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Group Theoretical Treatment of Crystal Vibrations; Application to Orthorhombic Polyethylene

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Irreducible representations of $\boldsymbol{k}$ groups of the space group *Pnam* were derived with Slater's method. Degeneracies of crystal vibrations due to space symmetry and time reversal symmetry were treated on the basis of Maradudin's theory. With irreducible representations of $\boldsymbol{k}$ groups, symmetry coordinates of the carbon atoms of orthorhombic polyethylene were constructed from translational-symmetry coordinates with nonintegral index vectors. A general matrix method was worked out for treating crystal vibrations of any phase-difference vector. Useful methods were derived for treating molecular crystals and chain polymer crystals and for approximate treatment of low frequency lattice vibrations.

For orthorhombic polyethylene crystal, various experimental data have become available, including infrared bands due to CH_2 bending and rocking vibrations,[1] for infrared bands due to lattice vibrations,[2,3] elastic and inelastic scattering cross sections of thermal neutrons[4-6] and low temperature specific heat.[7] All these data are related with the force field and normal vibrations of the crystal. For a molecular crystal, far infrared bands due to lattice vibrations arise from the intermolecular force field. Splitting of infrared bands due to intramolecular vibrations depends primarily on intermolecular force field but also on normal modes (atomic displacements) of the unperturbed vibrations concerned. Specific heat in the lowest temperature region is due to low frequency vibrations of three acoustic branches. On the other

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[1] R. G. Snyder, *J. Mol. Spectry.*, **4**, 411 (1960); *ibid.*, **7**, 116 (1961).

[2] J. E. Bertie and G. E. Whalley, *J. Chem. Phys.*, **41**, 575 (1964).

[3] S. Krimm and M. I. Bank, *ibid.*, **42**, 4059 (1965).

[4] H. R. Danner, G. J. Safford, H. Boutin and J. S. King, *ibid.*, **40**, 1417 (1964).

[5] W. Myers, J. L. Donovan and J. S. King, *ibid.*, **42**, 4299 (1965); W. Myers, G. C. Summerfield and J. S. King, *ibid.*, **44**, 184 (1966).

[6] L. A. Feldkamp, G. Venkataraman and J. S. King, "Neutron Inelastic Scattering," IAEA Symp., Copenhagen, Vol. 2, p. 159 (1968).

[7] J. E. Tucker and W. Reese, *J. Chem. Phys.*, **46**, 1388 (1967).

hand, elastic and inelastic scattering cross sections of thermal neutrons depend on the vibrational frequencies and also on vibrational displacements (of scattering nuclei) for all the acoustic and optical branches of crystal vibrations.

For an analysis of any one of these data, a highly simplified model may be useful, but often such a model is not necessarily applicable for analyses of other data. In our present series of studies on orthorhombic polyethylene crystal, available experimental data were all systematically treated on the basis of the intrachain and interchain force field and the acoustic and optical branches of crystal vibrations.

Chain-polymer crystals such as polyethylene are highly anisotropic and the restoring force along the chain axis is intramolecular in contrast with the intermolecular forces along two other directions. Accordingly these crystals form a special group of molecular crystals which practically behave as polymer molecules along the chain direction. A general method for treating molecular vibrations of helical polymer chains have been worked out previously,[8–10] and frequency-dispersion curves of the polyethylene chain[11] were obtained for analyzing band progression of intramolecular vibrations. However, for treating specific heat and neutron-scattering cross sections, normal coordinate treatments of the acoustic and optical vibrations of the three-dimensional crystal in the first Brillouin zone are required.

A dynamical theory of crystal lattices was established by Born and Huang[12] and a general method was worked out for treating crystal vibrations with Cartesian symmetry coordinates of any given wave vector ($\boldsymbol{k}$) [constructed in accordance with the translational symmetry of crystal lattices]. However, for crystal lattices of high space-group symmetry, crystal vibrations of special wave vectors may be grouped into symmetry classes and corresponding dynamical matrices may be factored into small matrices after unitary transformations. Accordingly computer time for numerical calculation is much reduced. Symmetry considerations are also required in drawing dispersion curves of the same symmetry class which should not intersect one another.

In the present study, therefore, group theoretical treatments were made of crystal vibrations of the space group *Pnam*. Furthermore, general matrix methods were worked out for treating molecular crystals and chain-polymer crystals and were applied to orthorhombic polyethylene crystal.

Space Group Operations and k Groups

For a crystal lattice, constituent atoms of a unit cell are classified into sets, each set consisting of equivalent atoms. In the case of orthorhombic polyethylene[13] (Fig. 1), two molecular chains pass through a unit cell along the c axis and there are four methylene groups per unit cell. There are two sets of hydrogen atoms and one set of carbon atoms. In the present paper, symmetry coordinates for carbon atoms will be described, but same considerations apply also for the other two sets of hydrogen atoms.

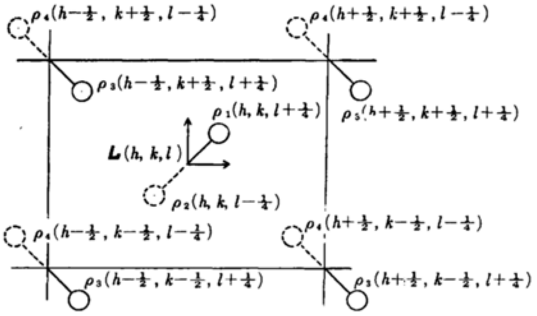

Fig. 1. Crystal structure and nonintegral index vectors ($\boldsymbol{\rho}$) of the carbon atoms of orthorhombic polyethylene (*Pnam*).

A unit cell of a crystal lattice is denoted with an index vector $\boldsymbol{L}$ with integral components (h,k,l). Then the ith atom of the $\boldsymbol{L}$th cell may be denoted with a nonintegral index

$$\boldsymbol{\rho}_i(\boldsymbol{L}) = \boldsymbol{L} + \boldsymbol{\rho}_i{}^0\,, \tag{1}$$

where components of the position vector $\boldsymbol{\rho}_i{}^0$ from the cell origin are given in units of lattice constants (a_0,b_0,c_0). For the crystal lattice of orthorhombic polyethylene (Fig. 1), the position vectors are given as

$$\boldsymbol{\rho}_1{}^0=\begin{bmatrix}0\\0\\1/4\end{bmatrix}\ \boldsymbol{\rho}_2{}^0=\begin{bmatrix}0\\0\\-1/4\end{bmatrix}\ \boldsymbol{\rho}_3{}^0=\begin{bmatrix}-1/2\\1/2\\1/4\end{bmatrix}\ \boldsymbol{\rho}_4{}^0=\begin{bmatrix}1/2\\-1/2\\-1/4\end{bmatrix} \tag{2}$$

and space group operations are listed in Table 1. Then, with respect to the translational-symmetry of the crystal lattice, the Cartesian symmetry coordinate vector $\boldsymbol{\sigma}$ for the ith atom is constructed as

$$\boldsymbol{\sigma}_i(\boldsymbol{\delta}) = N^{-1/2}\sum_{\boldsymbol{L}}\boldsymbol{X}(\boldsymbol{\rho}_i)\exp(-i\boldsymbol{\rho}_i\cdot\boldsymbol{\delta})\,, \tag{3}$$

where $\boldsymbol{\delta}$ is a phase difference vector (corresponding to a wave vector $\boldsymbol{k}$; $\delta_a=a_0k_a$, $\delta_b=b_0k_b$, $\delta_c=c_0k_c$), N is the total number of unit cells and $\boldsymbol{X}(\boldsymbol{\rho}_i)$ is the Cartesian coordinate vector (x,y,z) of the $\boldsymbol{\rho}_i$th

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[8] P. Higgs, *Proc. Roy. Soc. (London)*, **A220**, 472 (1953).

[9] T. Miyazawa, *J. Chem. Phys.*, **35**, 693 (1961).

[10] H. Sugeta and T. Miyazawa, *ibid.*, **47**, 2034 (1967).

[11] M. Tasumi, T. Shimanouchi and T. Miyazawa, *J. Mol. Spectry.*, **9**, 261 (1962); *ibid.*, **11**, 422 (1963).

[12] M. Born and K. Huang, "Dynamical Theory of Crystal Lattices," Clarendon Press, Oxford (1954).

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

TABLE 1. SYMMETRY OPERATIONS* $[R_u(\boldsymbol{\alpha}_u, \boldsymbol{\tau}_u)]$ OF THE SPACE GROUP *Pnam*

		$\boldsymbol{\alpha}_u$	$\boldsymbol{\tau}_u$
R_1	E	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	(0, 0, 0)
R_2	C_2^a	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	(1/2, 1/2, 1/2)
R_3	C_2^b	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	(1/2, 1/2, 0)
R_4	C_2^c	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	(0, 0, 1/2)
R_5	i	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	(0, 0, 0)
R_6	$\sigma_g(bc)$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	(1/2, 1/2, 1/2)
R_7	$\sigma_g(ac)$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	(1/2, 1/2, 0)
R_8	$\sigma_g(ab)$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	(0, 0, 1/2)

* Components of a nonprimitive translation vector $\boldsymbol{\tau}_u$ are given in units of lattice constants a_0, b_0 and c_0.

atom.

