt concentration. The excellent agreement with the theoretical model is evident. For the NaDS solutions, the experimental $D_{Cl^-}/D_{Cl^-}^0$ points in Figure 6 decrease from $X = 0$ to $X = 1$, followed by a leveling off for $X > 1$. An ionic strength dependence of $D_{Cl^-}/D_{Cl^-}^0$ is noted and upon comparing the $D_{Cl^-}/D_{Cl^-}^0$ at the lowest simple salt concentration with the theoretical line, agreement is not good. It is interesting that the experimental points for $D_{SO_4^{2-}}/D_{SO_4^{2-}}^0$ for NaH and NaDS which are shown in Figures 7 and 8, respectively, are close in value to their corresponding points for $D_{Cl^-}/D_{Cl^-}^0$. Similar findings have been reported for sodium poly(styrene sulfonate),[7] sodium ι-carrageenan,[13] and sodium alginate.[13] It appears that the Cl^- and SO_4^{2-} ions interact with each polyelectrolyte to the same extent. It is evident from Figures 7 and 8 that the diffusion ratios for SO_4^{2-} ions do not appear to approach unity as X tends to zero. This also is evident for SO_4^{2-} and $Fe(CN)_6^{4-}$ ions in sodium carrageenan and sodium alginate solutions,[13] but it was not found for these coions in sodium poly(styrene sulfonate) solutions at low simple salt concentrations. It is tempting to attribute this to greater experimental error at X less than unity because of low polyelectrolyte concentration. Because this region is of particular importance theoretically, experiments are in progress to evaluate the initial slopes of the curves. The Manning theory appears to be a good representation for monovalent–polyelectrolyte interactions but overemphasizes the interactions of multivalent coions with the polyelectrolyte.

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Calculation of Three-Dimensional Elastic Constants of Polymer Crystals. 1. Method of Calculation

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ABSTRACT: A new set of equations for calculating three-dimensional elastic constants of polymer crystals has been derived by using the **B** matrix in the normal coordinate treatments. Contrary to the methods by previous workers which need the parameters concerning all atoms in one unit cell, the number of parameters in the present method is reduced to that necessary to describe one crystallographic asymmetric unit by employing the space group symmetry of the crystal. This saves a great amount of memory size of computer and therefore becomes applicable to the cases with complicated crystal structure. Derivation of the equations has been illustrated by the case of orthorhombic polyethylene.

The crystallite moduli and compressibilities have been measured by many investigators for a wide variety of crystalline polymers.[1-3] It is very important to interpret these experimental results theoretically from the standpoint of the crystal structures determined by X-ray analysis and to clarify the relationship among crystal structures, intra- and intermolecular forces, and mechanical properties.

In the polymer crystal the chain molecules, the atoms which are linked tightly by the covalent bonds, are as-

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sembled together by the weaker intermolecular forces. Therefore the crystallite modulus in the chain direction is due mainly to that of the single chain. In previous papers[4,5] we derived a new method of calculation of the modulus of the single chain and discussed the factors affecting the modulus. Based on these results, we could understand the macroscopic moduli in the chain direction of poly(*p*-phenyleneterephthalamide) [Kevlar], poly(*m*-phenyleneisophthalamide) [Nomex], poly(ethylene oxybenzoate), and so on from the viewpoint of the molecular conformation.

In order to interpret the properties of the intermolecular interactions as well as the intramolecular ones, however, it is much more important to focus our attention on the three-dimensional crystallite moduli. Several methods of theoretical calculation of the elastic constants of the three-dimensionally arrayed polymer crystal have been proposed,[6-8] but these methods require the parameters concerning all atoms in one unit cell, and therefore need a great capacity of memory size of computer. Thus the application of the methods has been restricted so far to the simplest case of orthorhombic polyethylene. In order to make the equations applicable to more complicated cases, it is necessary to reduce the number of parameters to that sufficient to describe one crystallographic asymmetric unit by taking into account the space group symmetry of the crystal lattice. In the present paper we will derive a new set of theoretical equations for calculating the three-dimensional elastic constants. Application to some typical polymer crystals such as polyethylene, poly(vinyl alcohol), and poly(vinylidene fluoride) will be described in a later paper.[9]

Principles

Elastic constant matrix **C** is factorized into some blocks belonging to each symmetry species of the point group isomorphous to the factor group of the space group of the crystal.[8,10] For example, elastic constants for the case of orthorhombic systems are factorized into four blocks as shown in eq 1.

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & & & 0 \\ c_{21} & c_{22} & c_{23} & & & \\ c_{31} & c_{32} & c_{33} & & & \\ & & & c_{44} & & \\ & & & & c_{55} & \\ 0 & & & & & c_{66} \end{bmatrix} \begin{matrix} A_g \text{ species} \\ \\ \\ B_{1g} \text{ species} \\ B_{2g} \text{ species} \\ B_{3g} \text{ species} \end{matrix} \quad (1)$$

Shiro and Miyazawa[8] have already proposed the method of calculating the elastic constants which are represented by the force constant matrix $\mathbf{F_R}$ with the help of the **B** matrix used in the normal coordinate treatments, and the elastic constant matrix is factorized into blocks by using the transformation matrix of the internal displacement coordinates to the internal displacement symmetry coordinates. Their method, however, needs the whole set of parameters of the unit cell as stated above. In the present method, only one asymmetric unit is taken into consideration and the equations are developed by employing the symmetry properties of the crystal so as to obtain each block of elastic constant matrix belonging to the specific symmetry species from the first stage of calculation. Therefore it saves to a great extent the complicated calculations of elastic constants.

