Unit cell variations of polyethylene crystal with temperature and pressure

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The unit cell dimensions for the drawn and the extended chain crystal samples of polyethylene (PE) have been measured at temperatures between 20° and 130°C under hydrostatic high pressures up to 4000 kg/cm^2, by the use of high pressure and high temperature X-ray diffraction apparatus. A clear difference was found in the variation of *a*, *b* and *c* dimensions of orthorhombic unit cell in PE with temperature and pressure. The temperature changes of linear compressibility for each axis direction of the unit cell and for cell volume were determined on the bases of the variation of cell dimensions. For the *a*-axis direction, a drastic increase of the compressibility was observed above ~90°C but for the *b*- and *c*-axis directions, it was constant for all the temperature region of the measurement. The values of Grüneisen constant, γ, were evaluated at various temperatures from the compressibility data for both samples. The value of γ of the ECC sample was nearly constant below 90°C and gradually increased above 90°C; in the drawn sample, however, a rather steep increase was observed above 90°C.

INTRODUCTION

Various studies have been made of $P-V-T$ relations of polyethylene (PE)$^{1-7}$. In general, the work was performed using a dilatometer under high pressure or by the piston displacement method. The compressibility data obtained by the above methods include the compression of the amorphous region, or cavity, included in the sample in addition to the compression in the crystalline region. Therefore, in order to find the compression behaviour in the crystal lattice, X-ray diffraction under high pressure should be used. A considerable amount of work has recently been undertaken in this field. Ito$^{8-10}$ studied strain behaviours of PE and other polymers under hydrostatic high pressures up to 8000 kg/cm^2 at 20°C by this method. He obtained three corresponding equations which represent lattice strain *versus* pressure for the three axes of the unit cell. Hikosaka *et al.*^{11} studied the strain behaviours of PE under high pressures up to about 45 000 kg/cm^2 by means of diamond anvils and X-ray diffraction at 20°C.

The physical properties of polymers change with temperature. In PE, crystalline dispersion occurs near 90°C so that it is very interesting to investigate the $P-V-T$ relations including the temperature region. A recently developed high pressure X-ray diffraction apparatus^{12}, which enables us to obtain the fibre pattern of the crystalline sample at high temperature, is useful in the above study. In this paper, the change of cell dimensions of the orthorhombic unit cell of the PE crystal with temperature and pressure is shown. Furthermore, the temperature dependence of compressibility and of physical properties drawn from the $P-V-T$ data is presented.

EXPERIMENTAL

Sample preparation

Commercial high density PE, Hizex 2200J, in pellet form (M_w = 40 000) was used as starting material. Drawn samples were prepared by drawing the sheet of PE more than 8 times from its original length at 90°C in a water bath and annealing at 127°C at constant length.

The so-called extended chain crystal (*ECC*) sample was prepared by isothermal crystallization of PE rod under a pressure of 5000 kg/cm^2 according to the method reported in an earlier paper^{13}.

X-ray measurements

The description of the high pressure X-ray apparatus used in this study has been given in detail elsewhere^{12,14}. In our case, only the equatorial lines of reflection were needed so that a semicylindrical slit 1.5 mm in width was set in front of the semicylindrical camera. As the camera was designed to slide upwards following the method of Ito^{15}, it was possible to take a series of X-ray diffraction photographs on the same film.

The temperature was measured by an alumel–chromel sheathed thermocouple (1ϕ, Philips Co.) located near the sample and it was controlled by an SCR heat regulator to within an accuracy of ±0.3°C.

As a pressure transmitting fluid, a low viscosity silicone oil (Shinetsu Kagaku KF96, 10 cs) was used. Pressure measurement was performed with a calibrated manganin resistance manometer^{16}.

In the experiment, the X-ray exposure was started after holding the sample for 15 min at the desired temperature and pressure. The exposure time ranging from 20 min (110 and 200 reflections) to 2 h (002 reflection) was required to produce satisfactory patterns at a power of 40 kV and 20 mA. Ni-filtered CuKα radiation was used in all the experiments. The diffraction photograph from the plane parallel to the fibre axis was taken by setting the fibre axis of the drawn sample parallel to the cylindrical axis of the camera; the diffraction photograph from 002 was taken by setting the fibre axis perpendicular to the cylindrical axis and inclined to the direction of incident beam. The 110, 200, 020 and 002 diffraction lines from each exposure