A symmetry operation of a crystal lattice consists of a rotation $(\boldsymbol{\alpha}_u)$ and a nonprimitive translation$(\boldsymbol{\tau}_u)$.[14] For the crystal lattice of orthorhombic polyethylene, symmetry operations are listed in Table 1. A symmetry operation R_u (at the lattice origin $\boldsymbol{L}=0$) will transform the Cartesian coordinate vector $\boldsymbol{X}$ of the $\boldsymbol{\rho}_i$th atom as

$$R_u\boldsymbol{X}(\boldsymbol{\rho}_i) = \boldsymbol{\alpha}_u\boldsymbol{X}(\boldsymbol{\alpha}_u\boldsymbol{\rho}_i+\boldsymbol{\tau}_u) = \boldsymbol{\alpha}_u\boldsymbol{X}(\boldsymbol{\rho}_j) \tag{4}$$

and accordingly will transform the translational-symmetry coordinate $\boldsymbol{\sigma}_i(\boldsymbol{\delta})$ as

$$R_u\boldsymbol{\sigma}_i(\boldsymbol{\delta}) = N^{-1/2}\sum_{\boldsymbol{L}}\boldsymbol{\alpha}_u\boldsymbol{X}(\boldsymbol{\alpha}_u\boldsymbol{\rho}_i+\boldsymbol{\tau}_u)\exp(-i\boldsymbol{\rho}_i\cdot\boldsymbol{\delta}). \tag{5}$$

However, since

$$\boldsymbol{\rho}_i\cdot\boldsymbol{\delta} = (\boldsymbol{\alpha}_u\boldsymbol{\rho}_i)\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta}) \tag{6}$$

the exponential factor in Eq. (5) may be rewritten as

$$\begin{aligned} \exp(-i\boldsymbol{\rho}_i\cdot\boldsymbol{\delta}) &= \exp[-i(\boldsymbol{\alpha}_u\boldsymbol{\rho}_i)\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})] \\ &= \exp[-i(\boldsymbol{\alpha}_u\boldsymbol{\rho}_i+\boldsymbol{\tau}_u)\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})] \times \exp[i\boldsymbol{\tau}_u\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})]. \end{aligned} \tag{7}$$

From Eqs. (3)—(5) and (7), the effect of R_u may finally be given as

$$R_u\boldsymbol{\sigma}_i(\boldsymbol{\delta}) = \boldsymbol{\alpha}_u\boldsymbol{\sigma}_j(\boldsymbol{\alpha}_u\boldsymbol{\delta}) \times \exp[i\boldsymbol{\tau}_u\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})]. \tag{8}$$

Accordingly, the phase-difference vector is now transformed into a vector $\boldsymbol{\alpha}_u\boldsymbol{\delta}$ and the translational-symmetry coordinate $\boldsymbol{\sigma}_i(\boldsymbol{\delta})$ of the ith atom is transformed into the translational-symmetry coordinate $\boldsymbol{\alpha}_u\boldsymbol{\sigma}_j(\boldsymbol{\alpha}_u\boldsymbol{\delta})$ of the jth atom as multiplied with the phase-factor of $\exp[i\boldsymbol{\tau}_u\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})]$. For the carbon atoms of orthorhombic polyethylene, atom-index transformations $i\rightarrow j$ and exponents of phase factors are listed in Table 2.

A $\boldsymbol{k}$ group[14] is defined as the ensemble of space-group operations (R_u) which satisfy the condition.

$$\boldsymbol{\alpha}_u\boldsymbol{\delta} = \boldsymbol{\delta} + 2\pi\boldsymbol{m}, \tag{9}$$

where $\boldsymbol{m}$ is a vector with integral components. Naturally $\boldsymbol{k}$ groups are subgroups of the factor group. Accordingly, the dynamical matrix of the phase-difference vector $\boldsymbol{\delta}$ may be factorized into submatrices, each belonging to an irreducible representation of the $\boldsymbol{k}$ group. For a general phase-difference vector $\boldsymbol{\delta}(\delta_a,\delta_b,\delta_c)$, however, only the identity operation constitutes the $\boldsymbol{k}$ group and the dynamical matrix is not factorized any further.

With the space group *Pnam*, all the eight operations of Table 1 satisfy the condition of Eq. (9) $[\boldsymbol{m}=0]$ for $\boldsymbol{\delta}=0$ and accordingly the $\boldsymbol{k}$ group is the factor group D_{2h} itself. However, for $\boldsymbol{\delta}(\delta_a,0,0)$, only four operations, R_1 (identity), R_2 (twofold

TABLE 2. TRANSFORMATIONS OF ATOM INDICES $(i\rightarrow j)$ AND PHASE-DIFFERENCE VECTORS $(\boldsymbol{\delta}\rightarrow\boldsymbol{\alpha}_u\boldsymbol{\delta})$ AND EXPONENTS $\boldsymbol{\tau}_u\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})$ OF PHASE-FACTORS INVOLVED IN THE EFFECTS OF FACTOR-GROUP OPERATIONS (R_u) UPON TRANSLATIONAL-SYMMETRY COORDINATES $\boldsymbol{\sigma}_i(\boldsymbol{\delta})$

R_u	$i \rightarrow j$				$\boldsymbol{\alpha}_u\boldsymbol{\delta}$	$\boldsymbol{\tau}_u\cdot(\boldsymbol{\sigma}_u\boldsymbol{\delta})$
	$i=1$	2	3	4		
R_1	1	2	3	4	$(\delta_a,\ \delta_b,\ \delta_c)$	0
R_2	3	4	1	2	$(\delta_a,\ -\delta_b,\ -\delta_c)$	$(\delta_a-\delta_b-\delta_c)/2$
R_3	4	3	2	1	$(-\delta_a,\ \delta_b,\ -\delta_c)$	$(-\delta_a+\delta_b)/2$
R_4	2	1	4	3	$(-\delta_a,\ -\delta_b,\ \delta_c)$	$\delta_c/2$
R_5	2	1	4	3	$(-\delta_a,\ -\delta_b,\ -\delta_c)$	0
R_6	4	3	2	1	$(-\delta_a,\ \delta_b,\ \delta_c)$	$(-\delta_a+\delta_b+\delta_c)/2$
R_7	3	4	1	2	$(\delta_a,\ -\delta_b,\ \delta_c)$	$(\delta_a-\delta_b)/2$
R_8	1	2	3	4	$(\delta_a,\ \delta_b,\ -\delta_c)$	$-\delta_c/2$

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[14] J. C. Slater, "Quantum Theory of Molecules and Solid," Vol. 2, McGraw-Hill Company, New York (1965).

TABLE 3. $\boldsymbol{k}$ GROUPS (SYMMETRY OPERATIONS R_u)* FOR THE SPACE GROUP *Pnam*

D_{2h} (R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8)	$\Gamma(0,0,0)$, $X(\pi,0,0)$, $Z(0,\pi,0)$, $Y(0,0,\pi)$ $R(\pi,\pi,\pi)$, $T(0,\pi,\pi)$, $S(\pi,0,\pi)$, $U(\pi,\pi,0)$
C_{2v} (R_1, R_2, R_7, R_8)	$\Sigma(\delta_a,0,0)$, $A(\delta_a,\pi,0)$, $C(\delta_a,0,\pi)$, $E(\delta_a,\pi,\pi)$
C_{2v} (R_1, R_3, R_6, R_8)	$\Lambda(0,\delta_b,0)$, $H(0,\delta_b,\pi)$, $G(\pi,\delta_b,0)$, $Q(\pi,\delta_b,\pi)$
C_{2v} (R_1, R_4, R_6, R_7)	$\Delta(0,0,\delta_c)$, $D(\pi,0,\delta_c)$, $B(0,\pi,\delta_c)$, $F(\pi,\pi,\delta_c)$
C_s (R_1, R_6)	$(0,\delta_b,\delta_c)$, (π,δ_b,δ_c)
C_s (R_1, R_7)	$(\delta_a,0,\delta_c)$, (δ_a,π,δ_c)
C_s (R_1, R_8)	$(\delta_a,\delta_b,0)$, (δ_a,δ_b,π)
C_1 (R_1)	$(\delta_a,\delta_b,\delta_c)$

* $0<\delta<\pi$

screw axis along the a axis), R_7 (glide plane normal to the b axis) and R_8 (glide plane normal to the c axis) satisfy Eq. (9) [$\boldsymbol{m}=0$] and therefore the $\boldsymbol{k}$ group is C_{2v}. Finally, for $\boldsymbol{\delta}(\pi,0,0)$, remaining four operations of R_3 (twofold screw axis along the b axis), R_4 (twofold screw axis along the c axis), R_5 (inversion) and R_6 (glide plane normal to the a axis) satisfy Eq. (9) [$\boldsymbol{m}=(-1,0,0)$] and the $\boldsymbol{k}$ group again becomes D_{2h}. All the $\boldsymbol{k}$ groups of the space group *Pnam* are given in Table 3, where BSW notation[15] was followed for special phase-difference vectors.

Irreducible Representations

Irreducible representations of $\boldsymbol{k}$ groups were given by Slater[14] for 20 space groups including D_{2h}^{16}-*Pnam*. On the other hand, Kovalev[16] treated all the 230 space groups with the use of multiplier representation method. However, for polymer-chain crystals, it is a common practice to take the c axis parallel to the chain-direction and accordingly the space group of orthorhombic polyethylene is preferably taken as *Pnam* rather than *Pnam*. Furthermore, in the field of molecular dynamics, the effect of symmetry operations given in Eq. (8) is more intelligible than the reverse one (Slater[14]). In the present study, therefore, basis functions and irreducible representations for all the $\boldsymbol{k}$ groups of *Pnam* were derived on the basis of multiplication tables.