Displacements of Atoms

In this section, we derive the equations with the illustration of the case of orthorhombic polyethylene (PE) as shown in Figure 1. The crystallographic data determined by Bunn[11] are as follows: space group *Pnam*-D_{2h};[16] cell

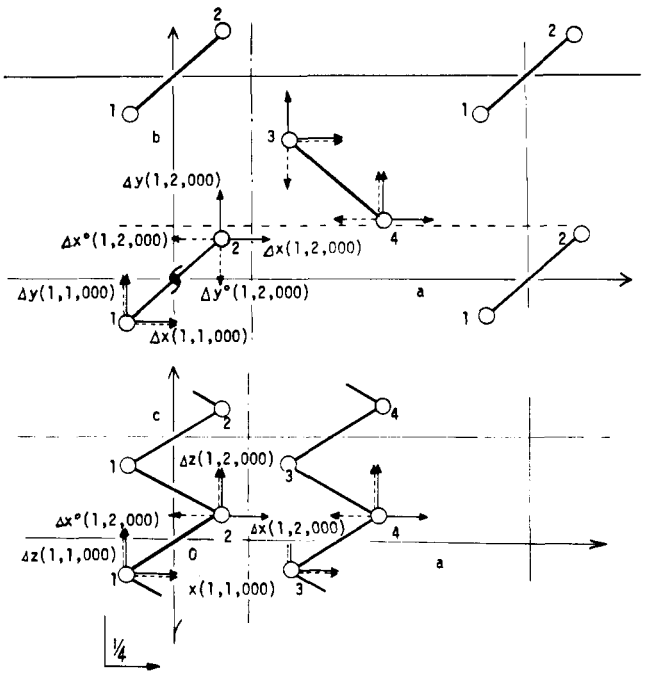

Figure 1. Crystal structure of orthorhombic polyethylene. Solid and broken arrows represent the Cartesian displacement coordinates of atoms in the coordinate system fixed on the 1st unit in the (000)'th unit cell and fixed on the *m*th unit itself, respectively. The coordinate system fixed on the *m*th unit is constructed by the transformation of the coordinate system fixed on the 1st unit using the transformation matrix $\mathbf{A}(m)$ shown in Table I. The figure shows the case of symmetry species A_g.

constants a = 7.40 Å, b = 4.93 Å, c(fiber axis) = 2.54 Å; and four CH_2 units per unit cell. There exist eight asymmetric units in a unit cell from the requirement of the space group and therefore one-half CH_2 unit becomes one asymmetric unit. But we will assume one CH_2 unit as one asymmetric unit since it is on the mirror plane.

We represent the Cartesian position vector and the Cartesian displacement vector of the *i*th atom in the *m*th unit of the $\mathbf{k} = (k_1, k_2, k_3)$'th unit cell as $\mathbf{X}(i,m,\mathbf{k})$ and $\Delta\mathbf{X}(i,m,\mathbf{k})$, respectively, in the coordinate system fixed on the 1st unit in the (0,0,0)'th unit cell (see Figure 1). According to the theory of elasticity,[10] in a homogeneous deformation of a crystal lattice, the displacement of an atom is given as

$$\Delta x(i,m,\mathbf{k}) = \rho_x(i,m) + x(i,m,\mathbf{k})u_{xx} + y(i,m,\mathbf{k})u_{xy} + z(i,m,\mathbf{k})u_{xz}$$

$$\Delta y(i,m,\mathbf{k}) = \rho_y(i,m) + x(i,m,\mathbf{k})u_{yx} + y(i,m,\mathbf{k})u_{yy} + z(i,m,\mathbf{k})u_{yz}$$

$$\Delta z(i,m,\mathbf{k}) = \rho_z(i,m) + x(i,m,\mathbf{k})u_{zx} + y(i,m,\mathbf{k})u_{zy} + z(i,m,\mathbf{k})u_{zz}$$

or

$$\Delta\mathbf{X}(i,m,\mathbf{k}) = \rho(i,m) + \mathbf{W}(i,m,\mathbf{k})\mathbf{U} \quad (2)$$

where

$$\mathbf{X}(i,m,\mathbf{k}) = \begin{bmatrix} x(i,m,\mathbf{k}) \\ y(i,m,\mathbf{k}) \\ z(i,m,\mathbf{k}) \end{bmatrix}$$

$$\Delta\mathbf{X}(i,m,\mathbf{k}) = \begin{bmatrix} \Delta x(i,m,\mathbf{k}) \\ \Delta y(i,m,\mathbf{k}) \\ \Delta z(i,m,\mathbf{k}) \end{bmatrix}$$

$$\rho(i,m) = \begin{bmatrix} \rho_x(i,m) \\ \rho_y(i,m) \\ \rho_z(i,m) \end{bmatrix}$$

$$\tilde{\mathbf{W}}(i,m,\mathbf{k}) = \begin{bmatrix} x(i,m,\mathbf{k}) & 0 & 0 \\ y(i,m,\mathbf{k}) & 0 & 0 \\ z(i,m,\mathbf{k}) & 0 & 0 \\ 0 & x(i,m,\mathbf{k}) & 0 \\ 0 & y(i,m,\mathbf{k}) & 0 \\ 0 & z(i,m,\mathbf{k}) & 0 \\ 0 & 0 & x(i,m,\mathbf{k}) \\ 0 & 0 & y(i,m,\mathbf{k}) \\ 0 & 0 & z(i,m,\mathbf{k}) \end{bmatrix} = \begin{bmatrix} \mathbf{X}(i,m,\mathbf{k}) & 0 & 0 \\ 0 & \mathbf{X}(i,m,\mathbf{k}) & 0 \\ 0 & 0 & \mathbf{X}(i,m,\mathbf{k}) \end{bmatrix}$$

$$\tilde{\mathbf{U}} = [u_{xx}, u_{xy}, u_{xz}, u_{yx}, u_{yy}, u_{yz}, u_{zx}, u_{zy}, u_{zz}]$$

