

Determination of Mean Square Displacements of Polyethylene Molecules in Crystal Lattice

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ABSTRACT: X-ray scattering intensities of bulk crystallized polyethylene were measured at temperatures from -165°C to 120°C . Mean square displacements of carbon atoms from their average locations were represented by the symmetric tensor U having four independent elements, U_{aa} , U_{bb} , U_{cc} , and U_{ab} . These elements and the atomic coordinates were determined as a function of temperature by the least square method. The displacement of the carbon atom was a maximum in the direction perpendicular to the skeletal zigzag plane. The minimum displacement was found in the direction along the the molecular axis. The mean square displacements of atoms were separated into contributions from the molecular vibration and the lattice imperfection by extrapolating the elements of tensor U to the temperature of absolute zero. The amplitudes of molecular vibration obtained by X-ray measurements agreed fairly well with the theoretical values calculated on the assumption of the harmonic oscillator model by Kitagawa and Miyazawa at the temperatures below 0°C . The atomic coordinates did not change below 0°C . The skeletal plane of polyethylene molecule tended to deflect slightly toward the a axis above 0°C with increasing temperature.

KEY WORDS X-rays / Atomic Coordinate / Atomic Displacement / Vibrational Amplitude / Lattice Imperfection / Anharmonicity / Polyethylene /

Mean square amplitudes of molecular vibrations in polyethylene crystals have been studied by several authors,¹⁻⁵ who determined the temperature factors related to the X-ray diffraction intensity. Kilian^{2,3} determined the temperature factor by using Ruland's method,⁶ showing the increase of vibration amplitudes of molecules with increasing temperature. He indicated that the observed temperature factor is the sum of the terms due to molecular vibration and to statistical lattice imperfection, and that the two terms could be separated by extrapolating the temperature factor to absolute zero. However, since the anisotropy of the temperature factor was not considered by him, the information concerning the direction of atomic displacements was not obtained. Aoki, *et al.*,⁴ took into account the anisotropy of atomic displacements of molecules and determined the mean square displacements along the a , b and c axes by using the integrated

intensities of three Bragg reflections. They compared their results with the theoretical temperature factors calculated by Kitagawa and Miyazawa,⁷ and indicated that the molecular vibration was anharmonic above 0°C . However, the values of observed vibration amplitudes were not the absolute ones but shifted conveniently to fit the theoretical values. The variation of the atomic coordinates was not considered in their treatment. These parameters are however expected to have a considerable effect on the intensities of Bragg reflections. Kavesh and Schultz⁵ determined the atomic coordinates and the temperature factors using the integrated intensities of ten Bragg reflections. They indicated that the plane of the zigzag chain tends to deflect slightly toward the a axis with increasing temperature. However, since the temperature factors were approximated by them using only two parameters, K_{AB} and K_C (the factors in the

directions perpendicular and parallel to the molecular axis respectively), they could not produce detailed information on the directions of the atomic displacements.

In order to clarify the molecular motions in the crystal lattice, it is necessary to obtain more detailed information concerning the directions and the amplitudes of molecular vibrations. For this purpose, it is useful to represent the temperature factors by the tensor ellipsoid as proposed by Cruickshank.⁸ It is intended in this paper to determine all of the parameters including the atomic coordinates and the elements of the temperature factor tensor for a polyethylene crystal as a function of temperature. The directions and amplitudes of thermal vibrations of molecules will be discussed as well as the harmonicity of the thermal vibration as compared with the theoretical value.⁷

THEORETICAL

The structure factor of the unit cell for the (*hkl*) reflection is defined by

$$F(hkl) = \sum_r f_r D_r \exp \{-2\pi i(hx_r + ky_r + lz_r)\} \quad (1)$$

where f_r is the scattering factor of the r -th atom and x_r , y_r , and z_r are the fractional coordinates of that atom. If X_r , Y_r , and Z_r are the component displacements of the r -th atom from the unit cell origin in the a , b , and c lattice directions measured in Angstroms respectively, then x_r , y_r , and z_r are defined as

$$x_r = \frac{X_r}{a} \quad y_r = \frac{Y_r}{b} \quad z_r = \frac{Z_r}{c} \quad (2)$$