Successive applications of point-group operations is equivalent to one of point-group operations, whereas for a space group, effects of nonprimitive translations ($\boldsymbol{\tau}_u$) are involved. Suppose a symmetry operation R_u operates on a translational-symmetry coordinate vector and then R_v operates on the resulting coordinate vector, then from Eq. (8), we have

$$\begin{aligned} R_vR_u\boldsymbol{\sigma}_i(\boldsymbol{\delta}) &= R_v[\boldsymbol{\alpha}_u\boldsymbol{\sigma}_j(\boldsymbol{\alpha}_u\boldsymbol{\delta})]\exp[i\boldsymbol{\tau}_u\cdot(\boldsymbol{\alpha}_u\boldsymbol{\delta})] \\ &= \boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\sigma}_k(\boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\delta})\exp[i\boldsymbol{\tau}_v\cdot(\boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\delta})]\exp[i\boldsymbol{\tau}_u\cdot\boldsymbol{\alpha}_u\boldsymbol{\delta})] \\ &= \boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\sigma}_k(\boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\delta})\exp[i(\boldsymbol{\alpha}_v\boldsymbol{\tau}_u+\boldsymbol{\tau}_v)\cdot(\boldsymbol{\alpha}_v\boldsymbol{\alpha}_u\boldsymbol{\delta})]\,, \end{aligned} \tag{10}$$

where the symmetry operation R_v transfers $\boldsymbol{\rho}_j$th atom to the site of a $\boldsymbol{\rho}_k$th atom. The multiplication rule for the rotational parts is identical with the case of point-group operations

$$\boldsymbol{\alpha}_v\boldsymbol{\alpha}_u = \boldsymbol{\alpha}_w. \tag{11}$$

However with a space group, $\boldsymbol{\tau}_v+\boldsymbol{\alpha}_v\boldsymbol{\tau}_u$ is not necessarily equal to $\boldsymbol{\tau}_w$. Accordingly, the effect of two successive space-group operations on a translational-symmetry coordinate may be written as

$$R_vR_u\boldsymbol{\sigma}_i(\boldsymbol{\delta}) = \exp[i(\Delta\boldsymbol{\tau})\cdot(\boldsymbol{\alpha}_w\boldsymbol{\delta})]R_w\boldsymbol{\sigma}_i(\boldsymbol{\delta}), \tag{12}$$

where

$$\Delta\boldsymbol{\tau} = \boldsymbol{\alpha}_v\boldsymbol{\tau}_u + \boldsymbol{\tau}_v - \boldsymbol{\tau}_w. \tag{13}$$

For the space-group *Pnam*, $\Delta\boldsymbol{\tau}$ vectors were derived for all possible combinations of symmetry operations (R_1—R_8) and the multiplication table is shown in Table 4. From this table, basis functions for irreducible representations may be constructed. Irreducible representations for all the $\boldsymbol{k}$ groups of *Pnam* were described by Kitagawa.[17] In the present paper, however, representations of a few $\boldsymbol{k}$ groups will now be discussed.

For the phase-difference vector of $\boldsymbol{\delta}(\delta_a,0,0)$, the $\boldsymbol{k}$ group includes four operations, R_1, R_2, R_7 and R_8 (Table 3). The operations R_2 and R_7 are associated with nonzero components of $\boldsymbol{\tau}_u$ along the a axis but the operations R_1 and R_8 are not (Table 1). Accordingly, basis functions were constructed as

$$\left.\begin{aligned} \phi_1 &= [R_1+R_8+\omega_a{}^*(R_2+R_7)]\phi_0 \\ \phi_2 &= [R_1+R_8-\omega_a{}^*(R_2+R_7)]\phi_0 \\ \phi_3 &= [R_1-R_8+\omega_a{}^*(R_2-R_7)]\phi_0 \\ \phi_4 &= [R_1-R_8-\omega_a{}^*(R_2-R_7)]\phi_0 \end{aligned}\right\}, \tag{14}$$

where

$$\omega_a = \exp(i\delta_a/2). \tag{15}$$

According to the multiplication table (Table 4), these basis functions are transformed with symmetry operations as

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15) L. P. Bouckaert, R. Smoluchowski and E. Wigner, *Phys. Rev.*, **50**, 58 (1936).

16) O. Kovalev (originally published in Russian in 1958 and later translated into English by A. M. Gross), "Irreducible Representations of the Space Groups," Gordon and Breach, Ltd., New York (1965).

17) T. Kitagawa, "Crystal Dynamics and Related Solid State Properties of Polymers," Thesis, Osaka University, Chapter IV and Appendix I (1969).

TABLE 4. MULTIPLICATION TABLE* FOR THE SPACE GROUP OPERATIONS (R_vR_u) OF *Pnam*

R_v	R_u							
	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
R_1	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
R_2	R_2	$e^{a}R_1$	$e^{-a}R_4$	R_3	R_6	$e^{-a}R_5$	$e^{a}R_8$	R_7
R_3	R_3	$e^{-b-c}R_4$	$e^{b}R_1$	$e^{c}R_2$	R_7	$e^{b+c}R_8$	$e^{-b}R_5$	$e^{-c}R_6$
R_4	R_4	$e^{a-b-c}R_3$	$e^{-a+b}R_2$	$e^{c}R_1$	R_8	$e^{-a+b+c}R_7$	$e^{a-b}R_6$	$e^{-c}R_5$
R_5	R_5	$e^{a-b-c}R_6$	$e^{-a+b}R_7$	$e^{c}R_8$	R_1	$e^{-a+b+c}R_2$	$e^{a-b}R_3$	$e^{-c}R_4$
R_6	R_6	$e^{-b-c}R_5$	$e^{b}R_8$	$e^{c}R_7$	R_2	$e^{b+c}R_1$	$e^{-b}R_4$	$e^{-c}R_3$
R_7	R_7	$e^{a}R_8$	$e^{-a}R_5$	R_6	R_3	$e^{-a}R_4$	$e^{a}R_1$	R_2
R_8	R_8	R_7	R_6	R_5	R_4	R_3	R_2	R_1

* For example, $e^{\pm a}=\exp(\pm i\delta_a)$, $e^{-a+b}=\exp(-i\delta_a+i\delta_b)$, $e^{a-b}=\exp(i\delta_a-i\delta_b)$, $e^{b+c}=\exp(i\delta_b+i\delta_c)$, $e^{-b-c}=\exp(-i\delta_b-i\delta_c)$, $e^{a-b-c}=\exp(i\delta_a-i\delta_b-i\delta_c)$, and $e^{-a+b+c}=\exp(-i\delta_a+i\delta_b+i\delta_c)$.

TABLE 5. MATRIX ELEMENTS* FOR IRREDUCIBLE REPRESENTATIONS OF $\Sigma(\delta_a,0,0)$, $A(\delta_a,\pi,0)$, $C(\delta_a,0,\pi)$, $E(\delta_a,\pi,\pi)$, $\Lambda(0,\delta_b,0)$, $G(\pi,\delta_b,0)$, and $\Delta(0,0,\delta_c)$

				R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
Σ_1	A_1	C_1	E_1	1	ω_a					ω_a	1
Σ_2	A_2	C_2	E_2	1	$-\omega^a$					$-\omega_a$	1
Σ_3	A_3	C_3	E_3	1	ω_a					$-\omega_a$	-1
Σ_4	A_4	C_4	E_4	1	$-\omega_a$					ω_a	-1
Λ_1		G_1		1		ω_b			ω_b		1
Λ_2		G_2		1		$-\omega_b$			ω_b		-1
Λ_3		G_3		1		ω_b			$-\omega_b$		-1
Λ_4		G_4		1		$-\omega_b$			$-\omega_b$		1
Δ_1				1			ω_c		ω_c	1	
Δ_2				1			$-\omega_c$		ω_c	-1	
Δ_3				1			ω_c		$-\omega_c$	-1	
Δ_4				1			$-\omega_c$		$-\omega_c$	1	

* $0<\delta_a, \delta_b, \delta_c<\pi$; $\omega_a=\exp(i\delta_a/2)$, $\omega_b=\exp(i\delta_b/2)$ and $\omega_c=\exp(i\delta_c/2)$.

TABLE 6. IRREDUCIBLE REPRESENTATIONS OF $\Gamma(0,0,0)$

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
$\Gamma_1(A_g)$	1	1	1	1	1	1	1	1
$\Gamma_2(A_u)$	1	1	1	1	-1	-1	-1	-1
$\Gamma_3(B_{3g})$	1	-1	-1	1	1	-1	-1	1
$\Gamma_4(B_{3u})$	1	-1	-1	1	-1	1	1	-1
$\Gamma_5(B_{1g})$	1	1	-1	-1	1	1	-1	-1
$\Gamma_6(B_{1u})$	1	1	-1	-1	-1	-1	1	1
$\Gamma_7(B_{2g})$	1	-1	1	-1	1	-1	1	-1
$\Gamma_8(B_{2u})$	1	-1	1	-1	-1	1	-1	1

$$\left.\begin{array}{llll}
R_1\phi_1=\phi_1 & R_2\phi_1=\omega_a\phi_1 & R_7\phi_1=\omega_a\phi_1 & \\
 & & & R_8\phi_1=\phi_1 \\
R_1\phi_2=\phi_2 & R_2\phi_2=-\omega_a\phi_2 & R_7\phi_2=-\omega_a\phi_2 & \\
 & & & R_8\phi_2=\phi_2 \\
R_1\phi_3=\phi_3 & R_2\phi_3=\omega_a\phi_3 & R_7\phi_3=-\omega_a\phi_3 & \\
 & & & R_8\phi_3=-\phi_3 \\
R_1\phi_4=\phi_4 & R_2\phi_4=-\omega_a\phi_4 & R_7\phi_4=\omega_a\phi_4 & \\
 & & & R_8\phi_4=-\phi_4
\end{array}\right\} \tag{16}$$

For the **k** group of $\Sigma(\delta_a,0,0)$, the irreducible representations are all one-dimensional (see Table 5) where ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are basis functions of Σ_1, Σ_2, Σ_3, and Σ_4, respectively (these correspond to the species A_1, B_2, A_2, and B_1 of the point group C_{2v}). The multiplication tables for $A(\delta_a,\pi,0)$, $C(\delta_a,0,\pi)$ and $E(\delta_a,\pi,\pi)$ are common with the table for $\Sigma(\delta_a,0,0)$ and accordingly the matrix elements of irreducible representations are shown commonly in Table 5.

