The Crystal Structure of Polyethylene at 4.5°K

Akiyoshi KAWAGUCHI,* Ryoh MATSUI,** and Keinosuke KOBAYASHI*

A cryostat for X-ray diffraction work with a diffractometer was constructed. This apparatus was utilized for the crystal structure analysis of polyethylene. Polyethylene was crystallized at 129°C and its X-ray measurements were carried out at 4.5°K. The crystal parameters were refined by the least squares method. The cell dimensions are: $a=7.12_8$ Å, $b=4.85_2$ Å and $c=2.55_5$ Å. The setting angle is $45.5\pm3°$.

INTRODUCTION

In 1939, the crystal structure of polyethylene was analysed in detail for the first time by Bunn.[1] Since his classic work, the crystal structure analyses of the melt-crystallized and drawn samples[2~6]an d the folded chain single crystals[7] were carried out intensively. It has been found out from these analyses that single crystals have the crystal structure with a large setting angle of 48° differing from that of other crystals whose crystal structure are significantly due to the preparation.

Polyethylene lattice expands in the a-axis direction with temperature and simultaneously the setting angle increases. Polymer crystals are inherently not perfect and become inevitably more disordered with the increase of temperature due to the thermal motion of atoms. The lattice disorder of the *first kind* can be estimated from the temperature factors on the X-ray diffraction analysis, and this is the overall disorder in which in addition to the disorder of thermal origin the statistical imperfections due to molecular displacements from the ideal positions are included. The disorder of the *second kind* (paracrystalline disorder) exists characteristically in polymer crystals. The disorder of the *second kind* can be measured from the integral breadths of a reflection of X-ray diffraction pattern and higher order reflections.[8] There is no suitable method to extract the disorder due to thermal molecular motions from these inherent disorders of crystals. If the structure of a crystal with frozen molecular motion is known, it will be possible to distinguish thermal disorder. Thus, the structure analysis of crystal should be done at a temperature close to 0°K to know the exact temperature dependence of the properties and structure of crystals.

A mechanical relaxation called the δ dispersion has been observed in polyethylene crystals in the temperature range as low as 20°K.[9] Its relaxation mechanism is not yet sufficiently clear and thus the structure analysis of crystal at a sufficiently low temperature is urgently needed to reveal the crystal structure without any thermal vibration. Although much progress has been made recently in the studies of properties and structures of materials at low temperatures in space research, few research works of the low temperature structure analysis of polymer crystals have been carried out except the works

* 河口昭義, 小林恵之助 : Laboratory of Polymer Crystals, The Institute for Chemical Research, Kyoto University, Uji, Kyoto.
** 松居りょう : Polyester Factory, Asahi Chemical Industry Co. Ltd., Nobeoka, Miyazaki.

by Shen *et al.*,[10] Höhne and Wilke,[11] and Avitabile *et al.*[6] Avitabile *et al.* have carried out the precise structure analysis of deuterated polyethylene crystal by the neutron diffraction method at 4°K.