The summation in eq 1 extends to all atoms in the unit cell. D_r represents the Debye—Waller factor which is a smearing function caused by displacements of atoms, and is given by

$$D_r = \exp \left\{ -\frac{1}{4} (\mathbf{s} \cdot \mathbf{B}_r \cdot \tilde{\mathbf{s}}) \right\} \quad (3)$$

where \mathbf{s} is the reciprocal lattice vector, which is written as

$$\mathbf{s} = \left(\frac{h}{a}, \frac{k}{b}, \frac{l}{c} \right) \quad (4)$$

\mathbf{B}_r is the temperature factor and is represented by the symmetric tensor having six independent

elements.⁸

$$\mathbf{B}_r = \begin{pmatrix} B_{aa,r} & B_{ab,r} & B_{ac,r} \\ & B_{bb,r} & B_{bc,r} \\ & & B_{cc,r} \end{pmatrix} \quad (5)$$

When atomic displacements are harmonic or small enough, \mathbf{B}_r is related to the tensor \mathbf{U}_r , which gives the amplitude of atomic displacement, as follows.

$$\mathbf{B}_r = 8\pi^2 \mathbf{U}_r = 8\pi^2 \begin{pmatrix} U_{aa,r} & U_{ab,r} & U_{ac,r} \\ & U_{bb,r} & U_{bc,r} \\ & & U_{cc,r} \end{pmatrix} \quad (6)$$

The mean square displacement in the direction specified by the unit vector $\mathbf{p} = (p_a, p_b, p_c)$ is written as⁸

$$\langle u^2 \rangle_r = \sum_i \sum_j U_{ij,r} p_i p_j \quad (i, j = a, b, c) \quad (7)$$

Figure 1 shows the crystal structure and the symmetry elements of polyethylene determined

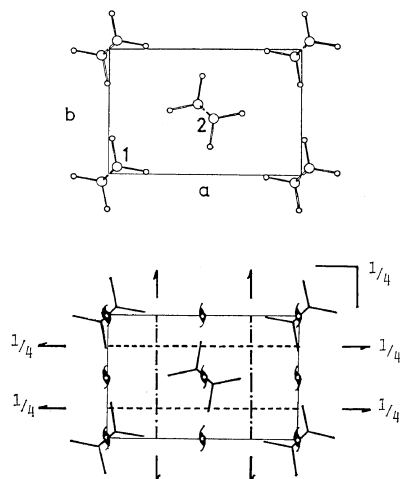


Figure 1. Structure and symmetry elements of a polyethylene crystal.

by Bunn.¹ Polyethylene crystals belong to the orthorhombic system having four methylene groups in the unit cell. X-ray scattering by hydrogen atoms were neglected because the X-ray scattering power of the hydrogen atoms is much smaller than that of carbon atoms.⁹ Since the polyethylene crystal is centro-symmetric, the summation in eq 1 is done for the carbon atom-1 located at (x, y, z) and the carbon atom-

2 at $[(1/2)+x, (1/2)-y, z]$. The crystal has a symmetry of mirror plane parallel to ab plane at $z=1/4$. Therefore, the following parameters are determined *a priori*.

$$z = \frac{1}{4} \quad U_{ac,r} = U_{bc,r} = 0 \quad (r=1, 2) \quad (8)$$

The crystal has a symmetry of glide plane a parallel to ac plane at $y=1/4$. Therefore, the following parameters are related with each other.