The definition of some components of strain **U** is illustrated in Figure 2. A tilde indicates transposed matrix or vector. Each atom is displaced from its equilibrium position by an external force, by an amount proportional to the product of the strain **U** and the Cartesian coordinate $\mathbf{X}(i,m,\mathbf{k})$, i.e., the second term in eq 2. However, the external deformation is not necessarily the most stable deformation and it is assumed that the atoms further change their relative positions in the unit cell so as to minimize the energy increment due to the external deformation (Theorem of Minimum Potential Energy).[10] This displacement corresponds to $\rho(i,m)$ of the first term in eq 2, which is called "internal strain" vector. Under the assumption of homogeneous deformation, $\rho(i,m)$ is common to all unit cells. That is, $\rho(i,m)$ is equivalent to the atomic displacement in the optically active vibration with the phase difference between the unit cells $\delta = \mathbf{0}$.[8] Figure 3 shows the atomic displacements when the a axis of the PE crystal is deformed by a tensile strain.

We assume $\rho^{\Gamma}(i)$ as the internal strain of the ith atom belonging to a certain symmetry species Γ of the point group isomorphous to the factor group of the space group of the crystal as follows

$$\rho^{\Gamma}(i) = (1/N)\sum_{m}\rho^{\Gamma}(i,m) \tag{3}$$

where $\rho^{\Gamma}(i,m)$ is the internal strain of the ith atom in the mth asymmetric unit, belonging to the symmetry species Γ, and N is a normalization constant. $\rho^{\Gamma}(i,m)$ can be related to $\rho^{\Gamma}(i,1)$ in the following equation[12,13]

$$\rho^{\Gamma}(i,m) = c(m)^{\Gamma}\mathbf{A}(m)\rho^{\Gamma}(i,1) \tag{4}$$

Here $\mathbf{A}(m)$ is a transformation matrix of unit 1 to unit m and $c(m)^{\Gamma}$ is a character for the symmetry operation $\mathbf{A}(m)$ and belongs to the symmetry species Γ.[14] $\mathbf{A}(m)$ and $c(m)^{\Gamma}$ are shown in Tables I and II, respectively, for the case of the PE crystal. As shown in Table II, the nine strain components u_{ij} ($i, j = x, y$, and z) belong to one of the species symmetric with respect to the center of symmetry.[8,10] Thus we can classify the four symmetry species A_g, B_{1g}, B_{2g}, and B_{3g} by only the four kinds of character, not by the eight kinds, because we do not need to consider the ungerade species A_u, B_{1u}, B_{2u}, and B_{3u}.

If we substitute eq 4 into eq 2, we obtain

$$\Delta\mathbf{X}(i,m,\mathbf{k}) = c(m)^{\Gamma}\mathbf{A}(m)\rho^{\Gamma}(i,1) + \mathbf{W}(i,m,\mathbf{k})\mathbf{U}^{\Gamma} \tag{5}$$

where $\mathbf{U}^{\Gamma}$ is used instead of **U** in eq 2. $\mathbf{U}^{\Gamma}$ is the vector consisting of only the strain components belonging to the symmetry species Γ (Table II). For example,

$$\mathbf{U}^{A_g} = [u_{xx}, 0, 0, 0, u_{yy}, 0, 0, 0, u_{zz}]$$

Since the external deformation parameters include the rotation of the crystal as a whole, pure elastic deformation (σ) is constructed from the following equations,[8,10]

$$\sigma_1 = u_{xx}, \quad \sigma_2 = u_{yy}, \quad \sigma_3 = u_{zz},$$

$$\sigma_4 = u_{yz} + u_{zy}, \quad \sigma_5 = u_{xz} + u_{zx},$$

$$\sigma_6 = u_{xy} + u_{yx}$$

$$\omega_1 = u_{yz} - u_{zy}, \quad \omega_2 = u_{xz} - u_{zx}, \quad \omega_3 = u_{xy} - u_{yx}$$

where ω_1, ω_2, and ω_3 represent the rotations of the crystal about the x, y, and z axes, respectively, and are omitted

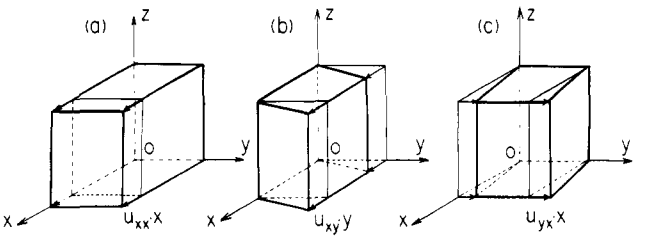

Figure 2. Definition of some components of strain **U**; (a) u_{xx}, (b) u_{xy}, and (c) u_{yx}, respectively.