The crystal structure has been predicted theoretically from minimizing the potential energy by assuming a suitable interaction between the non-bonded atoms. The structure thus derived corresponds to that polymer may have at 0°K. These predicted structures have been compared with the data observed at liquid nitrogen temperature or those extraporated to 0°K to check their validities. Naturally, it is more desirable to compare the predicted structure with the data obtained on a large and perfect crystal at a temperature
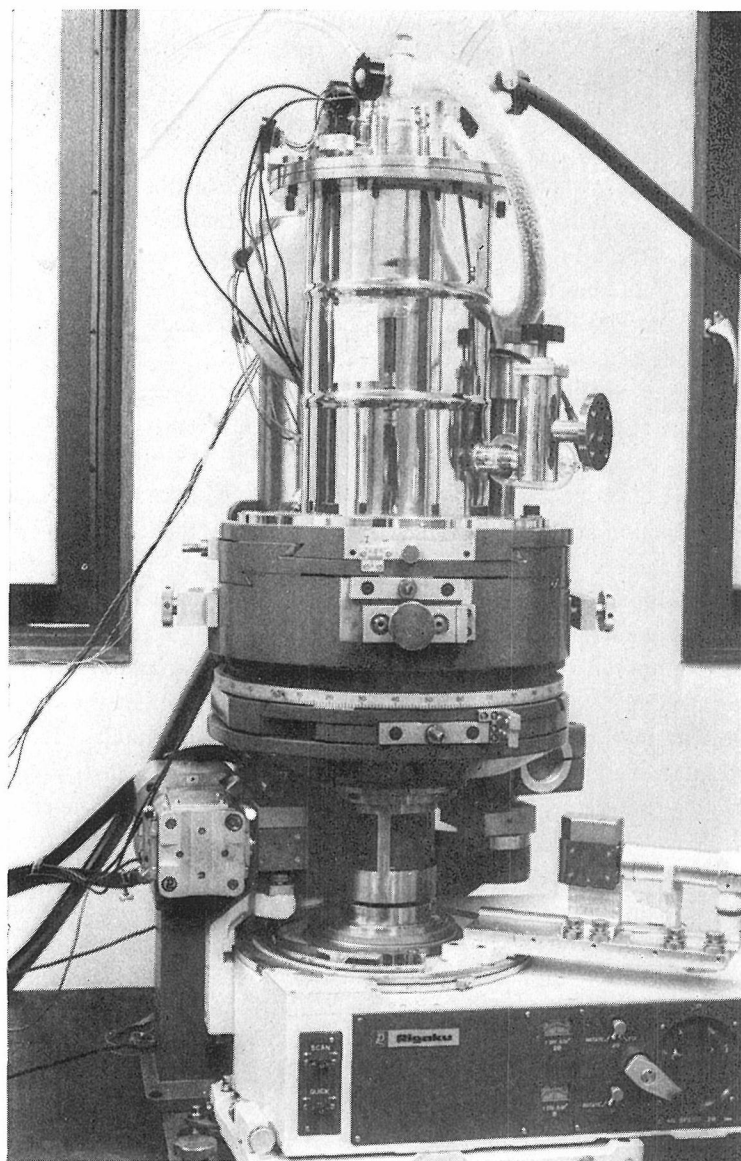

Fig. 1. The whole appearance of the cryostat.

as close to 0°K as possible.

Thus the analysis of the crystal structure at liquid helium temperature was undertaken in the present work. First, the cryostat was constructed to take the X-ray diffraction pattern at this temperature. The crystal structure analysis of polyethylene was carried out with the X-ray diffraction data obtained by this apparatus. The detail of the apparatus and the obtained results are presented in the following sections.

EXPERIMENTAL

Sample

Unfractionated linear polyethylene Sholex 6050 (produced by Showadenko Inc.) was once melted at 145°C for some tens minutes. The melts were transferred to an oil bath kept at 129°C and crystallized for three days. A plate of 1 mm thickness was used as a specimen for diffraction work.

Apparatus

Figure 4 shows the whole appearance of the apparatus. This is designed for the convenience of the measurment with X-ray diffractometer and was constructed by Rigaku-denki Inc. The cryostat is a conventional double Dewar vessel consisting of a liquid helium vessel surrounded by a liquid nitrogen vessel (Fig. 2). A radiation shield made of alminium foil of about 10 μ thickness is attached to the these vessels to screen the specimen from thermal radiation. The outside window is made of vacuum-tight beryllium (which
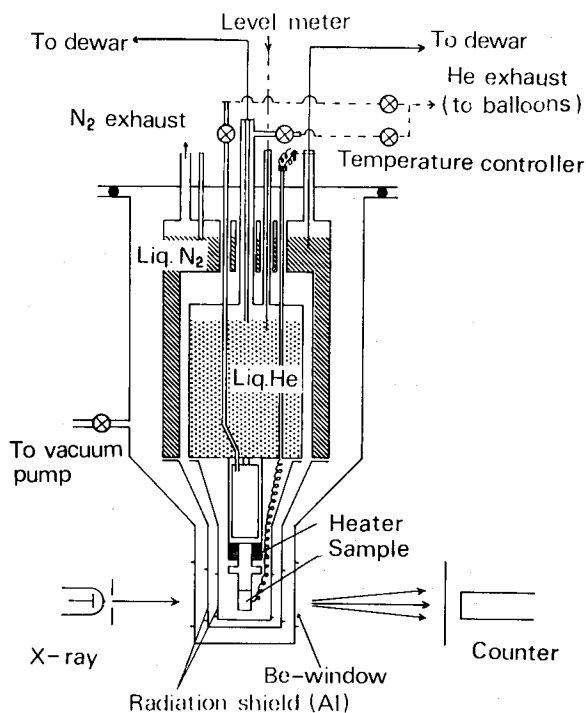