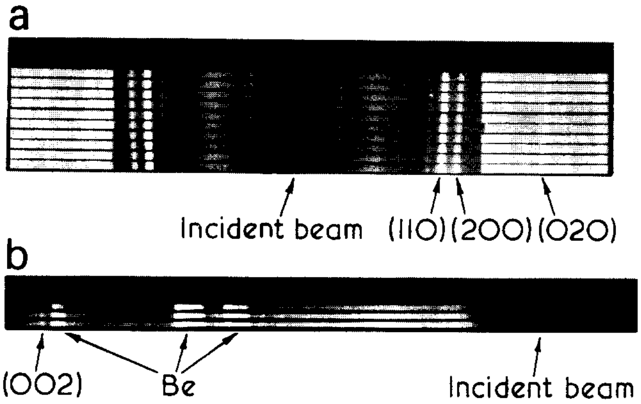

Figure 1 (a) X-ray diffraction photographs of equatorial lines of the drawn sample at 60°C. Corresponding pressures are 1 (atm), 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000 and 4500 kg/cm^2 from the bottom to the top. (b) X-ray diffraction photographs of 002 reflection lines of drawn sample at 50°C. Corresponding pressures are 1 (atm), 2000, and 4000 kg/cm^2 from the bottom to the top

were measured to calculate the parameters a, b and c for the orthorhombic unit cell. The distance of the diffraction lines of the same index in each exposure on the film was determined to within an accuracy of ±0.02 mm using a travelling microscope. A Rigaku 114.6 cm powder camera was also used to check the unit cell dimensions of the drawn sample and *ECC* samples at room temperature and atmospheric pressure. The error included in the final lattice spacing was ±0.005 Å in the a and b dimensions and ±0.001 Å in the c dimension.

The experiments were performed over the temperature range from 20° to 130°C under hydrostatic high pressures up to 4000 kg/cm^2. Powder or equatorial reflection photographs of seven or ten exposures for different pressures were taken on the same film at each temperature.

RESULTS AND DISCUSSION

Change of lattice parameters

Figure 1a is the X-ray diffraction photograph of the equatorial reflection of the drawn sample of PE taken at 60°C, as an example of multi-exposed film (the fibre axis is parallel to the cylindrical axis of the camera). A shift of the diffraction lines with increasing pressure is observed. We have obtained multi-exposed photographs at 5° or 10°C intervals in the temperature range 20°–130°C for both samples. *Figure 1b* is the X-ray diffraction photograph of the 002 reflection of PE taken at 50°C (the fibre axis is perpendicular to the cylindrical axis of the camera and inclined at 60° to the incident beam). The shift of the diffraction lines with increasing pressure is very small in this case.

Figure 2 shows the temperature and pressure changes of the a dimension of the orthorhombic unit cell of a drawn sample of PE. The thermal expansion behaviour of the a dimension at atmospheric pressure corresponds to the data of Swan[17]. The slope of the curve becomes less steep with increasing pressure especially above ~90°C and the thermal expansion curve of the a dimension under high pressure is complicated. The thermal expansion curve of the a dimension obtained by temperature rise under constant pressures of 2000 and 4000 kg/cm^2 agrees with the curve in this Figure within experimental error. A slight difference is observed between the drawn sample and *ECC* samples, especially above 90°C and this is quantitatively expressed in terms of compressibility. The change of the curve of thermal expansion above 90°C appeared under high pressure in both samples and seems to be concerned with the crystalline dispersion of PE (see below).

Figure 3 shows the temperature and pressure changes of the b dimension of the orthorhombic unit cell of the drawn sample. The thermal expansion behaviour of the b dimension at atmospheric pressure corresponds to the data of Swan as in the case of the a dimension. However, in this case, the shape of the curve does not change with pressure and the effect of crystalline dispersion is not found in the curve of thermal expansion when the pressure changes.

Figure 4 shows the change of the c dimension of the drawn sample with temperature and pressure. The curve at atmospheric pressure is on the extension of the curve obtained by Davis *et al.*[18] and the shape of the curve corresponds to the curve of thermal shrinkage of Kobayashi and Keller[19]. The shift of the curve with pressure is very small compared with the shift in the a and b dimensions. The shape of the curve does not change with pressure.