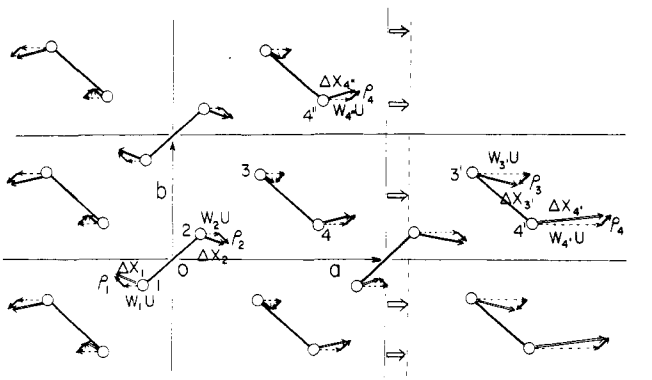

Figure 3. Atomic displacements when the a axis of the PE crystal is deformed by a tensile strain. Solid, broken, and double arrows represent respectively internal strain ρ, external strain **WU**, and the sum of the former two vectors or atomic displacement $\Delta\mathbf{X}$.

Table I
Transformation Matrices of CH_2 Units of Polyethylene Crystal

transformation of units	transformation matrices $\mathbf{A}(m)$
$1 \rightarrow 1$	$\mathbf{E} = \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$
$1 \rightarrow 2$	$\mathbf{C}_2^s(c) = \begin{bmatrix} -1 & & \\ & -1 & \\ & & 1 \end{bmatrix}$
$1 \rightarrow 3$	$\sigma_g(ac) = \begin{bmatrix} 1 & & \\ & -1 & \\ & & 1 \end{bmatrix}$
$1 \rightarrow 4$	$\sigma_g(bc) = \begin{bmatrix} -1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$

Table II
Characters $c(m)^{\Gamma}$ for Orthorhombic Polyethylene Crystal

species Γ	E	C_2^s (c)	σ_g (ac)	σ_g (bc)	C_2^s (b)	C_2^s (a)	σ (ab)	i	strain/stress tensors
A_g	1	1	1	1	1	1	1	1	xx, yy, zz
B_{1g}	1	−1	−1	1	−1	1	−1	1	yz
B_{2g}	1	−1	1	−1	1	−1	−1	1	xz
B_{3g}	1	1	−1	−1	−1	−1	1	1	xy
A_u	1	1	−1	−1	1	1	−1	−1	
B_{1u}	1	−1	1	−1	−1	1	1	−1	
B_{2u}	1	−1	−1	1	1	−1	1	−1	
B_{3u}	1	1	1	1	−1	−1	−1	−1	

hereafter. In a matrix form,

$$\mathbf{U} = \mathbf{T}_\sigma \sigma \tag{6}$$

where

$$\mathbf{T}_\sigma = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 \\ 0 & 0 & 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{bmatrix} \qquad \sigma = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix}$$

If we assume σ^Γ as the strain vector having the pure strain components which belong to the symmetry species Γ, we can write $\mathbf{U}^\Gamma$ as follows,

$$\mathbf{U}^\Gamma = \mathbf{T}_\sigma \sigma^\Gamma = \mathbf{T}_\sigma \Lambda^\Gamma \sigma \tag{7}$$

where Λ^Γ is the 6×6 diagonal matrix indicating the pure strain components belonging to the symmetry species Γ. In the case of PE, for example, σ_1 ($= u_{xx}$), σ_2 ($= u_{yy}$), and σ_3 ($= u_{zz}$) belong to the A_g species and therefore

$$\sigma^{A_g} = \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & & & & & 0 \\ & 1 & & & & \\ & & 1 & & & \\ & & & 0 & & \\ & & & & 0 & \\ 0 & & & & & 0 \end{bmatrix} \begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \Lambda^{A_g} \sigma$$

For the B_{1g} species,

$$\Lambda^{B_{1g}} = \begin{bmatrix} 0 & & & & & 0 \\ & 0 & & & & \\ & & 0 & & & \\ & & & 1 & & \\ & & & & 0 & \\ 0 & & & & & 0 \end{bmatrix}$$

By substituting eq 7 into eq 5, we can obtain the following equation:

$$\Delta\mathbf{X}(i,m,\mathbf{k}) = c(m)^\Gamma \mathbf{A}(m) \rho^\Gamma(i,1) + \mathbf{W}(i,m,\mathbf{k}) \mathbf{T}_\sigma \Lambda^\Gamma \sigma \tag{8}$$

Internal Displacement Coordinates

In the next step we construct the internal displacement coordinates (i.e., the changes of bond lengths, bond angles, and so on) from the Cartesian displacement coordinates $\Delta\mathbf{X}(i,m,\mathbf{k})$, just when we must consider the symmetry properties of $\mathbf{B}$ matrices. For the sake of it, we need rotate $\Delta\mathbf{X}(i,m,\mathbf{k})$ as follows. If we assume $\Delta\mathbf{X}^0(i,m,\mathbf{k})$ as the Cartesian displacement coordinate based on the coordinate system fixed on the mth unit itself, as defined in Figure 1,

$$\Delta\mathbf{X}^0(i,m,\mathbf{k}) = \tilde{\mathbf{A}}(m)\Delta\mathbf{X}(i,m,\mathbf{k}) = c(m)^\Gamma \rho^\Gamma(i,1) + \tilde{\mathbf{A}}(m)\mathbf{W}(i,m,\mathbf{k})\mathbf{T}_\sigma \Lambda^\Gamma \sigma \tag{9}$$