Fig. 2. Schematic representation of the cryostat.

hardly absorbs X-ray) to keep the sample chamber vacuum. This apparatus is also designed to perform the measurement at various temperatures. The temperature was controlled with an accuracy of $\pm 0.05°C$ by a controller using thermocouple. The thermocouple of copper in combination with an alloy of gold $+2.1\%$ cobalt was used. The temperature was measured with the resistance thermometer of germanium semiconductor. As for other experimental procedures at low temperature, the texts by White[12] and by Ros-Innes[13] were referred.

Liquid helium was used as cooling medium, but since the sample was cooled by conduction through the sample holder which was in thermal contact with the bottom of liquid helium vessel, the temperature $4.2°K$ of liquid helium was not achieved. The lowest temperature of the sample achieved by this apparatus was $4.5°K$. This type of cryostat has already been reported and its make-up and usage are practically same.

The X-ray generator was a conventional one with a sealed tube and was operated at $40\,kV$ and $25\,mA$. The diffraction intensities of the nickel filtered Cu-Kα ray were measured with a scintillation counter.

Method of Data Analysis

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

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

where f_r denotes the scattering factor of an atom and x_r, y_r, and z_r denote the fractional coordinates. The suffix r indicates the rth atom in the unit cell. These fractional coordinates are defined as follows:

$$x_r=X_r/a \qquad y_r=Y_r/b \qquad z_r=Z_r/c \tag{2}$$

where a, b, and c represent the lattice constants of unit cell and X_r, Y_r, and Z_r are the component displacements of rth atom from the origin of unit cell along a, b, and c directions, respectively. D_r denotes the Debye-Waller factor given by

$$D_r=\exp(-(h^2B_{11}+k^2B_{22}+l^2B_{33}+klB_{23}+lhB_{31}+hkB_{12})) \tag{3}$$

where $B_{ij}(i,j=1, 2, 3)$ denotes the anisotropic temperature factor. This factor is related to the smearing effect on reflections by the thermal agitation of atoms.

The vibration of an atom in an anisotropic potential field is characterized by a symmetric tensor with six independent components $U_{ij}(i,j=1, 2, 3)$, and the mean squared amplitude of vibration in the direction of unit vector l is given as

$$\langle u^2\rangle= \sum_i \sum_j U_{ij}l_i l_j \tag{4}$$

when $l_i(i=1, 2, 3)$ is a component of the vector l. The tensor component is connected with the temperature factor as follows:

$$B_{ii}=2\pi^2 x_i^* U_{ii} \ (i=1, 2, 3)$$

and $\quad B_{ij}=4\pi^2 x_i^* x_j^* U_{ij} \ (i, j=1, 2, 3)$ \hfill (5)

where x_1^*, x_2^*, and x_3^* are the reciprocal axis lengths, $i.e.$ a^*, b^*, and c^*.[14]

The precise parameters in Eq. (1) including the atomic coordinates and temperature factors were determined by the least squares method, which was generally used for a re-

finement of crystal structure.[15] The most probable values of these parameters are estimated to minimize the value R defined as follows:

$$R = \sum_{hkl} w(hkl)(KF_o{}'(hkl) - F_c(hkl))^2 \tag{6}$$

where $F_o{}'$ and F_c denote the square root of the observed integral intensity with the same sign as F_c and the calculated structure factor respectively, K is the scale factor and w (hkl) is the weight to (hkl) reflection. The iteration was repeated until the index RE converged on a suitable value. Here the index RE is a measure of reliability and defined as follows:

$$RE = \frac{\sum_{hkl} (|F_o(hkl)| - |F_c(hkl)|)}{\sum_{hkl} |F_o(hkl)|} \tag{7}$$

where F_o (hkl) is the observed structure factor equal to $KF_o{}'$ (hkl). Partly overlapped reflections were separated by means of the peak separation method based on the least squares.[16] When the separation could not be done by the method mentioned above, then the peak was separated in propotion to the ratio of calculated intensities. After correcting the observed integral intensities for the Lorentz-polarization factor and the absorption effect, $F_o{}'$ (hkl) was determined.