Compressibility

From the change of the lattice parameters with pressure at a given temperature, the change of the lattice strain ϵ

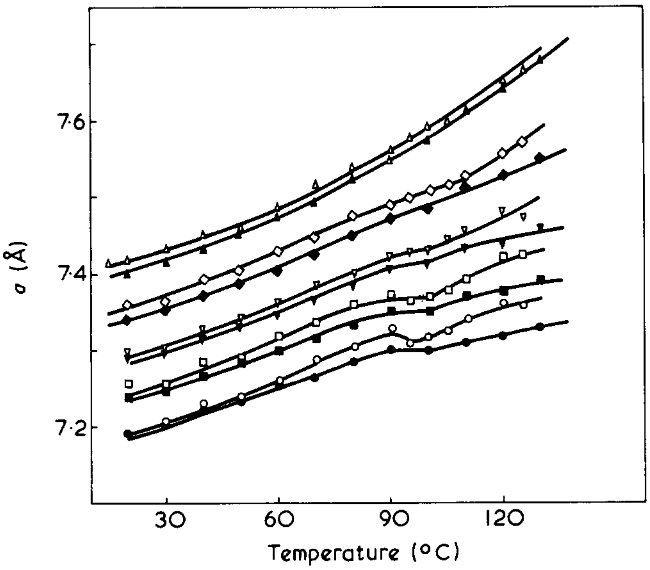

Figure 2 Variation of a dimension with temperature and pressure for drawn sample and *ECC* sample, (200) reflection. △, 1; ◇, 1000; ▽, 2000; □, 3000; ○, 4000 kg/cm^2. (▲, ♦, ▼, ■, ●), *ECC* sample; (△, ◇, ▽, □, ○) drawn sample

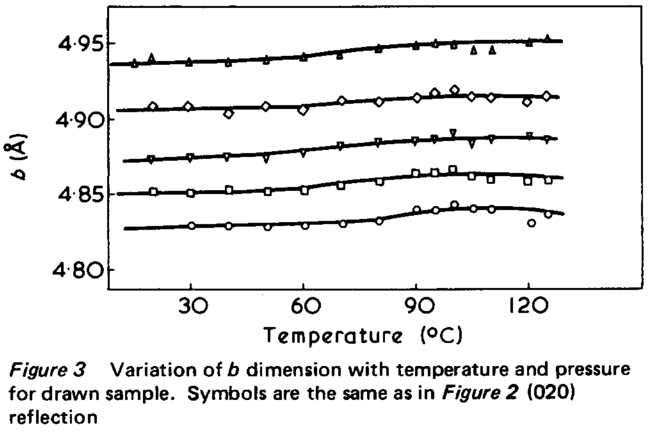

Figure 3 Variation of b dimension with temperature and pressure for drawn sample. Symbols are the same as in *Figure 2* (020) reflection

with pressure can be determined by the following equation:

$$-\epsilon_p = \frac{a_0 - a_p}{a_0} \qquad (1)$$

where a_0 is the lattice dimension at atmospheric pressure and a_p is the lattice dimension at pressure p. The relation expressed in equation (1) is also useful in the case of b- and c-axes.

Figure 5 shows the pressure dependence of the lattice strain along the a-axis at various temperatures for both samples. The numerical values are listed in *Table 1*. In the Figure, the curve at 20°C corresponds to the curve obtained by Ito[10]. A change in the shape of the curve with temperature is observed above 90°C. The ϵ values are represented by the polynomial expression in p as follows:

$$-\epsilon = A_a p - B_a p^2 + C_a p^3 \qquad (2)$$

where the coefficients, A_a, B_a and C_a are determined by means of the least squares method. The value of A_a represents the initial linear compressibility along the a-axis in the orthorhombic unit cell. The temperature dependence of A_a, B_a and C_a for both samples is shown in *Figure 6*. The initial linear compressibility gradually increases from 20° to ~90°C and abruptly increases above ~90°C. This drastic increase of the initial compressibility corresponds to the decrease of modulus in this temperature region of PE which is called the crystalline dispersion region. The temperature changes of B_a and C_a show a similar tendency to the variation of A_a with temperature.