When the number of atoms in one asymmetric unit is p, we can write eq 9 as

$$\begin{bmatrix} \Delta\mathbf{X}^0(1,m,\mathbf{k}) \\ \Delta\mathbf{X}^0(2,m,\mathbf{k}) \\ \vdots \\ \Delta\mathbf{X}^0(p,m,\mathbf{k}) \end{bmatrix} = c(m)^\Gamma \begin{bmatrix} \rho^\Gamma(1,1) \\ \rho^\Gamma(2,1) \\ \vdots \\ \rho^\Gamma(p,1) \end{bmatrix} + \begin{bmatrix} \tilde{\mathbf{A}}(m)\mathbf{W}(1,m,\mathbf{k}) \\ \tilde{\mathbf{A}}(m)\mathbf{W}(2,m,\mathbf{k}) \\ \vdots \\ \tilde{\mathbf{A}}(m)\mathbf{W}(p,m,\mathbf{k}) \end{bmatrix} \mathbf{T}_\sigma \Lambda^\Gamma \sigma \tag{10}$$

or

$$\Delta\mathbf{X}^0(m,\mathbf{k}) = c(m)^\Gamma \rho^\Gamma + \mathbf{W}(m,\mathbf{k})\mathbf{T}_\sigma \Lambda^\Gamma \sigma \tag{11}$$

where

$$\rho^\Gamma = \begin{bmatrix} \rho^\Gamma(1,1) \\ \rho^\Gamma(2,1) \\ \vdots \\ \rho^\Gamma(p,1) \end{bmatrix} = \begin{bmatrix} \rho^\Gamma(1) \\ \rho^\Gamma(2) \\ \vdots \\ \rho^\Gamma(p) \end{bmatrix}$$

and

$$\mathbf{W}(m,\mathbf{k}) = \begin{bmatrix} \tilde{\mathbf{A}}(m)\mathbf{W}(1,m,\mathbf{k}) \\ \tilde{\mathbf{A}}(m)\mathbf{W}(2,m,\mathbf{k}) \\ \vdots \\ \tilde{\mathbf{A}}(m)\mathbf{W}(p,m,\mathbf{k}) \end{bmatrix}$$

$\mathbf{W}(m,\mathbf{k})$ can be obtained easily from the Cartesian coordinates of unit 1 by the symmetry operation (rotation + translation) matrix. Thus we can represent $\Delta\mathbf{X}^0(m,\mathbf{k})$ by using only the parameters of unit 1.

$\Delta\mathbf{R}^\Gamma$, the internal displacement symmetry coordinate vector belonging to the symmetry species Γ, is defined as follows,

$$\Delta\mathbf{R}^\Gamma = (1/N)\sum_l \Delta\mathbf{R}(l) \tag{12}$$

where $\Delta\mathbf{R}(l)$ is the internal displacement coordinate vector of the lth unit. $\Delta\mathbf{R}(l)$ and $\Delta\mathbf{X}^0(m,\mathbf{k})$ can be related to each other by $\mathbf{B}$ matrices as follows:

$$\begin{array}{c} \\ \Delta\mathbf{R}(1) \\ \Delta\mathbf{R}(2) \\ \vdots \end{array} \begin{array}{c} \begin{array}{cccc} \Delta\tilde{\mathbf{X}}^0(1,\mathbf{k}) & \Delta\tilde{\mathbf{X}}^0(2,\mathbf{k}) & \Delta\tilde{\mathbf{X}}^0(3,\mathbf{k}) & \cdots \end{array} \\ \begin{bmatrix} \mathbf{B}(1,\mathbf{k}) & \mathbf{B}(2,\mathbf{k}) & \mathbf{B}(3,\mathbf{k}) & \cdots \\ \mathbf{B}(0,\mathbf{k}) & \mathbf{B}(1,\mathbf{k}) & \mathbf{B}(2,\mathbf{k}) & \cdots \\ \vdots & \vdots & \vdots & \vdots \end{bmatrix} \end{array}$$

That is,

$$\Delta\mathbf{R}(l) = \sum_{m,\mathbf{k}} \mathbf{B}(m,\mathbf{k})\Delta\mathbf{X}^0(m,\mathbf{k}) \tag{13}$$

Then, from eq 11, 12, and 13 we obtain

$$\begin{aligned} \Delta\mathbf{R}^\Gamma &= (1/N)\sum_l \Delta\mathbf{R}(l) = \\ &(1/N)\sum_l [\sum_{m,\mathbf{k}} \mathbf{B}(m,\mathbf{k})\Delta\mathbf{X}^0(m,\mathbf{k})] = \\ &(1/N)\sum_l [\sum_{m,\mathbf{k}} c(m)^\Gamma \mathbf{B}(m,\mathbf{k})\rho^\Gamma + \sum_{m,\mathbf{k}} \mathbf{B}(m,\mathbf{k})\mathbf{W}(m,\mathbf{k})\mathbf{T}_\sigma \Lambda^\Gamma \sigma] \\ &= [\sum_{m,\mathbf{k}} c(m)^\Gamma \mathbf{B}(m,\mathbf{k})][(1/N)\sum_l \rho^\Gamma] + \\ &[\sum_{m,\mathbf{k}} \mathbf{B}(m,\mathbf{k})\mathbf{W}(m,\mathbf{k})\mathbf{T}_\sigma \Lambda^\Gamma][(1/N)\sum_l \sigma] = \mathbf{B}_\rho{}^\Gamma \rho^\Gamma + \mathbf{B}_\sigma{}^\Gamma \sigma \end{aligned} \tag{14}$$

Here

$$\mathbf{B}_\rho{}^\Gamma = \sum_{m,\mathbf{k}} c(m)^\Gamma \mathbf{B}(m,\mathbf{k})$$

$$\mathbf{B}_\sigma{}^\Gamma = \sum_{m,\mathbf{k}} \mathbf{B}(m,\mathbf{k})\mathbf{W}(m,\mathbf{k})\mathbf{T}_\sigma \Lambda^\Gamma \tag{15}$$