$$\begin{aligned} U_{aa,1} = U_{aa,2} &\equiv U_{aa} & U_{bb,1} = U_{bb,2} &\equiv U_{bb} \\ U_{cc,1} = U_{cc,2} &\equiv U_{cc} & U_{ab,1} = -U_{ab,2} &\equiv U_{ab} \end{aligned} \quad (9)$$

By taking into account eq 3, 4, 6, 8, and 9, eq 1 is rewritten as follows.

$$\begin{aligned} F(hkl) = 2f \left[\exp \left\{ -2\pi^2 \left(U_{aa} \left(\frac{h}{a} \right)^2 + U_{bb} \left(\frac{k}{b} \right)^2 \right. \right. \right. \\ \left. \left. \left. + U_{cc} \left(\frac{l}{c} \right)^2 + 2U_{ab} \frac{h}{a} \frac{k}{b} \right) \right\} \right. \\ \left. \times \cos 2\pi \left(hx + ky + \frac{l}{4} \right) \right. \\ \left. + (-1)^{h+k} \exp \left\{ -2\pi^2 \left(U_{aa} \left(\frac{h}{a} \right)^2 \right. \right. \right. \\ \left. \left. \left. + U_{bb} \left(\frac{k}{b} \right)^2 + U_{cc} \left(\frac{l}{c} \right)^2 \right. \right. \right. \\ \left. \left. \left. - 2U_{ab} \frac{h}{a} \frac{k}{b} \right) \right\} \cos 2\pi \left(hx - ky + \frac{l}{4} \right) \right] \quad (10) \end{aligned}$$

Thus, the structure factor of the polyethylene unit cell is represented by eq 10, which includes the atomic coordinates parameters, x and y , and the atomic displacement parameters, U_{aa} , U_{bb} , U_{cc} and U_{ab} .

EXPERIMENTAL

Sample Preparation

The sample used in this work is a commercial grade high-density linear polyethylene, Hizex 1200J, the product of Mitsui Petro-Chemical Industries Co., Ltd. Its molecular weight (M_w) was 30 800, melt index was 9.2, and the degree of branching was 2 $\text{CH}_3/1000 \text{CH}_2$. The sample was melted at 180°C and cooled to room temperature at the rate of $0.1^\circ\text{C}/\text{min}$. This bulk-crystallized sample was then annealed at 120°C for ten hours. No preferred orientation of crystal

planes was found by checking with the measurement of orientation function.

X-ray Scattering Measurement

X-ray scattering intensities were measured by the reflection method using an X-ray diffractometer with Ni-filtered $\text{Cu-K}\alpha$ radiation and a Geiger-Müller (GM) counter. The intensity of the incident beam was regulated so as to make its maximum on the GM counter less than 100 counts per second. Count miss of the GM counter was found to be less than 1.5%.

The specimen was attached to the Rigakudenki Company low temperature device. The scattering intensities were measured over the temperature range from -165°C to 120°C .

Method of Data Analysis

The parameters in eq 10 including the atomic coordinates and the elements of tensor U were determined according to the least squares method,¹⁰ which is generally used for a precise determination of crystal structure. The most probable values of these parameters are assumed to minimize the value of R defined by the following equation.

$$R \equiv \sum_{hkl} w(hkl) \{ |F_o(hkl)| - K |F_c(hkl)| \}^2 \quad (11)$$

where F_o and F_c are the observed and calculated structure factors respectively, K is the scale factor and $w(hkl)$ is the weight of (hkl) reflection.

The integrated intensities of 32 reflections were used. Reflections partly super-imposed were separated by the ratio of peak intensities. Reflections completely super-imposed were separated by the ratio of calculated intensities. After the corrections of the intensity data were made according to the conventional procedure,¹⁰ the observed structure factors, $F_o(hkl)$, were determined.

Table I lists the 32 crystal planes, the integrated intensities, and the weights employed at 28°C . As the weights of (110) and (200) reflections with strong intensities, the values of 0.2 and 0.5 were assigned respectively.¹⁰ The weights of superposed reflections were set to $1.0/n$, where n denotes the number of superposition.