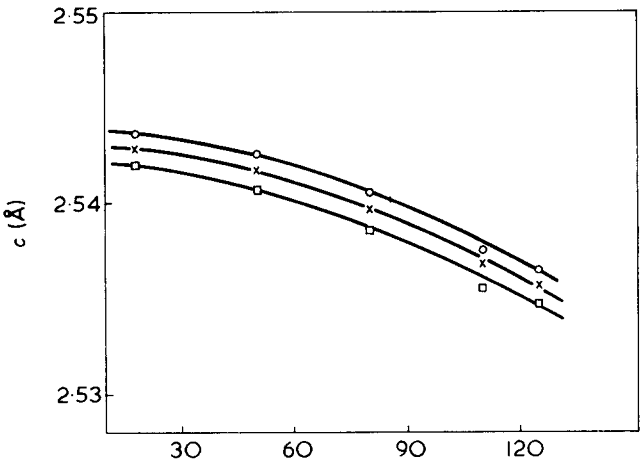

Figure 4 Variation of c dimension with temperature and pressure for drawn sample. ○, 1(atm); X, 2000; □, 4000 kg/cm². (002) reflection

Figure 7 shows the pressure dependence of the lattice strain along the b-axis for both samples and along the c-axis of the drawn sample. In the case of the b-axis direction, the ϵ-p relation does not change with temperature so that the relation is represented by only one equation for all the temperature region measured, as follows:

$$\text{Drawn sample} \quad -\epsilon_b = 6.84 \times 10^{-6} p - 0.30 \times 10^{-9} p^2 + 0.01 \times 10^{-12} p^3 \qquad (3a)$$

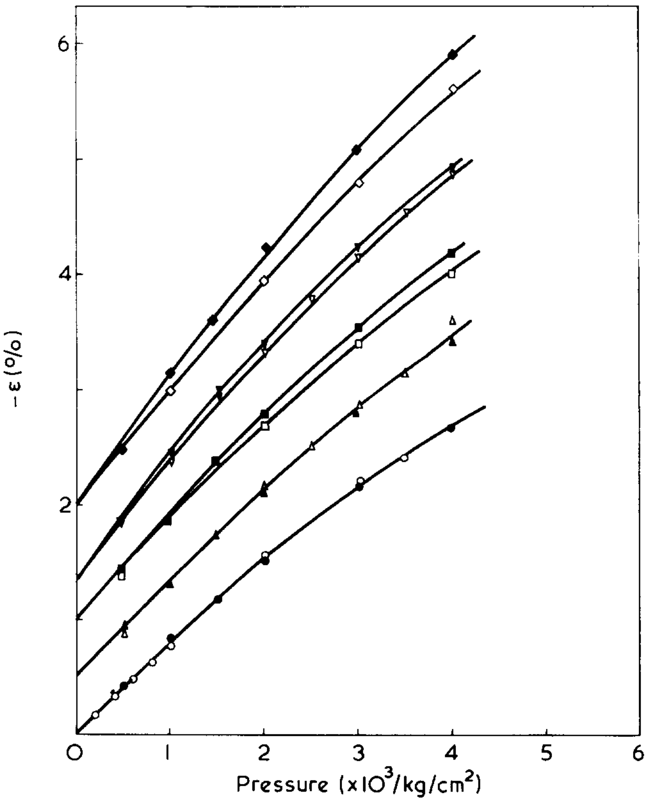

Figure 5 Change of strain *versus* pressure curve with temperature along the a-axis for both samples. ○, 20; △, 50; □, 90; ▽, 100; ◇, 120°C. (○, △, □, △, ◇), drawn sample; (●, ▲, ■, ▼, ◆), *ECC* sample. The curves except for 20°C are shifted arbitrarily along vertical axis. (200) reflection

Table 1

	Drawn sample			*ECC* sample		
Temperature (°C)	$A_a \times 10^6$	$B_a \times 10^9$	$C_a \times 10^{12}$	$A_a \times 10^6$	$B_a \times 10^9$	$C_a \times 10^{12}$
20	8.86	0.68	0.070	9.11	0.75	0.032
30	9.08	0.50	0.009	9.16	0.67	0.047
40	8.88	0.51	0.037	9.12	0.74	0.053
50	9.24	0.69	0.074	9.16	0.73	0.067
60	9.18	0.52	0.041	9.51	0.70	0.036
70	9.54	0.62	0.034	9.47	0.69	0.039
80	9.55	0.60	0.047	10.45	0.72	0.029
90	10.40	0.69	0.006	11.03	0.91	0.054
95	11.81	0.79	0.021	–	–	–
100	12.80	1.36	0.112	13.30	1.33	0.079
105	13.52	1.67	0.144	–	–	–
110	12.96	1.40	0.115	13.50	1.30	0.098
120	14.08	1.91	0.203	15.01	1.58	0.109
125	16.20	2.49	0.239	–	–	–
130	–	–	–	18.16	2.45	0.183