For $\Lambda(0,\delta_b,0)$, $H(0,\delta_b,\pi)$, $G(\pi,\delta_b,0)$ and $Q(\pi,\delta_b,\pi)$, the **k** group (C_{2v}) includes four operations (R_1, R_3, R_6, and R_8). However, the multiplication table of Λ and G is different from that of H and Q.

TABLE 7. IRREDUCIBLE REPRESENTATION OF $X(\pi, 0, 0)$

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
X_1	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$
X_2	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&-1\end{bmatrix}$

TABLE 8. IRREDUCIBLE REPRESENTATIONS OF $U(\pi, \pi, 0)$

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
U_1	1	i	i	1	1	i	i	1
U_2	1	$-i$	$-i$	1	1	$-i$	$-i$	1
U_3	1	i	i	1	-1	$-i$	$-i$	-1
U_4	1	$-i$	$-i$	1	-1	i	i	-1
U_5	1	i	$-i$	-1	1	i	$-i$	-1
U_6	1	$-i$	i	-1	1	$-i$	i	-1
U_7	1	i	$-i$	-1	-1	$-i$	i	1
U_8	1	$-i$	i	-1	-1	i	$-i$	1

TABLE 9. IRREDUCIBLE REPRESENTATIONS OF $R(\pi, \pi, \pi)$

	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
R_1	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-i&0\\0&i\end{bmatrix}$	$\begin{bmatrix}0&i\\i&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-i\\i&0\end{bmatrix}$	$\begin{bmatrix}i&0\\0&i\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$
R_2	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}i&0\\0&-i\end{bmatrix}$	$\begin{bmatrix}0&-i\\-i&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&i\\-i&0\end{bmatrix}$	$\begin{bmatrix}-i&0\\0&-i\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$

The irreducible representations of Λ and G (Table 5) are one-dimensional whereas those of H and Q are two-dimensional.17)

For special points of $(0,\delta_b,\delta_c)$, (π,δ_b,δ_c), $(\delta_a,0,\delta_c)$, (δ_a,π,δ_c), $(\delta_a,\delta_b,0)$ and (δ_a,δ_b,π), the $\boldsymbol{k}$ group is C_s (Table 3) and the dynamical matrix is factorized into two matrices after suitable symmetry transformations (there are no BSW symbols for these special points in the first Brillouin zone).

For $\Gamma(0,0,0)$, the factor group D_{2h} is $\boldsymbol{k}$ group itself and the irreducible representations are shown in Table 6. For each of $X(\pi,0,0)$, $Z(0,\pi,0)$, $Y(0,0,\pi)$, and $T(0,\pi,\pi)$, the $\boldsymbol{k}$ group again becomes D_{2h}. However, in contrast with the one-dimensional representations of Γ (Table 6), irreducible representations of X (Table 7), Z, Y, and T are two-dimensional.

For $U(\pi,\pi,0)$, the $\boldsymbol{k}$ group is also D_{2h}. With the following basis functions,

$$\left.\begin{aligned}
\varphi_1(U_1') &= (R_1+R_4+R_5+R_8)\phi_0\\
\varphi_2(U_1') &= (R_2+R_3+R_6+R_7)\phi_0\\
\varphi_1(U_2') &= (R_1+R_4-R_5-R_8)\phi_0\\
\varphi_2(U_2') &= (R_2+R_3-R_6-R_7)\phi_0\\
\varphi_1(U_3') &= (R_1-R_4+R_5-R_8)\phi_0\\
\varphi_2(U_3') &= (R_2-R_3+R_6-R_7)\phi_0\\
\varphi_1(U_4') &= (R_1-R_4-R_5+R_8)\phi_0\\
\varphi_2(U_4') &= (R_2-R_3-R_6+R_7)\phi_0
\end{aligned}\right\}\qquad(17)$$

four two-dimensional representations (real) are obtained. However, from group theory, the sum of squared dimensionalities of irreducible representations should be equal to the number of symmetry operations. In fact, four two-dimensional representations are reduced to eight one-dimensional representations (Table 8). Finally for $S(\pi,0,\pi)$ and $R(\pi,\pi,\pi)$, a four-dimensional representation (real) is obtained with the following basis functions,

$$\left.\begin{aligned}
\varphi_1 &= (R_1+R_8+R_2+R_7)\phi_0\\
\varphi_2 &= (R_1+R_8-R_2-R_7)\phi_0\\
\varphi_3 &= (R_5+R_4+R_6+R_3)\phi_0\\
\varphi_4 &= (R_5+R_4-R_6-R_3)\phi_0.
\end{aligned}\right\}\qquad(18)$$

However, the four-dimensional representation is reduced to two two-dimensional representations (Table 9). Dimensionalities (f_s) of irreducible representations are summarized in Table 11.

Degeneracy of Crystal Vibrations

The relation between the dimensionality of irreducible representations and degeneracy of crystal vibrations was generally treated by Maradudin and Vosko18) with the use of the irreducible multiplier co-representation method. The pth frequency parameter $[\lambda_p(\boldsymbol{\delta})]$ and characteristic vector $[\boldsymbol{L}_p(\boldsymbol{\delta})]$ of the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ are given by

$$\lambda_p(\boldsymbol{\delta})\boldsymbol{L}_p(\boldsymbol{\delta}) = \boldsymbol{D}_S(\boldsymbol{\delta})\boldsymbol{L}_p(\boldsymbol{\delta}).\qquad(19)$$

The unitary matrix, $\boldsymbol{T}(\boldsymbol{\alpha}_u,\boldsymbol{\tau}_u)$, associated with the

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18) A. A. Maradudin and S. H. Vosko, *Rev. Modern Phys.*, **40**, 1 (1968)

uth operation of the space group was derived and a similarity transformation of the dynamical matrix may be carried out, yielding[18)]

$$\boldsymbol{T}(\boldsymbol{\alpha}_u,\ \boldsymbol{\tau}_u)\boldsymbol{D}_S(\boldsymbol{\delta})\boldsymbol{T}(\boldsymbol{\alpha}_u,\ \boldsymbol{\tau}_u)^{-1} = \boldsymbol{D}_S(\boldsymbol{\alpha}_u\boldsymbol{\delta}) \tag{20}$$

and accordingly

$$\boldsymbol{\Lambda}(\boldsymbol{\delta}) = \boldsymbol{\Lambda}(\boldsymbol{\alpha}_u\boldsymbol{\delta}). \tag{21}$$

Therefore the irreducible volume of the first Brillouin zone depends upon the factor-group symmetry. For D_{2h} systems, the irreducible volume is one-eighth of the first Brillouin zone and treatments of crystal vibrations for $0 \leq \delta_a, \delta_b, \delta_c \leq \pi$ are sufficient.

For a unitary-type operation R_u of the $\boldsymbol{k}$ group $(\boldsymbol{\alpha}_u\boldsymbol{\delta} = \boldsymbol{\delta})$, $\boldsymbol{T}(\boldsymbol{\alpha}_u, \boldsymbol{\tau}_u)$ commutes with $\boldsymbol{D}_S(\boldsymbol{\delta})$ so that Eq. (19) is transformed,

$$\lambda_p(\boldsymbol{\delta})\{\boldsymbol{T}(\boldsymbol{\alpha}_u,\ \boldsymbol{\tau}_u)\boldsymbol{L}_p(\boldsymbol{\delta})\} = \boldsymbol{D}_S(\boldsymbol{\delta})\{\boldsymbol{T}(\boldsymbol{\alpha}_u,\ \boldsymbol{\tau}_u)\boldsymbol{L}_p(\boldsymbol{\delta})\}. \tag{22}$$

On the other hand, for an antiunitary-type operation (R_w) of the space group which inverts the phase-difference vector $(\boldsymbol{\alpha}_w\boldsymbol{\delta} = -\boldsymbol{\delta})$, Eq. (19) is transformed into

$$\begin{aligned}\lambda_p(\boldsymbol{\delta})\{\boldsymbol{T}(\boldsymbol{\alpha}_w,\ \boldsymbol{\tau}_w)\boldsymbol{L}_p(\boldsymbol{\delta})\} &= \boldsymbol{D}_S(-\boldsymbol{\delta})\{\boldsymbol{T}(\boldsymbol{\alpha}_w,\ \boldsymbol{\tau}_w)\boldsymbol{L}_p(\boldsymbol{\delta})\} \\ &= \boldsymbol{D}_S(\boldsymbol{\delta})^*\{\boldsymbol{T}(\boldsymbol{\alpha}_w,\ \boldsymbol{\tau}_w)\boldsymbol{L}_p(\boldsymbol{\delta})\}.\end{aligned} \tag{23}$$