Calculations by the least square method were made by using the electronic computer, FACOM 230-60, in the Computer Center of Kyushu University. The atomic coordinates and the

Table I. Crystal planes, integrated intensities and weights used in the least square method at 28°C

(hkl)	Intensity	Weight
110	1000.0	0.2
200	316.2	0.5
210	16.4	1.0
020	35.7	1.0
120	9.3	1.0
011	39.8	1.0
310	31.7	1.0
111	27.1	1.0
201	33.3	1.0
220	13.6	1.0
211	19.1	1.0
400	6.5	1.0
410	3.4	0.3
320	7.5	0.3
121	21.7	0.3
311	17.3	1.0
221	6.0	0.5
130	3.3	0.5
230	1.7	0.3
401	6.0	0.3
420	1.4	0.3
411	0.8	0.3
321	4.7	0.3
510	0.9	0.3
031	5.3	0.5
330	0.4	0.5
231	5.4	0.3
520	1.6	0.3
002	6.9	0.3
511	7.8	0.3
112	7.9	0.3
202	6.6	0.3

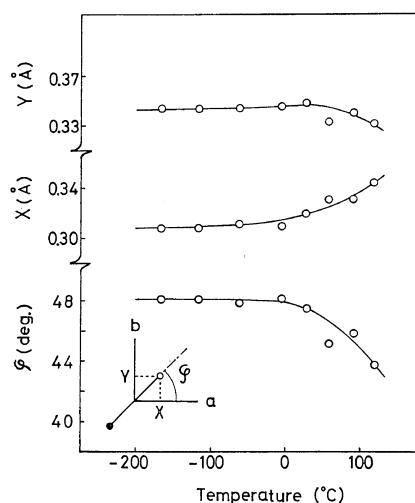
isotropic temperature factor reported by Bunn¹ were used as the starting values of the parameters. Thus, the most probable values of x , y , U_{aa} , U_{bb} , U_{cc} , and U_{ab} in eq 10 were determined.

RESULTS

Table II lists the atomic coordinates, x and y (fractional coordinates), and their standard deviations, $\sigma(x)$ and $\sigma(y)$, at temperatures from -165°C to 120°C . Figure 2 shows the temperature dependence of the atomic coordinates, X and Y (Angstrom unit), and the setting angle,

Table II. Fractional coordinates of carbon atom, x and y

Temp, °C	$x \pm \sigma(x)$	$y \pm \sigma(y)$
-165	0.042 ± 0.003	0.070 ± 0.004
-115	0.042 ± 0.002	0.070 ± 0.004
-60	0.042 ± 0.002	0.070 ± 0.004
-2	0.042 ± 0.002	0.070 ± 0.003
28	0.043 ± 0.002	0.069 ± 0.003
60	0.044 ± 0.003	0.067 ± 0.004
93	0.043 ± 0.003	0.068 ± 0.004
120	0.045 ± 0.003	0.066 ± 0.005

**Figure 2.** Atomic coordinates X , Y and setting angle φ vs. temperature.

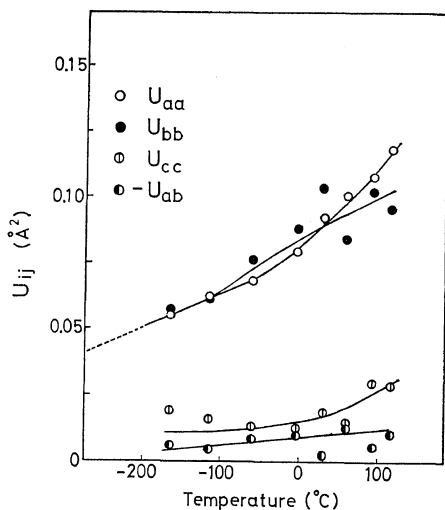
φ , between the a axis and the skeletal zigzag plane. As seen in Figure 2, X , Y and φ do not change below 0°C . On the other hand, increase in X and decreases in Y and φ are seen with increasing temperature in the temperature region above 0°C . These facts show that the skeletal zigzag plane of polyethylene molecule tends to deflect toward the a axis with increasing temperature. These observations agree with those reported by Kasai and Kakudo,¹¹ and Kavesh and Schultz.⁵