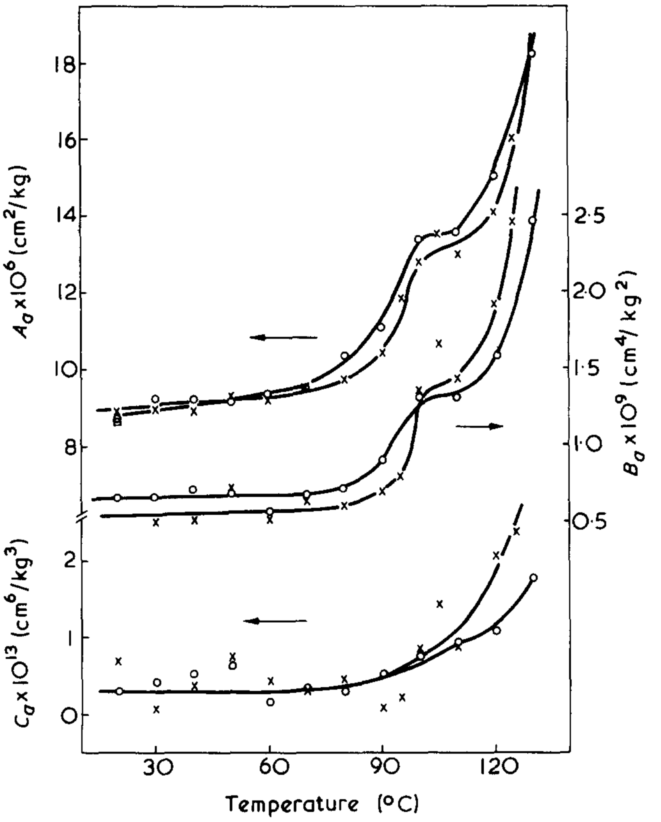

Figure 6 Variation of A_a, B_a and C_a with temperature. X, drawn sample; O, *ECC* sample

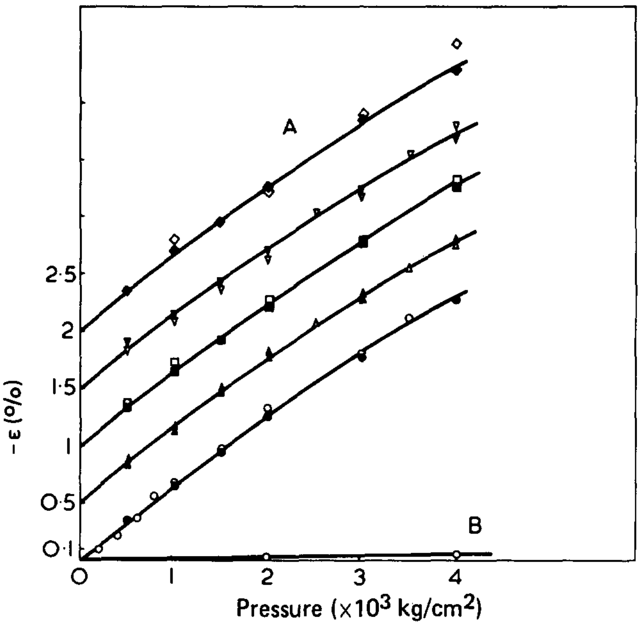

Figure 7 Change of strain *versus* pressure curve with temperature along the *b*-axis for both samples. Symbols are the same as in *Figure 5*. The curves except for 20°C are shifted arbitrarily along vertical axis. Strain *versus* pressure curve in *c*-axis is also shown in the Figure. A, (020); B, (002)

$$ECC\text{ sample:}\quad -\epsilon_b = 6.62 \times 10^{-6}p - 0.10 \times 10^{-9}p^2 - 0.02 \times 10^{-12}p^3 \qquad (3b)$$

Along the *c*-axis as in the case of the *b*-axis, the compressibility change with temperature was not observed. The change of lattice dimension with temperature and pressure is very small compared with the change in *a*- and *b*-axes and the ϵ–p curve for a drawn sample is represented by a linear equation in p for all the temperature region, as follows:

$$-\epsilon_c = 0.12 \times 10^{-6}p \qquad (4)$$

The very small value of the linear compressibility along the *c*-axis in comparison with the value along the *a*- and *b*-axes has been reported by Ito; the origin of the difference is ascribed to the extremely large value of the intrachain force constant along the *c*-axis in contrast with the value of the interchain force constant perpendicular to the chain axis in the PE crystal. The ϵ–p relation was not obtained for the *ECC* sample because the 002 diffraction lines in the film were very weak. However, if we assume that the ϵ–p relation along the *b*-axis for both samples is nearly the same and the value of linear compressibility along the *c*-axis is very small, we may consider that the relation along the *c*-axis is nearly the same for both samples.