Calculations by the least squares method were carried out with an electronic computer FACOM 230-48 in the Institute for Chemical Research of Kyoto University. The values given by Bunn were used as the starting values of parameters and the atomic coordinates and anisotropic temperature factors were refined to yield the most reliable values.

RESULTS

Polyethylene crystal undergoes no phase transition during cooling to 4.5°K where

Table I. The Observed Lattice Parameters of Polyethylene Crystal

Unit cell dimensions (Å)		
a	b	c
7.12$_8$	4.85$_2$	2.55$_3$
Coordinates of carbon atom		
x	y	z
0.04$_6$	0.06$_5$	0.25

Temperature factors (Å²)			
B_{11}	B_{22}	B_{33}	B_{12}
0.01$_2$	0.02$_5$	0.07$_6$	-0.001

Setting angle (°)
45.5° ±3°

Mean squared displacements (Å²)		
$\langle \Delta a^2 \rangle$	$\langle \Delta b^2 \rangle$	$\langle \Delta c^2 \rangle$
0.03$_2$	0.03$_0$	0.02$_5$

Table II. The Observed and Calculated Structure Factors

(h	k	l)	|Fo|	|F$_c$|
1	1	0	13.60	16.39
2	0	0	13.26	14.91
2	1	0	3.32	3.72
0	2	0	8.24	8.70
1	2	0	3.03	2.83
0	1	1	5.68	5.84
1	1	1	3.35	3.75
3	1	0	6.15	5.53
2	0	1	5.68	6.34
2	2	0	4.61	4.49
2	1	1	3.90	3.72
4	0	0	4.86	4.00
1	2	1	4.29	5.43
3	2	0	4.53	4.61
4	1	0	4.11	3.01
3	1	1	4.91	5.04
1	3	0	3.51	2.72
2	2	1	3.40	2.80
2	3	0	3.11	3.54
4	0	1	5.96	5.64
5	1	0	0.28	0.77
0	3	1	6.69	5.38
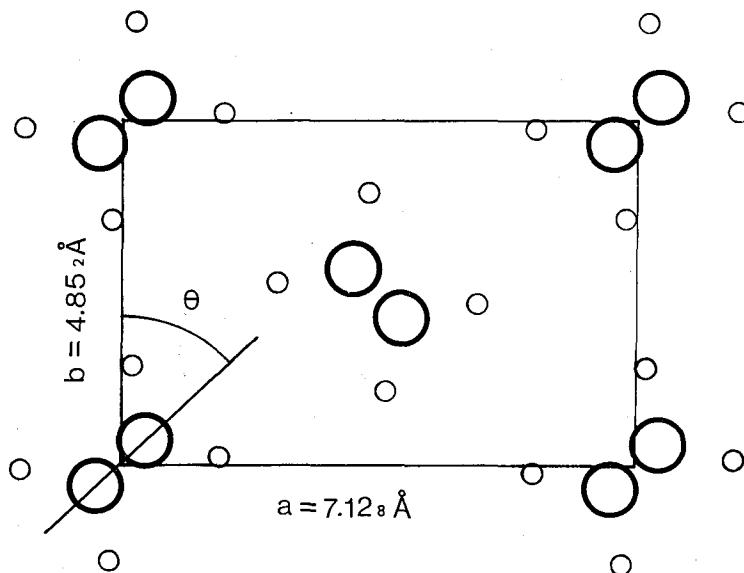
Fig. 3. The projection of orthorhombic unit cell of polyethylene at 4.5°K on (001) plane. θ is the setting angle.

the crystal system is orthorohmbic as at room temperature. Its space group is Pnam. The lattice dimensions of unit cell were determined from the observed peak positions of the wide angle X-ray diffraction pattern by the least squares method (see Table I).

In determining the coordinates and anisotropic temperature factors of the atoms by the method described above, hydrogen atoms were neglected. The coordinates and anisotropic temperature factors of the carbon atom are listed in Table I. B_{23} and B_{31} are *a priori* zero because of the symmetry of space group of crystal lattice. 22 reflections were used in this calculation. The observed and calculated structure factors are shown in Table II. Though several reflections such as (002), (520), (231) have the observable intensities, they are overlapped with the intense peak from the sample holder and the peaks can not be resolved into the respective components with a reliable accuracy. Those reflections are not used in the calculation and omitted in Table II. The reliability index RE was about 12%.