Table III lists the elements of the tensor U and their standard deviations at the temperatures from -165°C to 120°C . Figure 3 shows the temperature dependence of U_{aa} , U_{bb} , U_{cc} , and $-U_{ab}$. Here, U_{aa} , U_{bb} and U_{cc} indicate the mean square displacements along the a , b , and

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Table III. Values of U_{ij} in 10^{-2} \AA^2

Temp, °C	$U_{aa} \pm \sigma(U_{aa})$	$U_{bb} \pm \sigma(U_{bb})$	$U_{cc} \pm \sigma(U_{cc})$	$U_{ab} \pm \sigma(U_{ab})$
-165	5.5 ± 1.9	5.7 ± 1.8	1.9 ± 1.0	-0.6 ± 1.3
-115	6.2 ± 1.9	6.1 ± 1.8	1.6 ± 1.1	-0.4 ± 1.3
-60	6.8 ± 2.0	7.6 ± 1.9	1.3 ± 1.1	-0.8 ± 1.4
-2	7.9 ± 1.9	8.8 ± 1.8	1.2 ± 1.0	-1.0 ± 1.4
28	9.2 ± 1.9	10.4 ± 1.9	1.7 ± 1.0	-0.1 ± 1.3
60	10.0 ± 2.4	8.4 ± 2.0	1.5 ± 1.1	-1.2 ± 1.6
93	10.8 ± 2.5	10.2 ± 2.3	3.0 ± 1.3	-0.5 ± 1.6
120	11.8 ± 2.9	9.5 ± 2.4	2.9 ± 1.4	-1.0 ± 1.8


Figure 3. Elements of tensor U vs. temperature.

c axes, respectively. As seen in Figure 3, U_{aa} is nearly equal to U_{bb} and about five times as large as U_{cc} . In other words, the atomic displacements along the a and b axes are almost the same and much larger than that of c axis as reported by Aoki, *et al.*⁴ The equality of the displacements along the a and b axes seems to be reasonable, as far as the setting angle of the skeletal plane to the a axis is about 45° . The anisotropy of the molecular force field in the directions parallel and perpendicular to the molecular axis offers a reasonable explanation for the difference between the displacements along the a and c axes or b and c axes. The atoms are bonded by strong covalent bonds along the molecular axis compared with the rather weak intermolecular van der Waals bonds.

As shown in Table III, the cross element, U_{ab} , which has newly been introduced in this study,

has a negative value. This result is closely related to the fact that the displacement of the carbon atom is maximum in the direction perpendicular to the skeletal zigzag plane if the tensor U is diagonalized according to the transformation method to the principal axes. Figure 4 shows the direction of the two principal axes (LA and SA) and the root mean square displacements of the carbon atom along these axes at -115°C . The value in parentheses in Figure 4 is the root mean square displacement along the c -axis, the third principal axis. The fact that the direction of LA axis, that of the maximum

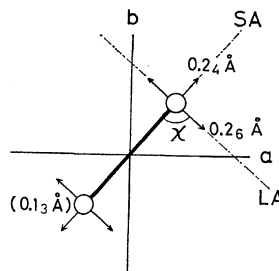

Figure 4. Root mean square displacements along the LA , SA and molecular axis (parentheses) at -115°C .