The equation for the volume compression of the unit cell is determined by summing the equations (2)–(4), as follows:

$$\frac{V_0 - V_p}{V_0} = Ap - Bp^2 + Cp^3 \qquad (5)$$

The coefficients A, B and C vary with temperature according to the variation of the coefficients A_a, B_a and C_a with temperature in equation (2). The change of the shape of the strain of the cell volume *versus* pressure curve at different temperatures for both samples is shown in *Figure 8*. The numerical values of A, B and C are listed in *Table 2*. It is clear that the shape of the curve resembles the shape of the curve for the *a*-axis at the corresponding tempera-

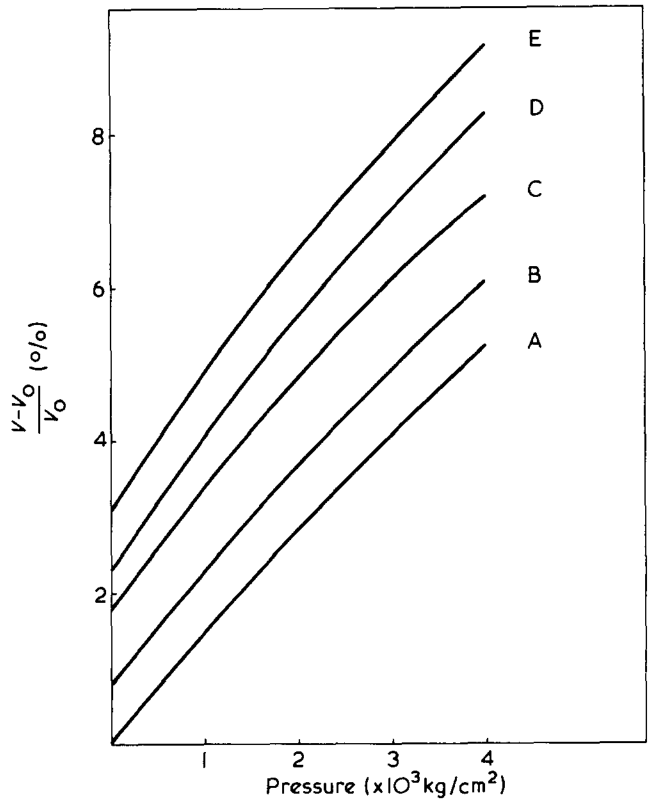

Figure 8 Change of strain *versus* pressure curve with temperature in volume for drawn sample. A, 20; B, 50; C, 90; D, 100; E, 120°C. Curves except for A are also shifted along vertical axis

Table 2

	Drawn sample			*ECC* sample		
Temperature (°C)	$A \times 10^6$	$B \times 10^9$	$C \times 10^{12}$	$A \times 10^6$	$B \times 10^9$	$C \times 10^{12}$
20	15.82	0.98	0.080	15.84	0.85	0.008
30	16.04	0.80	0.019	15.89	0.77	0.023
40	15.84	0.81	0.047	15.87	0.84	0.029
50	16.20	0.99	0.074	15.89	0.83	0.043
60	16.14	0.82	0.041	16.02	0.62	0.012
70	16.50	0.92	0.044	16.20	0.79	0.015
80	16.51	0.90	0.057	17.18	0.82	0.005
90	17.36	0.99	0.016	17.76	1.01	0.030
95	18.77	1.09	0.031	–	–	–
100	19.76	1.66	0.122	20.03	1.43	0.055
105	20.36	1.97	0.154	–	–	–
110	19.92	1.70	0.125	20.23	1.40	0.074
120	21.04	2.21	0.213	21.74	1.68	0.085
125	25.13	3.74	0.367	–	–	–
130	–	–	–	24.89	2.55	0.159

ture. *Figure 9* shows the variation of the initial volume compressibility with temperature. The comparison between *Figures 9* and *5* leads us to a conclusion that the variation of the initial volume compressibility with temperature is a reflection of the variation of the initial linear compressibility for the *a*-axis and not for *b*- and *c*-axes.