Figure 3 shows a projection of polyethylene unit cell at 4.5°K on the basal plane (001). The large open circles and small ones represent the carbon and hydrogen atoms, respectively. A C-H bond length of 1.1Å and an H-C-H bond angle of 110° are assumed. As shown in Fig. 3, the setting angle is the angle between the projection of planar zigzag chains and the b axis. This angle is calculated as about 45.5° from the coordinates x, y in Table I.

The mean squared displacements in the a, b, and c axis directions are estimated from the temperature factors according to Eqs. (4) and (5). (see Table I)

DISCUSSION

Lattice dimensions of polyethylene crystal observed or estimated at low temperature have been reported by many researchers.[6,10,17~18] They are shown in Table III with the

Table III. The Observed and Calculated Lattice Dimension and the Setting Angle

a(Å)	b(Å)	c(Å)	Temp. (°K)	setting angle	reference
[observed]					
7.16	4.86	2.538	10		(10)
7.121	4.852	2.548	4	49°	(6)
7.12₈	4.85₃	2.55₅	4.5	45.5±3°	present work
[estimated]					
7.14	4.87				(17)
7.103	4.853	2.553			(18)
[predicted]					
7.2	4.95			48°	(20)
7.118	4.855			46.9°	(21)*
7.1	5.0			45°	(22)**
7.156	4.894			46°19′	(23)
7.11	4.92			48°	(24)
7.15	4.84			47.5°	(25)***

* Parameters for Set IV
** Values of a and b are estimated from the given graph.
*** Parameters for Set II

present data. The values given by Hendus[17] and Davis *et al.*[18] are estimated by extraporation of the data at above liquid nitrogen temperatures to $0°K$. The sets by Davis *et al.* and Avitabile *et al.* are in good agreement with the present data. It should be emphasized that the values by us and Avitabile *et al.* are most reliable since the actual measurement was taken place at the lowest temperature.

The long periods of the sample used here were found to be over 400 Å from the measurement of the small angle X-ray scattering. The crystallite size and paracrystalline distortion were also estimated according to Hosemann's paracrystalline theory.[8] The paracrystalline distortion was about 2.0% in the [110] direction and the crystallite size in the same direction was about 400 Å. The crystallites composing the sample are sufficiently large as polymer crystal and their lattice distortion is fairly small. These lattice dimensions are thus nearly equal to those that a large perfect crystal of polyethylene is supposed to have at a temperature near $0°K$. Polyethylene lattice shrinks in the *a* and *b* axis directions during cooling to $4.5°K$, while the *c* axis length increases by about 0.01 Å in comparison with the values at room temperature (see Table I). This result suggests that the thermal expansion in the *c* axis direction is due to the fact that the thermal twisting of chains around C-C bonds is restricted. Davis *et al.* and Kobayashi and Keller[19] have also speculated this cause of thermal expansion in the *c* axis direction from the results at rather high temperature. Molecular chains oscillating between left- and right-handed helical conformations become rigid in planar zigzag conformation. The carbon-carbon bond length (1.568 ± 0.01 Å) and bond angle ($109 \pm 1°$) in the present molecular conformation were calculated from the atomic positions and the lattice dimensions. The present bond length is more extended than the usual value (1.54 Å) of polyethylene and paraffine at room temperature, but is comparable to that in some small molecules.[26] The bond angle is smaller and very close to the tetrahedral angle of diamond lattice, $109°27'$. (The extension of bond length and the narrowing of bond angle at low temperature have also found out by Avitabile *et al.* from the crystal structure analysis of deuterated polyethylene by the neutron diffraction: the bond length is 1.578 Å and the bond angle is $107.7°$). When light atoms such as hydrogen are not considered in the structure analysis by the least squares method, the refined coordinates of atoms intend to shift toward light atoms. Since hydrogen atoms are not considered in the present analysis, the coordinates of carbons may shift toward the positions of hydrogen atoms (cf. Fig. 3) and this shift may result in extending bond length and narrowing bond angle as the coordinates along the c axis are fixed. Molecular chains take an extended planar zigzag conformation as judged from the large *c* axis lattice dimension. Let us imagine the molecular conformation at rather high temperature. When a molecular chain oscillating between left- and right-handed helical conformation is projected on the plane normal to the molecular chain axis, the time-average position of carbon on the plane should shift to the molecular axis from that of planar zigzag molecules. Since the time-average molecular conformation remains in the planar zigzag, this shift of position leads to the apparent expansion of bond angle and the simultaneous shortening of bond length. Thus, the increase of the *c* axis lattice dimension, the extension of bond length and the narrowing of bond angle at low temperature are explained consistently in terms of change in molecular conformation.