Table IV. Values of U_{LA} , and U_{SA} in 10^{-2} \AA^2 , and χ in degree

Temp, °C	$U_{LA} \pm \sigma(U_{LA})$	$U_{SA} \pm \sigma(U_{SA})$	$\chi \pm \sigma(\chi)$
-165	6.2 ± 1.9	5.0 ± 1.8	81 ± 62
-115	6.6 ± 1.9	5.7 ± 1.9	90 ± 85
-60	8.1 ± 2.0	6.3 ± 1.9	74 ± 42
-2	9.4 ± 1.9	7.3 ± 1.9	75 ± 35
60	10.7 ± 2.5	7.7 ± 2.0	105 ± 30
93	11.1 ± 2.5	9.9 ± 2.2	103 ± 80
120	12.2 ± 2.9	9.1 ± 2.3	111 ± 34

displacement, is almost perpendicular to the skeletal zigzag plane suggests that the rotational vibration of molecules around their axes will contribute considerably to the temperature factor as discussed in a later part.

Table IV lists the values of U_{LA} , U_{SA} , and χ , and their standard deviations at various temperatures, where U_{LA} and U_{SA} denote the mean square displacements along the LA and SA axes, respectively, and χ is the angle between the LA axis and the skeletal zigzag plane.

DISCUSSION

It is generally known that the atoms in crystal lattice vibrate harmonically in the low temperature region, and that the square of vibration amplitude of a harmonic oscillator is proportional to absolute temperature except in the temperature region near absolute zero, where the quantum effect must be considered. In the case of a polyethylene crystal, the quantum effect on the molecular vibrations which determine the temperature factor is considered to be negligible in the temperature region of this study.⁷ Then, extrapolation of U_{ij} at the temperatures below 0°C should give zero value at absolute zero in Figure 3, if U_{ij} shows the mean square displacements of atoms due only to the molecular vibrations. As seen in Figure 3, the observed values of the elements of the tensor U seem to decrease with decreasing temperature. However, extrapolation of the curves of U_{ij} , especially U_{aa} and U_{bb} , to the temperature absolute zero gives considerably large values. This fact will be explained by taking into account the displacements of the carbon atoms caused by the lattice imperfections of the first kind as discussed by Kilian.³ In such a case, the displacements determined by X-ray measurements are separated into two kinds of contributions from the molecular vibrations and the lattice imperfections. According to the convolution theory, Debye-Waller factor is written as follows.³

$$D = \exp\{-2\pi^2(\mathbf{s} \cdot \mathbf{U} \cdot \tilde{\mathbf{s}})\} = \exp\{-2\pi^2(\mathbf{s} \cdot \mathbf{U}^T \cdot \tilde{\mathbf{s}})\} \times \exp\{-2\pi^2(\mathbf{s} \cdot \mathbf{U}^0 \cdot \tilde{\mathbf{s}})\} \quad (12)$$

Thus,

$$\mathbf{U} = \mathbf{U}^T + \mathbf{U}^0 \quad (13)$$

where \mathbf{U}^T and \mathbf{U}^0 are the tensors giving the mean square amplitudes of molecular vibrations and the mean square displacements of atoms due to the lattice imperfections, respectively. According to eq 13, \mathbf{U}^0 is obtained by extrapolation of the temperature dependence curve of U_{ij} to the absolute zero.

The extent of lattice imperfection may be different between samples with different preparation histories. Crystallization conditions, annealing conditions, γ -ray irradiations, etc., will strongly influence the imperfections of the crystal lattice. In the case of the bulk crystal sample used in this study, the mean square displacements due to the lattice imperfections were determined as follows.

$$U_{aa}^0 \simeq U_{bb}^0 \simeq 0.04 \text{ \AA}^2 \quad U_{ab}^0 \simeq 0 \text{ \AA}^2 \quad (14)$$

U_{cc}^0 could not be determined because U_{cc} shows an unexplainable increase with decreasing temperature. In any way, U_{cc}^0 is considered to be much smaller than U_{aa}^0 or U_{bb}^0 according to Figure 3. These results indicate that the lattice imperfections are almost isotropic in the direction perpendicular to the molecular axis, whereas the imperfections along the molecular axis are small because of the strong intrachain force field.