Accordingly, if $\boldsymbol{T}(\boldsymbol{\alpha}_w,\boldsymbol{\tau}_w)\boldsymbol{L}_p(\boldsymbol{\delta})$ and $\boldsymbol{T}(\boldsymbol{\alpha}_u,\boldsymbol{\tau}_u)\boldsymbol{L}_p(\boldsymbol{\delta})$ are linearly independent of each other, so-called time-reversal degeneracy arises over space degeneracy [dimensionality (f_s) of irreducible representation]. According to Maradudin,[18)] time-reversal degeneracy may be studied after treating

$$\Phi = \sum_u \phi(\boldsymbol{\delta}, R_aR_u)\chi^{\mu}(\boldsymbol{\delta}, R_aR_uR_aR_u), \tag{24}$$

where R_a is any antiunitary operation and $\phi(\boldsymbol{\delta},R_w)$ is the multiplier representation of an antiunitary operation $(R_w \leftarrow R_aR_u)$.

$$\phi(\boldsymbol{\delta},R_w) = \exp[-i(\boldsymbol{\delta}+\boldsymbol{\alpha}_w{}^{-1}\boldsymbol{\delta})\cdot\boldsymbol{\tau}_w]. \tag{25}$$

As an example of $\sum(\delta_a,0,0)$ of the space group *Pnam*, R_1, R_2, R_7, and R_8 are unitary-type operations whereas R_3, R_4, R_5, and R_6, are antiunitary-type operations. The inversion operation (R_5) always serves as an antiunitary operation for any phase-difference vector and is preferably used as R_a. In Eq. (24), $\chi^{\mu}(\boldsymbol{\delta},R_aR_uR_aR_u)$ is the character of the μth irreducible representation for the operation $R_aR_uR_aR_u$. Summation runs over all the operations of a $\boldsymbol{k}$ group, and if Φ is equal to the order (g) of the $\boldsymbol{k}$ group, time-reversal degeneracy does not arise but, if Φ is equal to $-g$ or equal to 0, time-reversal degeneracy arises.[18)] Accordingly with an f_s-dimensional representation of a $\boldsymbol{k}$ group, crystal vibrations are f_s-fold degenerate for $\Phi/g=1$ but are $2f_s$-fold degenerate for $\Phi/g=-1$ or 0. Formulas of $\phi(\boldsymbol{\delta},R_w)$ were obtained, as shown in Table 11, for symmetry operations of the space group *Pnam*, and the values of Φ/g were calculated as listed in Table 10. The time-reversal degeneracy $(t_s=2)$ is now expected for U, S, R, A, C, E, G, F, and Q. It may be remarked that crystal vibrations

TABLE 10. DEGENERACY DUE TO TIME REVERSAL SYMMETRY (t_s) AND TO SPACE SYMMETRY (f_s)

Point	Φ/g*	t_s	f_s	t_sf_s
$\Gamma(0,0,0)$	1	1	1	1
$X(\pi,0,0)$, $Z(0,\pi,0)$, $Y(0,0,\pi)$, $T(0,\pi,\pi)$	1	1	2	2
$U(\pi,\pi,0)$	0	2	1	2
$S(\pi,0,\pi)$, $R(\pi,\pi,\pi)$	0	2	2	4
$\sum(\delta_a,0,0)$, $\Lambda(0,\delta_b,0)$, $\Delta(0,0,\delta_c)$	1	1	1	1
$H(0,\delta_b,\pi)$, $B(0,\pi,\delta_c)$, $D(\pi,0,\delta_c)$	1	1	2	2
$A(\delta_a,\pi,0)$, $C(\delta_a,0,\pi)$, $E(\delta_a,\pi,\pi)$, $G(\pi,\delta_b,0)$, $F(\pi,\pi,\delta_c)$	0	2	1	2
$Q(\pi,\delta_b,\pi)$	−1	2	2	4
$(0,\delta_b,\delta_c)$, $(\delta_a,0,\delta_c)$, $(\delta_a,\delta_b,0)$	1	1	1	1
(π,δ_b,δ_c), (δ_a,π,δ_c), (δ_a,δ_b,π)	0	2	1	2
$(\delta_a,\delta_b,\delta_c)$	1	1	1	1

* $t_s=1$ for $\Phi/g=1$ but $t_s=2$ for $\Phi/g=-1$ or 0.

TABLE 11. MULTIPLIER REPRESENTATIONS FOR THE SPACE GROUP *Pnam* $(R_a=R_5,\ R_aR_u\rightarrow R_w)$

R_u	R_w	$\boldsymbol{\delta}+\boldsymbol{\alpha}_w{}^{-1}\boldsymbol{\delta}$	τ_w	$\phi(\boldsymbol{\delta},R_w)$
R_1	R_5	$(0,0,0)$	$(0,0,0)$	1
R_2	R_6	$(0,2\delta_b,2\delta_c)$	$(1/2,1/2,1/2)$	$\exp[-i(\delta_b+\delta_c)]$
R_3	R_7	$(2\delta_a,0,2\delta_c)$	$(1/2,1/2,0)$	$\exp[-i\delta_a]$
R_4	R_8	$(2\delta_a,2\delta_b,0)$	$(0,0,1/2)$	1
R_5	R_1	$(2\delta_a,2\delta_b,2\delta_c)$	$(0,0,0)$	1
R_6	R_2	$(2\delta_a,0,0)$	$(1/2,1/2,1/2)$	$\exp[-i\delta_a]$
R_7	R_3	$(0,2\delta_b,0)$	$(1/2,1/2,0)$	$\exp[-i\delta_b]$
R_8	R_4	$(0,0,2\delta_c)$	$(0,0,1/2)$	$\exp[-i\delta_c]$

are doulby-degenerate ($t_s f_s = 2$) if a component of the phase-difference vector is equal to π. If more than two components are equal to π, crystal vibrations are doubly-degenerate ($t_s f_s = 2$ for T, U, E, and F) or fourfold-degenerate ($t_s f_s = 4$ for S, R, and Q).

Symmetry Coordinates of Polyethylene

Symmetry coordinates of a crystal lattice for the μth symmetry species may be constructed from the sum of $\sum_u K_\mu(R_u)^* R_u \boldsymbol{\sigma}_i(\boldsymbol{\delta})$ over symmetry operations of the $\boldsymbol{k}$ group, where $K_\mu(R_u)^*$ is the complex conjugate of a matrix element (for R_u) of the μth irreducible representation of the $\boldsymbol{k}$ group.

The symmetry coordinates of orthorhombic polyethylene for $\Gamma(0,0,0)$ may be constructed from Tables 2 and 6, as follows.

$$\left.\begin{array}{ll}
\Gamma_1(A_g) & S_1 = (\sigma_1{}^x - \sigma_2{}^x + \sigma_3{}^x - \sigma_4{}^x)/2 \\
 & S_2 = (\sigma_1{}^y - \sigma_2{}^y - \sigma_3{}^y + \sigma_4{}^y)/2 \\
\Gamma_2(A_u) & S_3 = (\sigma_1{}^z + \sigma_2{}^z - \sigma_3{}^z - \sigma_4{}^z)/2i \\
\Gamma_3(B_{3g}) & S_4 = (\sigma_1{}^x - \sigma_2{}^x - \sigma_3{}^x + \sigma_4{}^x)/2 \\
 & S_5 = (\sigma_1{}^y - \sigma_2{}^y + \sigma_3{}^y - \sigma_4{}^y)/2 \\
\Gamma_4(B_{3u}) & S_6 = (\sigma_1{}^z + \sigma_2{}^z + \sigma_3{}^z + \sigma_4{}^z)/2i \\
\Gamma_5(B_{1g}) & S_7 = (\sigma_1{}^z - \sigma_2{}^z - \sigma_3{}^z + \sigma_4{}^z)/2 \\
\Gamma_6(B_{1u}) & S_8 = (\sigma_1{}^x + \sigma_2{}^x + \sigma_3{}^x + \sigma_4{}^x)/2i \\
 & S_9 = (\sigma_1{}^y + \sigma_2{}^y - \sigma_3{}^y - \sigma_4{}^y)/2i \\
\Gamma_7(B_{2g}) & S_{10} = (\sigma_1{}^z - \sigma_2{}^z + \sigma_3{}^z - \sigma_4{}^z)/2 \\
\Gamma_8(B_{2u}) & S_{11} = (\sigma_1{}^x + \sigma_2{}^x - \sigma_3{}^x - \sigma_4{}^x)/2i \\
 & S_{12} = (\sigma_1{}^y + \sigma_2{}^y + \sigma_3{}^y + \sigma_4{}^y)/2i
\end{array}\right\} \quad (26)$$

TABLE 12. SYMMETRY COORDINATES (S_1—S_{12}) FOR SYMMETRY SPECIES* OF $\boldsymbol{k}$ GROUPS**

	Γ	Σ	Λ	Δ
S_1	1	1	1	1
S_2	1	1	1	1
S_3	2	3	3	3
S_4	3	2	4	3
S_5	3	2	4	3
S_6	4	4	2	1
S_7	5	3	2	2
S_8	6	1	4	4
S_9	6	1	4	4
S_{10}	7	4	3	4
S_{11}	8	2	1	2
S_{12}	8	2	1	2
	0	δ_a	0	0
$\boldsymbol{\delta}$	0	0	δ_b	0
	0	0	0	δ_c

* For examples, numerals of 1, 2, 3,… in the column headed with Γ denote $\Gamma_1, \Gamma_2, \Gamma_3, \cdots$.