$\mathbf{B}(m,\mathbf{k})$ is based on the coordinate system fixed to the mth unit. From the input data concerning the structure parameters, we calculate $\mathbf{B}^0(m,\mathbf{k})$, i.e., $\mathbf{B}$ matrix constructed in the coordinate system of the 1st unit, from which we can obtain $\mathbf{B}(m,\mathbf{k})$ as follows.

$$\mathbf{B}(m,\mathbf{k}) = \mathbf{B}^0(m,\mathbf{k})[\mathbf{A}(m) \times \mathbf{E}] \tag{16}$$

where $\mathbf{A}(m) \times \mathbf{E}$ is a direct product of 3×3 matrix $\mathbf{A}(m)$ and p-ordered unit matrix $\mathbf{E}$.

Table III shows the $\mathbf{B}^0(m,\mathbf{k})$ in the case of the PE

Table III
B Matrices for Orthorhombic Polyethylene Crystal[a]

	$B_\alpha{}^0$			$B_\beta{}^0$			$B_\gamma{}^0$			$B_\delta{}^0$		
	Δx_1	Δy_1	Δz_1	$\Delta x_1'$	$\Delta y_1'$	$\Delta z_1'$	$\Delta x_1''$	$\Delta y_1''$	$\Delta z_1''$	$\Delta x_1'''$	$\Delta y_1'''$	$\Delta z_1'''$
Δr	−0.3676	−0.4186	−0.8306	0.3676	0.4186	0.8306	0	0	0	0	0	0
$\Delta\phi$	0.3585	0.4082	−0.3643	−0.7170	−0.8164	0	0.3585	0.4082	0.3643	0	0	0
$\Delta\tau$	−0.5312	0.4664	0	0.5312	−0.4664	0	0.5312	−0.4664	0	−0.5312	0.4664	0
Δp_1	0.8981	−0.4430	0	−0.8981	0.4430	0	0	0	0	0	0	0
Δp_2	0.1246	−0.9514	0.2816	−0.1246	0.9514	−0.2816	0	0	0	0	0	0
Δp_3	−0.7493	−0.5886	0.3032	0.7493	0.5886	−0.3032	0	0	0	0	0	0
Δp_4	−0.7493	−0.5886	−0.3032	0.7493	0.5886	0.3032	0	0	0	0	0	0

[a] $\Delta x_1'$, $\Delta y_1'$, etc., represent the displacements of the atoms of units which neighbor to the 1st unit and construct the internal coordinates. For example, $\Delta x_1' = \Delta x(1,3,\mathbf{k} = (0,\bar{1},0))$ for Δp_1.

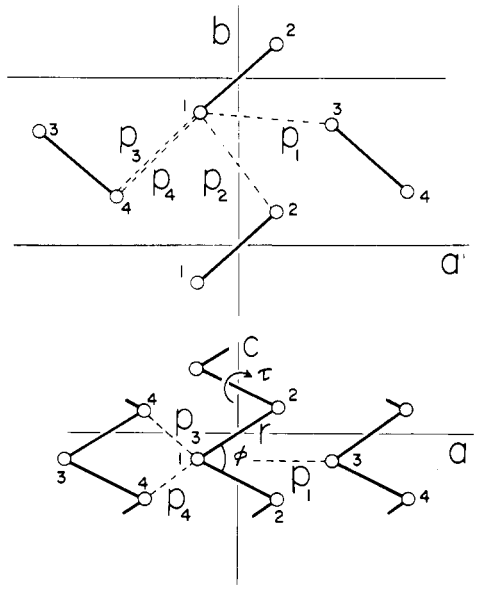

Figure 4. Intra- and intermolecular internal coordinates of the orthorhombic PE crystal.

crystal. Intramolecular and intermolecular internal coordinates are defined in Figure 4. The Cartesian coordinates of the basic atom or the 1st methylene unit are given as $\tilde{\mathbf{X}}(1,1,\mathbf{k=0})$ = [−0.281 Å, −0.320 Å, −0.635 Å]. The equilibrium values of the internal coordinates are as follows; r^0 = 1.529 Å, ϕ^0 = 112.3°, τ^0 = 180°, $p_1{}^0$ = 4.1256 Å, $p_2{}^0$ = 4.5092 Å, $p_3{}^0 = p_4{}^0$ = 4.1876 Å. From eq 15 and 16 and the values in Table III, we obtain $\mathbf{B}_\rho{}^{A_g}$ and $\mathbf{B}_\sigma{}^{A_g}$ belonging to the A_g species as seen in eq 17 and 18.

$$\mathbf{B}_\rho{}^{A_g} = \begin{array}{c} \\ \Delta r \\ \Delta\phi \\ \Delta\tau \\ \Delta p_1 \\ \Delta p_2 \\ \Delta p_3 \\ \Delta p_4 \end{array} \begin{array}{c} \begin{array}{ccc} \Delta x & \Delta y & \Delta z \end{array} \\ \begin{bmatrix} -0.7350 & -0.8371 & 0 \\ 1.4335 & 1.6324 & 0 \\ 0 & 0 & 0 \\ 0 & -0.8847 & 0 \\ 0.2493 & -1.9028 & 0 \\ -1.4987 & 0 & 0 \\ -1.4987 & 0 & 0 \end{bmatrix} \end{array} \tag{17}$$