Lattice parameters are predicted by many workers[20~25] from minimizing the lattice

energy which is the sum of intermolecular potential energies over all atomic pairs in crystal lattice (see Table III). The molecular chain folding is not considered in these calculations and a crystal lattice is assumed to be perfect and extended infinitely, so that the derived values correspond to those which polyethylene crystal may take at 0°K. The inherent disorder and finite size of a real crystal thus set the limitation in referring to the predicted structure. The difference of the lattice dimensions calculated by various workers is due to the difference of the potential functions in their calculation. The set given by Williams[21] is in good agreement with the present values. Williams has used the potential functions derived by the least squares method from the data on various crystals of simple chain molecules at liquid nitrogen temperature and his potential functions are considered to be closest to the real one. The setting angle of predicted parameters is generally larger than the present value and is smaller than the value (49°) given by Avitabile *et al*. Thus the lattice parameters comparable to the observed ones are predicted theoretically. It is noted, however, that the short bond length and large bond angle at room temperature as well as the temperature invariance of c axis length are assumed in these calculations.

The mean squared displacements of carbon atoms are estimated from the anisotropic temperature factors by Eqs. (4) and (5) (see Table I). $\langle \Delta a^2 \rangle$ is equal to $\langle \Delta b^2 \rangle$ and this result is consistent with the fact that the setting angle of molecular zigzag plane is set to about 45°. The displacement of carbon atom has two origins: (1) the net thermal disorder caused by thermal fluctuation of molecular chains around their regular positions and (2) the statistical lattice imperfection of the inherent molecular displacement from its registered position. The displacement of carbon atoms due to two different origins is not treated separately in Eq. (3) and thus each contribution to the X-ray diffraction cannot be known. Kitagawa and Miyazawa[27] calculated the temperature factors for X-ray scattering at 100°K by using the potential functions determined from the spectroscopic data at low temperature. The mean squared displacement caused only by the thermal agitation is estimated at 0.014 Å² in both a and b axis directions. This values must be smaller at 4.5°K. Though 4.5°K is not necessarily "low" in the field of low temperature physics, the present data may be regarded as those at 0°K from the view point of the thermal motions in molecular crystals. The lattice disorder estimated in the present work is too large to be considered solely due to thermal vibrations, so that the so-called temperature factors at 4.5°K may be treated as the "distortion factors" due to lattice imperfections including the zero-point vibration. Iohara *et al*. estimated this factor as 0.04 Å by the extraporation of the temperature factors obtained at several temperatures above liquid nitrogen temperature to 0°K. Their value is comparable to the present observed data of 0.03 Å² in the a and b axis directions. If the lattice imperfections are known quantitatively, then the lattice disorder due to thermal fluctuation can be estimated by the subtraction of the "disorder factor" from the overall temperature factor. The temperature dependence of disorder will be discussed elsewhere.

The disorder of the first kind due to the statistical lattice imperfections was measured by the structure analysis at low temperature. The result depends largely on the observed integral intensities and the contribution of the lattice disorder of the second kind to the observed intensities should be estimated. The disorder factor of the second kind is given by:[8]

$$D_h = 2 \exp(-2\pi^2 g_h^2 h^2)/\{1 + \exp(-2\pi^2 g_h^2 h^2)\} \qquad (8)$$

where D_h is the fractional reduction in the scattered intensity, g_h is the disorder of the second kind and h is the order of the reflection. Substituting $g_h=0.02$ into Eq. (8),

$$D_{110}=0.996$$

and $$D_{220}=0.984$$

Thus the paracrystalline disorder has a negligible effect on the measured intensities and can be neglected in the structure analysis. The disorder of the first kind (see Table I) plus the paracrystalline disorder (2%) is the total disorder of real crystal. Even when polyethylene is crystallized deliberately at high temperature over a long period, the crystal disorder is inevitably incorporated into crystallites and remains unremoved at low temperature.

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