** $0 < \delta_a, \delta_b, \delta_c < \pi$.

It may be recalled here that translational-symmetry coordinates ($\sigma_i{}^x, \sigma_i{}^y$, and $\sigma_i{}^z$) are functions of phase-difference vector $\boldsymbol{\delta}$ as shown in Eq. (3), so are $S_1(\boldsymbol{\delta})$—$S_{12}(\boldsymbol{\delta})$. From analyses of the effects of symmetry operations, these symmetry coordinates (S_1—S_{12}) are found useful, as themselves, for $\Sigma(\delta_a,0,0)$, $\Lambda(0,\delta_b,0)$, and $\Delta(0,0,\delta_c)$. As examples, symmetry coordinates of S_1, S_2, S_8, and S_9 may be used for the Σ_1 species, S_4, S_5, S_{11}, and S_{12} for the Σ_2 species, S_3 and S_7 for the Σ_3 species, and S_6 and S_{10} for the Σ_4 species. Furthermore the symmetry coordinates of Eq. (26) may be used for $(0,\delta_b,\delta_c)$, $(\delta_a,0,\delta_c)$, $(\delta_a,\delta_b,0)$, and $(\delta_a,\delta_b,\delta_c)$ and also for phase-difference vectors $\boldsymbol{\delta}$ on boundaries of the first Brillouin zone. It may be remarked that, for any phase difference vector, the real parts of the symmetry coordinates of Eq. (26) are symmetric with respect to the inversion operation whereas the imaginary parts are antisymmetric. Accordingly, the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ associated with $S_1(\boldsymbol{\delta})$—$S_{12}(\boldsymbol{\delta})$ are real. Elements of the dynamical matrix are functions of $\boldsymbol{\delta}(\delta_a,\delta_b,\delta_c)$ and the vibrational frequencies for a $\boldsymbol{\delta}$ vector may be calculated after diagonalization of the dynamical matrix.

As a few examples of $X(\pi,0,0)$, $U(\pi,\pi,0)$, and $R(\pi,\pi,\pi)$, degeneracy of crystal vibrations will now be discussed from analyses of symmetry coordinates. For $X(\pi,0,0)$, symmetry coordinates may be constructed from $\sum_u X_\mu(R_u)^* R_u \boldsymbol{\sigma}_i$ (Tables 2 and 7) as follows.

$$\left.\begin{array}{l}
S(X_1)_{1a} = (\sigma_1{}^x - i\sigma_4{}^x)/2^{1/2} \\
\qquad S(X_1)_{1b} = (-\sigma_2{}^x - i\sigma_3{}^x)/2^{1/2} \\
S(X_1)_{2a} = (-\sigma_2{}^x + i\sigma_3{}^x)/2^{1/2} \\
\qquad S(X_1)_{2b} = (\sigma_1{}^x + i\sigma_4{}^x)/2^{1/2} \\
S(X_1)_{3a} = (\sigma_1{}^y + i\sigma_4{}^y)/2^{1/2} \\
\qquad S(X_1)_{3b} = (-\sigma_2{}^y + i\sigma_3{}^y)/2^{1/2} \\
S(X_1)_{4a} = (-\sigma_2{}^y - i\sigma_3{}^y)/2^{1/2} \\
\qquad S(X_1)_{4b} = (\sigma_1{}^y - i\sigma_4{}^y)/2^{1/2} \\
S(X_2)_{5a} = (\sigma_1{}^z - i\sigma_4{}^z)/2^{1/2} \\
\qquad S(X_2)_{5b} = (\sigma_2{}^z + i\sigma_3{}^z)/2^{1/2} \\
S(X_2)_{6a} = (\sigma_2{}^z - i\sigma_3{}^z)/2^{1/2} \\
\qquad S(X_2)_{6b} = (\sigma_1{}^z + i\sigma_4{}^z)/2^{1/2}
\end{array}\right\} \quad (27)$$

Now, from Table 2 and Eqs. (2) and (3), effects of inversion (R_5) are

$$\left.\begin{array}{l}
R_5\boldsymbol{\sigma}_1(\pi,0,0) = -\boldsymbol{\sigma}_2(-\pi,0,0) = -\boldsymbol{\sigma}_2(\pi,0,0) \\
R_5\boldsymbol{\sigma}_3(\pi,0,0) = -\boldsymbol{\sigma}_4(-\pi,0,0) = \boldsymbol{\sigma}_4(\pi,0,0)
\end{array}\right\} \quad (28)$$

Accordingly, pairs (a and b) of symmetry coordinate vectors of $X(\pi,0,0)$ are transformed upon inversion as follows,

$$\left.\begin{array}{l}
S(X_1)_a \leftrightarrow S(X_1)_b \\
S(X_2)_a \leftrightarrow -S(X_2)_b
\end{array}\right\} \quad (29)$$

and crystal vibrations are doubly degenerate for X_1 and X_2.

Next, for $U(\pi,\pi,0)$, symmetry coordinates may be constructed from Tables 2 and 8 as follows.

$$\left.\begin{aligned}
S(U_1)_1 &= [(\sigma_1{}^x-\sigma_2{}^x) - i(\sigma_3{}^x-\sigma_4{}^x)]/2\\
S(U_1)_2 &= [(\sigma_1{}^y-\sigma_2{}^y) + i(\sigma_3{}^y-\sigma_4{}^y)]/2\\
S(U_2)_1 &= [(\sigma_1{}^x-\sigma_2{}^x) + i(\sigma_3{}^x-\sigma_4{}^x)]/2\\
S(U_2)_2 &= [(\sigma_1{}^y-\sigma_2{}^y) - i(\sigma_3{}^y-\sigma_4{}^y)]/2\\
S(U_3)_3 &= [(\sigma_1{}^z+\sigma_2{}^z) + i(\sigma_3{}^z+\sigma_4{}^z)]/2\\
S(U_4)_3 &= [(\sigma_1{}^z+\sigma_2{}^z) - i(\sigma_3{}^z+\sigma_4{}^z)]/2\\
S(U_5)_4 &= [(\sigma_1{}^z-\sigma_2{}^z) + i(\sigma_3{}^z-\sigma_4{}^z)]/2\\
S(U_6)_4 &= [(\sigma_1{}^z-\sigma_2{}^z) - i(\sigma_3{}^z-\sigma_4{}^z)]/2\\
S(U_7)_5 &= [(\sigma_1{}^x+\sigma_2{}^x) - i(\sigma_3{}^x+\sigma_4{}^x)]/2\\
S(U_7)_6 &= [(\sigma_1{}^y+\sigma_2{}^y) + i(\sigma_3{}^y+\sigma_4{}^y)]/2\\
S(U_8)_5 &= [(\sigma_1{}^x+\sigma_2{}^x) + i(\sigma_3{}^x+\sigma_4{}^x)]/2\\
S(U_8)_6 &= [(\sigma_1{}^y+\sigma_2{}^y) - i(\sigma_3{}^y+\sigma_4{}^y)]/2
\end{aligned}\right\} \qquad (30)$$

However, since translational-symmetry coordinate vectors $\boldsymbol{\sigma}_1$—$\boldsymbol{\sigma}_4$ are all real for $U(\pi,\pi,0)$, symmetry coordinates of (U_1 and U_2), (U_3 and U_4), (U_5 and U_6) and (U_7 and U_8) are mutually conjugate and accordingly crystal vibrations of these pairs are doubly degenerate due to time-reversal symmetry ($t_s=2$, see Table 10).

Finally, for $R(\pi,\pi,\pi)$, symmetry coordinates may be obtained from Tables 2 and 9 as follows.

$$\left.\begin{aligned}
S(R_1)_{1a} &= (\sigma_1{}^x+i\sigma_3{}^x)/2^{1/2}\\
S(R_1)_{2a} &= (\sigma_1{}^y-i\sigma_3{}^y)/2^{1/2}\\
S(R_1)_{3a} &= (-\sigma_2{}^z-i\sigma_4{}^z)/2^{1/2}\\[4pt]
S(R_1)_{1b} &= (-i\sigma_2{}^x+\sigma_4{}^x)/2^{1/2}\\
S(R_1)_{2b} &= (-i\sigma_2{}^y-\sigma_4{}^y)/2^{1/2}\\
S(R_1)_{3b} &= (-i\sigma_1{}^z+\sigma_3{}^z)/2^{1/2}\\[4pt]
S(R_2)_{1c} &= (\sigma_1{}^x-i\sigma_3{}^x)/2^{1/2}\\
S(R_2)_{2c} &= (\sigma_1{}^y+i\sigma_3{}^y)/2^{1/2}\\
S(R_2)_{3c} &= (\sigma_2{}^z-i\sigma_4{}^z)/2^{1/2}\\[4pt]
S(R_2)_{1d} &= (-i\sigma_2{}^x-\sigma_4{}^x)/2^{1/2}\\
S(R_2)_{2d} &= (-i\sigma_2{}^y+\sigma_4{}^y)/2^{1/2}\\
S(R_2)_{3d} &= (i\sigma_1{}^z+\sigma_3{}^z)2^{1/2}
\end{aligned}\right\} \qquad (31)$$

However, from Table 2 and Eqs. (2) and (3), effects of inversion (R_5) are

$$\left.\begin{aligned}
R_5\boldsymbol{\sigma}_1(\pi,\pi,\pi) &= -\boldsymbol{\sigma}_2(-\pi,-\pi,-\pi) = i\boldsymbol{\sigma}_2(\pi,\pi,\pi)\\
R_5\boldsymbol{\sigma}_3(\pi,\pi,\pi) &= -\boldsymbol{\sigma}_4(-\pi,-\pi,-\pi) = i\boldsymbol{\sigma}_4(\pi,\pi,\pi)
\end{aligned}\right\} \qquad (32)$$

and therefore symmetry coordinate vectors are transformed upon inversion, as follows,

$$\boldsymbol{S}(R_1)_a \leftrightarrow -\boldsymbol{S}(R_1)_b \qquad \boldsymbol{S}(R_2)_c \leftrightarrow -\boldsymbol{S}(R_2)_d. \qquad (33)$$

Furthermore, for the phase-difference vector of (π,π,π),

$$\boldsymbol{S}(R_1)_a = -i\boldsymbol{S}(R_2)_c{}^* \qquad \boldsymbol{S}(R_1)_b = -i\boldsymbol{S}(R_2)_d{}^* \qquad (34)$$

and accordingly, the symmetry coordinate vectors of R_1 and R_2 form doubly-degenerate pairs (a–c and b–d) due to time-reversal symmetry. However, since the symmetry coordinate vectors of R_1 and R_2 form doubly degenerate pairs (a–b and c–d) due to space symmetry, crystal vibrations of $R(\pi,\pi,\pi)$ are four-fold degenerate (see Table 10, $f_s=2$, $t_s=2$).