$$\mathbf{B}_\sigma{}^{A_g} = \begin{array}{c} \\ \Delta r \\ \Delta\phi \\ \Delta\tau \\ \Delta p_1 \\ \Delta p_2 \\ \Delta p_3 \\ \Delta p_4 \end{array} \begin{array}{c} \begin{array}{cccccc} \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 & \sigma_5 & \sigma_6 \end{array} \\ \begin{bmatrix} 0.2065 & 0.2679 & 1.0548 & 0 & 0 & 0 \\ -0.4028 & -0.5224 & 0.9252 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -3.3183 & -0.8073 & 0 & 0 & 0 & 0 \\ -0.0700 & -4.0815 & -0.3577 & 0 & 0 & 0 \\ -2.3515 & -1.4510 & -0.3852 & 0 & 0 & 0 \\ -2.3515 & -1.4510 & -0.3852 & 0 & 0 & 0 \end{bmatrix} \end{array} \tag{18}$$

Potential Energy and Elastic Constants

The potential energy per asymmetric unit is written as

$$V^\Gamma = \tfrac{1}{2}\Delta\tilde{\mathbf{R}}^\Gamma\mathbf{F}_\mathbf{R}{}^\Gamma\Delta\mathbf{R}^\Gamma \tag{19}$$

where

$$\mathbf{F}_\mathbf{R}{}^\Gamma = \mathbf{F}(11) + \sum_m c(m)^\Gamma[\mathbf{F}(1m) + \tilde{\mathbf{F}}(1m)] \tag{20}$$

$\mathbf{F}(11)$ is the force constant matrix corresponding to the interactions within one asymmetric unit and $\mathbf{F}(1m)$ is the matrix indicating the interactions between the 1st and the mth units. In the case of the PE crystal, we consider the interactions shown in eq 21a. The values of the intra- and

$$\begin{array}{c} \\ \Delta r \\ \Delta\phi \\ \Delta\tau \\ \Delta p_1 \\ \Delta p_2 \\ \Delta p_3 \\ \Delta p_4 \end{array} \begin{array}{c} \begin{array}{ccccccccccc} \Delta r & \Delta\phi & \Delta\tau & \Delta p_1 & \Delta p_2 & \Delta p_3 & \Delta p_4 & \Delta r' & \Delta\phi' & \cdots \end{array} \\ \begin{bmatrix} K_r & F_{r\phi} & & & & & & F_{rr} & 0 & 0 \\ F_{r\phi} & H_\phi & & & 0 & & & F_{r\phi} & 0 & 0 \\ & & T_\tau & & & & & & & \\ & & & P_1 & & & & & & \\ & & & & P_2 & & & & & \\ & 0 & & & & P_3 & & & & 0 \\ & & & & & & P_4 & & & \end{bmatrix} \end{array} \tag{21a}$$

intermolecular force constants used are referred to ref 4 and 8. Therefore, see eq 21b for $\mathbf{F}_\mathbf{R}{}^{A_g}$. The units of the

$$\mathbf{F}_\mathbf{R}{}^{A_g} = \begin{bmatrix} K_r + 2F_{rr} & 2F_{r\phi} & & & & & \\ 2F_{r\phi} & H_\phi & & & 0 & & \\ & & T_\tau & & & & \\ & & & P_1 & & & \\ & & & & P_2 & & \\ & 0 & & & & P_3 & \\ & & & & & & P_4 \end{bmatrix}$$

$$= \begin{bmatrix} 4.410 & 0.432 & & & & & \\ 0.432 & 1.523 & & & 0 & & \\ & & 0.095 & & & & \\ & & & 0.025 & & & \\ & & & & 0.003 & & \\ & & & & & 0.025 & \\ & 0 & & & & & 0.025 \end{bmatrix} \tag{21b}$$

force constants are mdyn/Å for stretching, mdyn Å/rad^2 for bending and torsion, and mdyn/rad for stretching–bending interactions, respectively.

By substituting eq 14 into 19, we obtain

$$V^\Gamma = \tfrac{1}{2}[\tilde{\rho}^\Gamma\tilde{\mathbf{B}}_\rho{}^\Gamma + \tilde{\sigma}\tilde{\mathbf{B}}_\sigma{}^\Gamma]\mathbf{F}_\mathbf{R}{}^\Gamma[\mathbf{B}_\rho{}^\Gamma\rho^\Gamma + \mathbf{B}_\sigma{}^\Gamma\sigma] \tag{22}$$

Since V^Γ is minimized by ρ^Γ,

$$\partial V^\Gamma/\partial\rho^\Gamma{}_\alpha(i) = 0 \tag{23}$$

where $\alpha = x$, y, and z. Therefore

$$\tilde{\mathbf{B}}_\rho{}^\Gamma\mathbf{F}_\mathbf{R}{}^\Gamma\mathbf{B}_\rho{}^\Gamma\rho^\Gamma + \tilde{\mathbf{B}}_\rho{}^\Gamma\mathbf{F}_\mathbf{R}{}^\Gamma\mathbf{B}_\sigma{}^\Gamma\sigma = 0$$

Thus

$$\rho^{\Gamma} = -[\tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathrm{R}}{}^{\Gamma}\mathbf{B}_{\rho}{}^{\Gamma}]^{-1}\tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\sigma}{}^{\Gamma}\sigma \quad (24)$$

The matrix $\tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\rho}{}^{\Gamma}$ in eq 24 has the zero eigenvalues in the case that the symmetry species Γ has the coordinates T_x, T_y, or T_z, which correspond to the pure translations along the x, y, or z axes, respectively. The calculation of the inverse matrix of such a singular matrix is referred to ref 15.