Hereafter we assume that the imperfection of the crystal is frozen and unchanged with

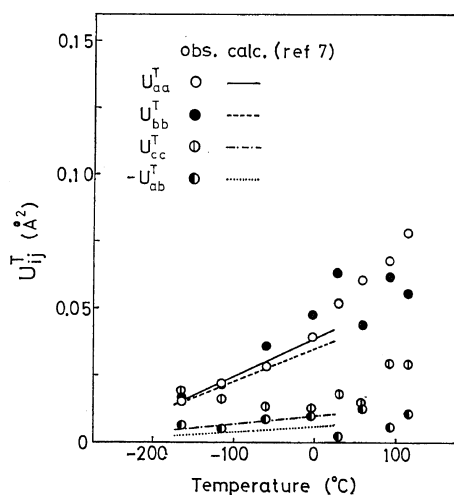


Figure 5. Elements of tensor U^T vs. temperature.

increasing temperature. This assumption is considered to be acceptable in the low temperature region as discussed later. Then, the elements U_{ij}^T of the tensor U^T , which give the mean square amplitudes of the molecular vibration can be determined by using eq 13. Figure 5 shows the temperature dependence of U_{ij}^T . Here, U_{cc}^T is assumed to be equal to U_{cc} because U_{cc}^0 cannot be determined.

Kitagawa and Miyazawa⁷ have calculated the frequency distribution of the normal vibration in the polyethylene crystal and the amplitude of every vibrational mode on the basis of a harmonic oscillator model, and they derived the tensors of temperature factor of X-ray diffraction at -173°C and 25°C . Their results, which are converted to U_{ij}^T by using the relation of eq 6, are shown in Figure 5 by full line (U_{aa}^T), broken line (U_{bb}^T), chain line (U_{cc}^T) and dotted line (U_{ab}^T).

As seen in Figure 5, agreements between the elements of the tensors obtained by the X-ray measurements and the theoretical calculations are fairly good especially in the low temperature region below about 0°C . In order to determine U_{ij}^T , the lattice imperfection is assumed not to vary with temperature as already mentioned. The agreements with the calculated values seem to suggest that the assumption is reasonable at least in the low temperature region. Furthermore, the agreements seem to support the fact that the polyethylene molecules in the crystal vibrate almost harmonically at these low temperatures.

In the temperature region above 0°C , on the other hand, the values of U_{ij}^T evaluated by X-ray measurements increase rapidly with increasing temperature and show larger values than those of the theoretical U_{ij}^T . This fact can be ascribed to an increase of anharmonicity of molecular vibration as discussed by Aoki, *et al.*⁴.

The tensor U^T was diagonalized and the mean square amplitudes of molecular vibration along two principal axes of the tensor ellipsoid, U_{LA}^T and U_{SA}^T , were determined. Figure 6 shows the temperature dependence of U_{LA}^T and U_{SA}^T . U_{LA}^T , which indicates the maximum mean square amplitude of molecular vibration, is found in a direction almost perpendicular to the skeletal zigzag plane, and U_{SA}^T , which shows the minimum mean square amplitude in ab plane, is

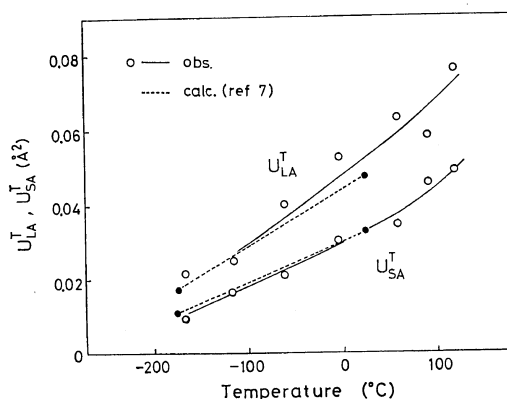


Figure 6. Mean square amplitudes along the LA and SA axes vs. temperature.

found in the direction including the skeletal plane and perpendicular to the molecular axis.