Normal Vibration Treatment

Symmetry Coordinates. For a crystal containing an atoms per unit cell, there are $3n$ normal modes of crystal vibrations for a given phase-difference vector $\boldsymbol{\delta}=(\delta_a,\delta_b,\delta_c)$. Accordingly, the Cartesian symmetry coordinate vector $\boldsymbol{S}(\boldsymbol{\delta})$ with $3n$ components may be constructed as

$$\boldsymbol{S}(\boldsymbol{\delta}) = \sum_{\rho}\boldsymbol{U}(\boldsymbol{\delta},\boldsymbol{\rho})\boldsymbol{X}(\boldsymbol{\rho}), \qquad (35)$$

where $\boldsymbol{U}(\boldsymbol{\delta},\boldsymbol{\rho})$ is a unitary transformation matrix and $\boldsymbol{X}(\boldsymbol{\rho})$ is the Cartesian coordinate vector (three components) of the $\boldsymbol{\rho}$th atom. For the case of orthorhombic polyethylene, real parts of the Cartesian symmetry coordinates of Eq.(26) may be used, *viz.*,

$$\boldsymbol{S}(\boldsymbol{\delta})^\dagger = (S_1\,S_2\,S_3\,S_4\,S_5\,S_6\,S_8\,S_9\,S_7\,S_{11}\,S_{12}\,S_{10}) \qquad (36)$$

so that

$$\boldsymbol{S}(\boldsymbol{\delta}) = (2N)^{-1/2}\sum_{L}\begin{bmatrix}\boldsymbol{u}_1{}^c & \boldsymbol{u}_2{}^c & \boldsymbol{u}_3{}^c & \boldsymbol{u}_4{}^c\\ \boldsymbol{u}_1{}^c & \boldsymbol{u}_2{}^c & -\boldsymbol{u}_3{}^c & -\boldsymbol{u}_4{}^c\\ \boldsymbol{u}_1{}^s & -\boldsymbol{u}_2{}^s & \boldsymbol{u}_3{}^s & -\boldsymbol{u}_4{}^s\\ \boldsymbol{u}_1{}^s & -\boldsymbol{u}_2{}^s & -\boldsymbol{u}_3{}^s & \boldsymbol{u}_4{}^s\end{bmatrix}\begin{bmatrix}\boldsymbol{X}(\boldsymbol{\rho}_1)\\ \boldsymbol{X}(\boldsymbol{\rho}_2)\\ \boldsymbol{X}(\boldsymbol{\rho}_3)\\ \boldsymbol{X}(\boldsymbol{\rho}_4)\end{bmatrix} \qquad (37)$$

$$\left.\begin{aligned}
\boldsymbol{u}_1{}^c &= \begin{bmatrix} c_1 & 0 & 0\\ 0 & c_1 & 0\\ 0 & 0 & s_1\end{bmatrix} & \boldsymbol{u}_1{}^s &= \begin{bmatrix} s_1 & 0 & 0\\ 0 & s_1 & 0\\ 0 & 0 & c_1\end{bmatrix}\\
\boldsymbol{u}_2{}^c &= \begin{bmatrix} -c_2 & 0 & 0\\ 0 & -c_2 & 0\\ 0 & 0 & s_2\end{bmatrix} & \boldsymbol{u}_2{}^s &= \begin{bmatrix} -s_2 & 0 & 0\\ 0 & -s_2 & 0\\ 0 & 0 & c_2\end{bmatrix}\\
\boldsymbol{u}_3{}^c &= \begin{bmatrix} c_3 & 0 & 0\\ 0 & -c_3 & 0\\ 0 & 0 & -s_3\end{bmatrix} & \boldsymbol{u}_3{}^s &= \begin{bmatrix} s_3 & 0 & 0\\ 0 & -s_3 & 0\\ 0 & 0 & -c_3\end{bmatrix}\\
\boldsymbol{u}_4{}^c &= \begin{bmatrix} -c_4 & 0 & 0\\ 0 & c_4 & 0\\ 0 & 0 & -s_4\end{bmatrix} & \boldsymbol{u}_4{}^s &= \begin{bmatrix} -s_4 & 0 & 0\\ 0 & s_4 & 0\\ 0 & 0 & -c_4\end{bmatrix}
\end{aligned}\right\} \qquad (38)$$

where

$$\left.\begin{aligned} c_i &= \cos(\boldsymbol{\rho}_i\cdot\boldsymbol{\delta})\\ s_i &= \sin(\boldsymbol{\rho}_i\cdot\boldsymbol{\delta})\end{aligned}\right\} \qquad (39)$$

Dynamical Matrix. The potential energy (V) of crystal vibrations may be expressed with internal coordinates $\boldsymbol{R}$ (bond lengths, bond angles, internal-rotation angles, and others) as

$$2V = \tilde{\boldsymbol{R}}\boldsymbol{F}_R\boldsymbol{R}, \qquad (40)$$

where $\boldsymbol{F}_R$ is the potential energy matrix. With the use of the $\boldsymbol{B}(\boldsymbol{\rho})$ matrix,[19] the $\boldsymbol{R}$ vector is derived from Eq. (35) as

$$\boldsymbol{R} = \sum_{\rho}\boldsymbol{B}(\boldsymbol{\rho})\boldsymbol{X}(\boldsymbol{\rho}) = \sum_{\rho}\boldsymbol{B}(\boldsymbol{\rho})\sum_{\delta}\tilde{\boldsymbol{U}}(\boldsymbol{\delta},\boldsymbol{\rho})\boldsymbol{S}(\boldsymbol{\delta}). \qquad (41)$$

Then, the potential energy for the phase-difference

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[19] E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); *ibid.*, **9**, 76 (1942).

$\boldsymbol{\delta}$ is derived as

$$2V(\boldsymbol{\delta}) = \tilde{\boldsymbol{S}}(\boldsymbol{\delta})\boldsymbol{F}_S(\boldsymbol{\delta})\boldsymbol{S}(\boldsymbol{\delta}) \tag{42}$$

$$\boldsymbol{F}_S = \sum_{\rho'}\sum_{\rho} \boldsymbol{U}(\boldsymbol{\delta},\ \boldsymbol{\rho}')\tilde{\boldsymbol{B}}(\boldsymbol{\rho}')\boldsymbol{F}_R\boldsymbol{B}(\boldsymbol{\rho})\tilde{\boldsymbol{U}}(\boldsymbol{\delta},\boldsymbol{\rho}), \tag{43}$$

where a transposed conjugate vector (or matrix) is denoted with a tilde. On the other hand, the kinetic energy (T) for $\boldsymbol{\delta}$ is given as

$$2T(\boldsymbol{\delta}) = \tilde{\dot{\boldsymbol{S}}}(\boldsymbol{\delta})\boldsymbol{M}_S\dot{\boldsymbol{S}}(\boldsymbol{\delta}), \tag{44}$$

where $\dot{\boldsymbol{S}}$ is the time derivative of $\boldsymbol{S}$ and $\boldsymbol{M}_S$ is the diagonal mass matrix whose elements are masses of constituent atoms of a unit cell.

The dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ for $\boldsymbol{\delta}$ is then derived as

$$\boldsymbol{D}_S(\boldsymbol{\delta}) = \boldsymbol{M}_S{}^{-1/2}\boldsymbol{F}_S(\boldsymbol{\delta})\boldsymbol{M}_S{}^{-1/2}, \tag{45}$$

where $\boldsymbol{M}_S{}^{-1/2}$ is a diagonal matrix whose elements are square root of reciprocal masses of atoms.

Diagonalization. A general method for diagonalizing hermitian matrices $\boldsymbol{D}_S(\boldsymbol{\delta})$ has been described,[20] although dynamical matrices of polyethylene are real if the symmetry-coordinates of Eq. (36) are used. After diagonalizing $\boldsymbol{D}_S(\boldsymbol{\delta})$,

$$\tilde{\boldsymbol{L}}_S(\boldsymbol{\delta})\boldsymbol{D}_S(\boldsymbol{\delta})\boldsymbol{L}_S(\boldsymbol{\delta}) = \boldsymbol{\Lambda}(\boldsymbol{\delta}) \tag{46}$$

the diagonal frequency-parameter matrix $\boldsymbol{\Lambda}(\boldsymbol{\delta})$ is obtained whose elements are squared angular frequencies. With the unitary eigenvector matrix $\boldsymbol{L}_S(\boldsymbol{\delta})$, the transformation from the $\boldsymbol{S}(\boldsymbol{\delta})$ vector to the normal coordinate vector $\boldsymbol{Q}(\boldsymbol{\delta})$ is given as

$$\boldsymbol{S}(\boldsymbol{\delta}) = \boldsymbol{M}_S{}^{-1/2}\boldsymbol{L}_S(\boldsymbol{\delta})\boldsymbol{Q}(\boldsymbol{\delta}) \tag{47}$$

and, from Eq. (35), the Cartesian coordinate vector $\boldsymbol{X}(\boldsymbol{\rho})$ of the $\boldsymbol{\rho}$th atom is finally given as

$$\boldsymbol{X}(\boldsymbol{\rho}) = \sum_{\delta}\tilde{\boldsymbol{U}}(\boldsymbol{\delta},\ \boldsymbol{\rho})\boldsymbol{M}_S{}^{-1/2}\boldsymbol{L}_S(\boldsymbol{\delta})\boldsymbol{Q}(\boldsymbol{\delta}). \tag{48}$$

In actual numerical treatments for a number of phase-difference vectors in the first Brillouin zone, computation time is consumed primarily in diagonalization of dynamical matrices and careful procedure is desirable for reducing computation time.