By substituting eq 24 into eq 22, we obtain

$$V^{\Gamma} = \tfrac{1}{2}\tilde{\sigma}\{\tilde{\mathbf{B}}_{\sigma}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\sigma}{}^{\Gamma} - \tilde{\mathbf{B}}_{\sigma}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\rho}{}^{\Gamma}[\tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathrm{R}}{}^{\Gamma}\mathbf{B}_{\rho}{}^{\Gamma}]^{-1}\tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\sigma}{}^{\Gamma}\}\sigma = \tfrac{1}{2}\tilde{\sigma}\{\mathbf{F}_{\sigma}{}^{\Gamma} - \tilde{\mathbf{F}}_{\rho\sigma}{}^{\Gamma}[\mathbf{F}_{\rho}{}^{\Gamma}]^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\}\sigma \quad (25)$$

where

$$\mathbf{F}_{\rho}{}^{\Gamma} = \tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\rho}{}^{\Gamma}$$

$$\mathbf{F}_{\rho\sigma}{}^{\Gamma} = \tilde{\mathbf{B}}_{\rho}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\sigma}{}^{\Gamma} \quad (26)$$

$$\mathbf{F}_{\sigma}{}^{\Gamma} = \tilde{\mathbf{B}}_{\sigma}{}^{\Gamma}\mathbf{F}_{\mathbf{R}}{}^{\Gamma}\mathbf{B}_{\sigma}{}^{\Gamma}$$

If we represent the elastic constant matrix belonging to the symmetry species Γ as $\mathbf{C}^{\Gamma}$,

$$V^{\Gamma} = (v/2)\tilde{\sigma}\mathbf{C}^{\Gamma}\sigma \quad (27)$$

where v is the effective volume per asymmetric unit. When the unit cell with the volume v_{cell} contains n units, $v = v_{\mathrm{cell}}/n$. By comparing eq 25 with 27,

$$\mathbf{C}^{\Gamma} = \{\mathbf{F}_{\sigma}{}^{\Gamma} - \tilde{\mathbf{F}}_{\rho\sigma}{}^{\Gamma}[\mathbf{F}_{\rho}{}^{\Gamma}]^{-1}\mathbf{F}_{\rho\sigma}{}^{\Gamma}\}/v \quad (28)$$

In the case of the PE crystal, we can obtain $\mathbf{C}^{\mathrm{A_g}}$ by substituting eq 17, 18, and 21 into eq 28, as follows, where 10^{10} dyn/cm^2 = 1 GPa. The elastic constants belonging to the other symmetry species can be calculated the same way as for the $\mathrm{A_g}$ species.

$$\mathbf{C}^{\mathrm{A_g}} = \begin{bmatrix} 22.0 & 9.8 & 1.9 & 0 & 0 & 0 \\ 9.8 & 7.5 & 1.4 & 0 & 0 & 0 \\ 1.9 & 1.4 & 294.6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \times 10^{10}\ \mathrm{dyn/cm^2} \quad (29)$$

In the next paper, we will discuss the calculated results for the various typical polymer crystals such as polyethylene, poly(vinyl alcohol), and poly(vinylidene fluoride).[9]

Appendix. The Relationship between One-Dimensional and Three-Dimensional Lattice Deformations

In the previous paper,[5] we derived a new set of equations for calculating the crystallite modulus of an isolated single chain under the constraining condition of preserving the helical symmetry, i.e., $\Delta\theta = 0$, where θ is a helical rotation angle per monomeric unit around the chain axis. [We should correct here eq 22 in ref 5 as follows: $\Delta\phi = fd \cot(\phi/2)/(2H_{\phi}\sin^2(\theta/2))$ and $\Delta\tau = fd \cot(\tau/2)\cos^2(\phi/2)/(2F_{\tau}\sin^2(\theta/2))$. Accompanied with this correction, the theoretical curve (broken line) in Figure 2 in ref 5 calculated under the condition of $\Delta\theta \neq 0$ increases. But the solid curve ($\Delta\theta = 0$) does not change and the good agreement of the solid curve with the observed results is not affected.] Now we can understand the physical meaning of $\Delta\theta = 0$ from the viewpoint of symmetry properties of the one-dimensional single chain in connection with those of the three-dimensional crystal lattice. As stated in the section Displacements of Atoms in the present paper, the homogeneous deformation of the crystal lattice (one-dimensional and three-dimensional) results in the preservation of translational symmetry of lattice and the corresponding units in each unit cell are deformed in phase as is likely in the case of optically active lattice vibrations; that is, the symmetry property of the deformation of translational lattice is isomorphous to the so-called factor group symmetry. In an infinitely long one-dimensional lattice, the external stress tensor considered in the calculation of Young's modulus is only the zz component which should belong to the total symmetry species of the factor group, where z is the chain axis. Therefore we can say that the preservation of helical symmetry ($\Delta\theta = 0$) is an inevitable consequence of the assumption of homogeneous deformation, because the "totally" symmetric property means the maintenance of the all symmetry elements (including helical symmetry) on the deformation of the single chain by the external tensile stress (zz) along the chain axis. In the three-dimensional lattice, the factor group treatment can also be applied. Different from the case of the single chain, however, there exist other tensor components of external stress such as xx, xy, and so on, which belong to the various symmetry species of the factor group as well as the "totally" symmetric species. Then the elastic constant matrix is factored into some blocks of these symmetry species as shown in the text. In this way we can understand the correlation between the one-dimensional and the three-dimensional elastic deformations.

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