According to the calculation by Kitagawa and Miyazawa,⁷ the temperature factor is mainly determined by the intermolecular vibration modes with low frequencies as found in translational or rotational vibration of molecular chains and does not relate to the high frequency intramolecular vibrations. Then, U_{LA}^T is considered to be mainly determined by the translational mode in the LA direction as indicated in Figure 7a and the rotational mode around the molecular axis as indicated in Figure 7b, whilst U_{SA}^T is dependent on the translational

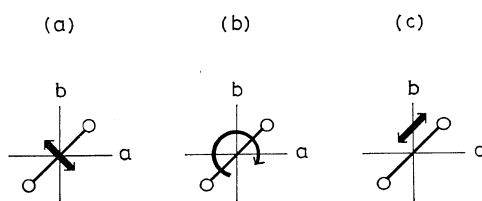


Figure 7. Vibration modes along the LA and SA axes: (a) translational mode along LA axis; (b) rotational mode around molecular axis; (c) translational mode along SA axis.

mode in the SA direction as indicated in Figure 7c.

In Figure 6, the theoretical values calculated on the assumption of harmonic oscillation⁷ (filled circles and broken lines) are compared with the values found based on the X-ray measurements

(open circles and full lines). The observed values of U_{SA}^T agree fairly well with the theoretical ones until about 60°C. This fact indicates that the translational mode of molecules in the SA direction is harmonic up to relatively high temperatures. On the other hand, the observed values of U_{LA}^T are larger than the calculated ones even at temperatures as low as 0°C. If it is assumed that the harmonicity of the translational mode along the LA direction is not very different from that along the SA direction, the above fact leads to the conclusion that the rotational mode around the molecular axis becomes anharmonic more easily than the translational mode.

It is impossible to separate the amplitude of rotational vibration and that of translational vibration along the LA axis from the observed U_{LA}^T and criticize their harmonicity without any assumptions. The theoretical value of the ratio of the mean square amplitudes of these two vibration modes was estimated after the calculation of Kitagawa and Miyazawa.⁷ By using the theoretical ratio, the translational and rotational vibration amplitudes can be separated from the observed values of U_{LA}^T . The mean square amplitudes of rotational vibration, $\langle \omega^2 \rangle$, evaluated based on this assumption are plotted against temperature in Figure 8.

As shown in Figure 2, the skeletal plane turns slightly toward the a axis in the temperature region above 0°C. Such a tendency is related to the anharmonic vibration of molecules above 0°C.

The vibration amplitude along the molecular axis, U_{cc}^T , was not determined, because the extent of the lattice imperfection in this direction, U_{cc}^0 , could not be estimated. Therefore, the comparison of the observed U_{cc}^T with the theoretical values⁷ was not made. The rapid increase in U_{cc} at the temperatures above 60°C as shown in Figure 3 may be considered as an indication

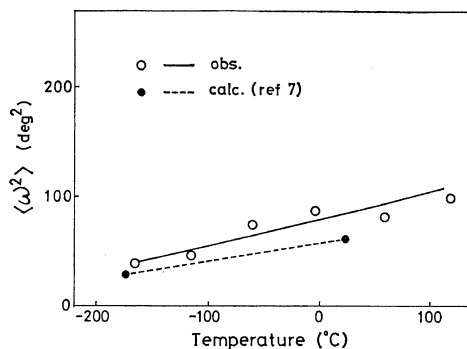


Figure 8. Mean square amplitude of rotational vibration $\langle \omega^2 \rangle$ vs. temperature.

that the anharmonicity of the translational mode along the molecular axis becomes considerable at high temperatures. The strong intrachain force field will not be so easily affected by temperature as the van der Waals intermolecular force field is.

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