Molecular Crystals. In three-dimensional molecular crystals, high-frequency intramolecular vibrations are primarily due to intramolecualr force field and weak intermolecular interactions give rise to small band-splitting. Usually the force field of a free molecule is brought over to the crystalline state and the potential energy matrix ($\boldsymbol{F}_R$) of a molecular crystal is expressed as a sum of the intramolecular part ($\boldsymbol{F}_R{}^M$) and the intermolecular part ($\boldsymbol{F}_R{}^C$),

$$\boldsymbol{F}_R = \boldsymbol{F}_R{}^M + \boldsymbol{F}_R{}^C. \tag{49}$$

From Eqs. (43), (45), and (49), it is readily seen that the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ is now expressed as a sum of the intramolecular part $\boldsymbol{D}_S{}^M(\boldsymbol{\delta})$ and intermolecular part $\boldsymbol{D}_S{}^C(\boldsymbol{\delta})$. If, however, each molecule of the crystal is brought inside a unit cell, the intramolecular force field of a molecule can be expressed with Cartesian coordinates of a common index vector and accordingly $\boldsymbol{D}_S{}^M$ becomes independent of $\boldsymbol{\delta}$,

$$\boldsymbol{D}_S(\boldsymbol{\delta}) = \boldsymbol{D}_S{}^M + \boldsymbol{D}_S{}^C(\boldsymbol{\delta}). \tag{50}$$

Then it is advisable to diagonalize $\boldsymbol{D}_S(\boldsymbol{\delta})$ in two steps, since large off-diagonal elements of $\boldsymbol{D}_S(\boldsymbol{\delta})$ are primarily from the intramolecular part. The first step is to diagonalize $\boldsymbol{D}_S{}^M$ that is independent of $\boldsymbol{\delta}$,

$$\tilde{\boldsymbol{L}}_S{}^M\boldsymbol{D}_S{}^M\boldsymbol{L}_S{}^M = \boldsymbol{\Lambda}^M \text{ (diagonal).} \tag{51}$$

Accordingly, the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ is now transformed into

$$\tilde{\boldsymbol{L}}_S{}^M\boldsymbol{D}_S(\boldsymbol{\delta})\boldsymbol{L}_S{}^M = \boldsymbol{\Lambda}^M + \tilde{\boldsymbol{L}}_S{}^M\boldsymbol{D}_S{}^C(\boldsymbol{\delta})\boldsymbol{L}_S{}^M \tag{52}$$

and the diagonalization of the second step is carried out to yield the frequency parameter matrix and eigenvector matrix,

$$\boldsymbol{\Lambda}(\boldsymbol{\delta}) = \tilde{\boldsymbol{L}}_S{}^C(\boldsymbol{\delta})[\boldsymbol{\Lambda}^M + \tilde{\boldsymbol{L}}_S{}^M\boldsymbol{D}_S{}^C(\boldsymbol{\delta})\boldsymbol{L}_S{}^M]\boldsymbol{L}_S{}^C(\boldsymbol{\delta}) \tag{53}$$

$$\boldsymbol{L}_S(\boldsymbol{\delta}) = \boldsymbol{L}_S{}^M\boldsymbol{L}_S{}^C(\boldsymbol{\delta}). \tag{54}$$

The off-diagonal elements meeting in the second step are due to the intermolecualr force field and are relatively small so that total computation involved in numerical treatments for many $\boldsymbol{\delta}$ vectors is thus greatly reduced.

Polymer-chain Crystals. For the dynamical matrix $\boldsymbol{D}_S(\boldsymbol{\delta})$ of polymer-chain crystals, the intrachain part $\boldsymbol{D}_S{}^M$ depends upon the phase-difference along the chain axis,

$$\boldsymbol{D}_S(\boldsymbol{\delta}) = \boldsymbol{D}_S{}^M(\delta_c) + \boldsymbol{D}_S{}^C(\delta_a,\delta_b,\delta_c). \tag{55}$$

Accordingly for each chosen value of δ_c, the first step is carried out to diagonalize $\boldsymbol{D}_S{}^M(\delta_c)$ and then the second step is carried out, for many values of δ_a and δ_b, to yield $\boldsymbol{\Lambda}(\boldsymbol{\delta})$ and $\boldsymbol{L}_S(\boldsymbol{\delta})$,

$$\begin{aligned}\boldsymbol{\Lambda}(\boldsymbol{\delta}) = \tilde{\boldsymbol{L}}_S{}^C(\boldsymbol{\delta})[&\boldsymbol{\Lambda}^M(\delta_c)\\ &+ \tilde{\boldsymbol{L}}_S{}^M(\delta_c)\boldsymbol{D}_S{}^C(\boldsymbol{\delta})\boldsymbol{L}_S{}^M(\delta_c)]\boldsymbol{L}_S{}^C(\boldsymbol{\delta})\end{aligned} \tag{56}$$

$$\boldsymbol{L}_S(\boldsymbol{\delta}) = \boldsymbol{L}_S{}^M(\delta_c)\boldsymbol{L}_S{}^C(\boldsymbol{\delta}). \tag{57}$$

Low Frequency Vibrations. Low frequency crystal vibrations are concerned with low temperature specific heat, neutron-scattering cross sections or mean squared amplitudes of atoms. In treating these properties theoretically, it is required to calculate vibrational frequencies and eigenvectors for a large number of phase-difference vectors. Accordingly, it is highly desirable to develop a useful approximation procedure for treating low frequency vibrations.

For orthorhombic polyethylene, however, a gap of frequency distribution[11] lies at 550—700 cm^{-1} and low-frequency vibrations may approximately

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[20] T. Miyazawa, K. Fukushima and Y. Ideguchi, *J. Chem. Phys.*, **38**, 2709 (1963).

be treated separately from high-frequency vibrations. Thus, from the eigenvector matrix $\boldsymbol{L}_S{}^M(\delta_c)$ of Eq. (51), columns associated with low-frequency modes are extracted to form a rectangular matrix $\boldsymbol{L}_l{}^M(\delta_c)$ and the corresponding minor matrix $\boldsymbol{\Lambda}_l(\delta_c)$ is extracted from the frequency-parameter matrix $\boldsymbol{\Lambda}^M(\delta_c)$. Then, the dynamical matrix $\boldsymbol{D}_l(\boldsymbol{\delta})$ for low-frequency modes is approximately obtained by a congruent transformation with $\boldsymbol{L}_l{}^M(\delta_c)$,

$$\boldsymbol{D}_l(\boldsymbol{\delta}) = \boldsymbol{\Lambda}_l(\delta_c) + \tilde{\boldsymbol{L}}_l{}^M(\delta_c)\boldsymbol{D}_S{}^C(\boldsymbol{\delta})\boldsymbol{L}_l{}^M(\delta_c) \tag{58}$$

and the frequency-parameter matrix and eigenvector matrix for low-frequency vibrations are given as

$$\boldsymbol{\Lambda}_l(\boldsymbol{\delta}) = \tilde{\boldsymbol{L}}_l{}^C(\boldsymbol{\delta})\boldsymbol{D}_l(\boldsymbol{\delta})\boldsymbol{L}_l{}^C(\boldsymbol{\delta}) \tag{59}$$

$$\boldsymbol{L}_l(\boldsymbol{\delta}) = \boldsymbol{L}_l{}^M(\delta_c)\boldsymbol{L}_l{}^C(\boldsymbol{\delta}). \tag{60}$$

For orthorhombic polyethylene, the order of dynamical matrices is reduced from 36 [$\boldsymbol{D}_S$] to 8 [$\boldsymbol{D}_l$] and therefore the approximate procedure stated above saves a lot of computation time, allowing vibration treatments over a greater number of phase-difference vectors in the first Brillouin zone.

Conclusion

Irreducible representations of $\boldsymbol{k}$ groups of the space group *Pnam* and degeneracies of crystal vibrations due to space symmetry and time-reversal symmetry were treated in the present study. Symmetry coordinates of carbon atoms of orthorhombic polyethylene were constructed from translational-symmetry coordinates with nonintegral index vectors. Similar coordinates may readily be constructed for sets of hydrogen atoms. Furthermore, general matrix methods were worked out for treating molecular crystals and chain-polymer crystals and for approximately treating low frequency lattice vibrations.

These methods are applicable for treating frequency distributions and specific heat, mean squared thermal amplitudes of scattering atoms (temperature factor for X ray scattering), and scattering cross sections (elastic and inelastic) of thermal neutrons. Symmetry considerations are indispensable for treating dispersion curves of optical and acoustic branches of crystal vibrations. These studies on orthorhombic polyethylene will be presented in forthcoming papers.