Temperature dependence of Grüneisen constant

The Grüneisen constant, γ, is a parameter which reflects the anharmonicity of solids. An understanding of γ would provide information on the nature of polymeric solids, therefore, a considerable interest has been taken in the study of γ of PE. A method of obtaining the value of γ from the volume compression data is to use the following equation:

$$\gamma = -\frac{1}{2} + \frac{B}{A^2} \tag{6}$$

where A and B are the coefficients which appear in equation (5). Equation (6) was derived by Pastine[20] by a slight modification of Slater's[21] original equation for three-dimensional solids to the approximately two-dimensional solid such as PE. Ito[10] obtained the value of 3 as the γ value for PE at 20°C by the use of the above equation.

As the coefficients A and B in the p–V equation (equation 5) have been obtained for various temperatures from 20°–130°C, we can determine the values of γ for various temperatures according to equation (6).

Figure 10 shows the variation of γ with temperature for the drawn and *ECC* samples. A large difference between the two samples occurs above 90°C. In the drawn sample, the value of γ increases rather rapidly with temperature above 90°C, but in *ECC* it increases gradually in the same temperature region. The tendency for the value of γ to increase for the *ECC* sample agrees with the tendency of the temperature change of γ in the *ECC* sample obtained by the dilatometric method under high pressure in the same temperature region by Kijima *et al.*[22]. However, the value of γ is different and their values are more than twice our value. They discussed the anharmonicity of molecular motions in PE crystal on the basis of the result of the symmetric tensor, **U**, which represents the mean square displacements of atoms in the lattice[23]. According to them, the increased value of γ near the crystalline dispersion region may be considerably ascribed to the increase of anharmonicity of translational vibrations along the molecular axis. The difference of the value seems to originate from the difference of the method of measurement, because the equation used by them to evaluate the value of γ is basically the same as equation (6). *Figure 11* shows the comparison of the pressure dependence of compressibility defined by:

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) \tag{7}$$

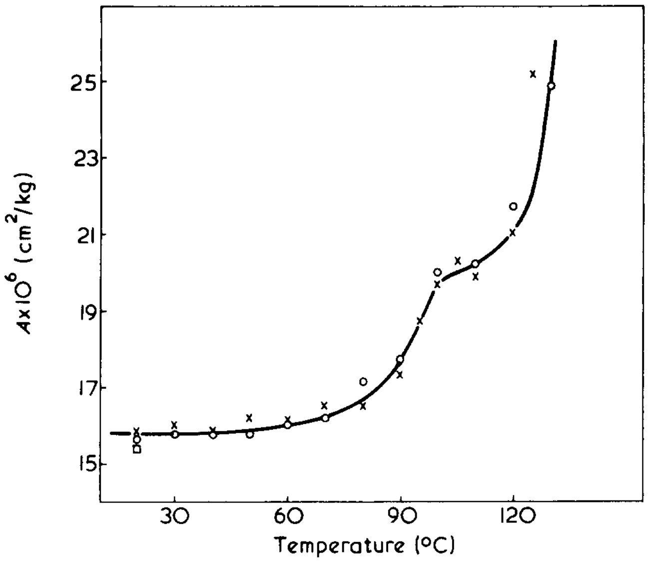

Figure 9 Variation of A with temperature. Symbols are the same as in *Figure 6*

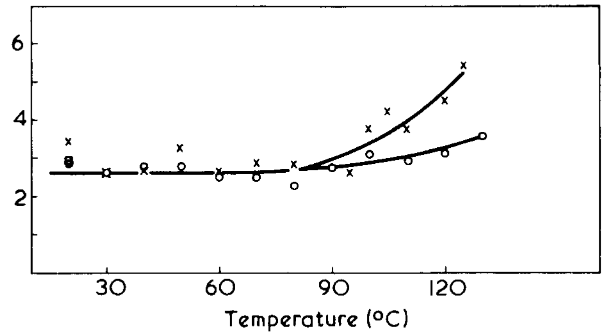

Figure 10 Variation of γ with temperature. Symbols are the same as in *Figure 6*

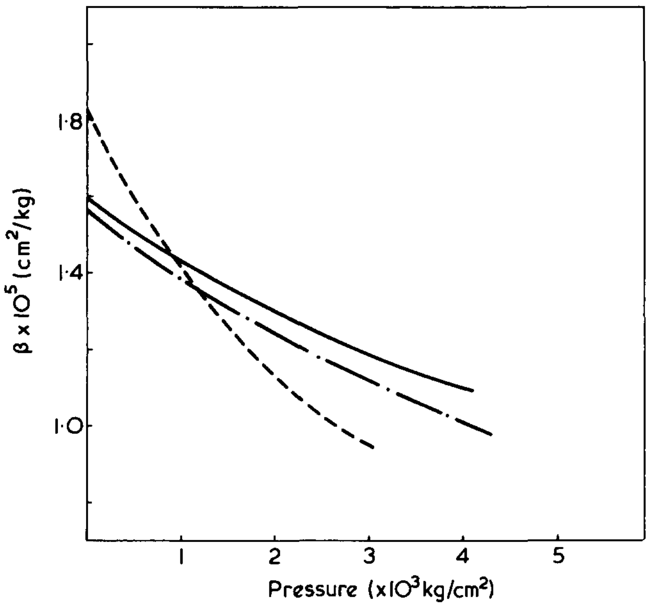

Figure 11 Variation of compressibility with pressure at 40°C: – – – –, ref 22; ——, this work; — · — ·, ref 9 (20°C)

A clear difference is observed between the volume compression curve obtained by the methods of dilatometry and X-ray diffraction under high pressure.

The tendency of γ to increase at about 90°C in the drawn sample may be mainly ascribed to the increased mobility of molecules in the interlamellar region or defect region in the crystal as described by Kijima *et al.*, because the crystal in the drawn sample is thought to be close to the imperfect crystal sample in their paper[22].

CONCLUSIONS

Considerable changes in lattice dimensions of the orthorhombic unit cell of PE for the drawn and *ECC* samples have been observed subsequent to changes of pressure and temperature. The appearance of the change of the lattice dimension for each direction in the three principal axes of the orthorhombic unit cell with temperature and pressure was different.

A difference was observed between the temperature dependence of the shape of lattice strain *versus* pressure curve for the *a*-axis and the other axes. The initial linear compressibility for the *a*-axis changes with temperature and an abrupt increase of its value was observed above 90°C. Its value did not change with temperature along *b*- and *c*-axes. The change of initial volume compressibility with temperature depended on the change of the linear compressibility with temperature along the *a*-axis.

The variation of the Grüneisen constant, γ, with temperature was obtained for both samples. The value of γ was nearly constant below 90°C for both samples and it increased gradually above 90°C for the *ECC* sample and rather rapidly for drawn sample.

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REFERENCES

1 Weir, C. E. *J. Res. Nat. Bur. Stand.* 1951, **46**, 207
2 Weir, C. E. *J. Res. Nat. Bur. Stand.* 1954, **53**, 245
3 Matsuoka, S. and Maxwell, B. *J. Polym. Sci.* 1958, **32**, 131
4 Matsuoka, S. *J. Polym. Sci.* 1962, **57**, 569
5 Hellwege, K. H., Knappe, W. and Lehman, P. *Kolloid Z.* 1962, **183**, 110
6 Warfield, R. W. *J. Appl. Chem.* 1967, **17**, 263
7 Olabisi, O. and Simha, R. *Macromolecules* 1975, **8**, 206
8 Ito, T. and Marui, H. *Polym. J.* 1971, **2**, 768
9 Ito, T. *J. Crystallogr. Soc. Jpn* 1974, **16**, 318
10 Ito, T. *High Polym. Jpn.* 1976, **25**, 750
11 Hikosaka, M., Seto, T. and Minomura, S. *Polym. Prepr. Jpn.* 1977, **26**, 421
12 Nakafuku, C. and Takemura, T. *Jpn J. Appl. Phys.* 1975, **14**, 599
13 Yasuniwa, M., Nakafuku, C. and Takemura, T. *Polym. J.* 1973, **4**, 526
14 Yasuniwa, M., Enoshita, R. and Takemura, T. *Jpn J. Appl. Phys.* 1976, **15**, 1421
15 Ito, T. *Rev. Sci. Instrum.* 1974, **45**, 1560
16 Nakafuku, C., Takamizawa, K. and Takemura, T. *Rev. Sci. Instrum.* 1976, **47**, 229
17 Swan, P. R. *J. Polym. Sci.* 1962, **56**, 403
18 Davis, G. T., Eby, R. K. and Colson, J. P. *J. Appl. Phys.* 1970, **41**, 4316
19 Kobayashi, Y. and Keller, A. *Polymer* 1970, **11**, 114
20 Pastine, D. J. *J. Chem. Phys.* 1968, **49**, 3012
21 Slater, J. C. 'Introduction to Chemical Physics', Dover, New York, 1970, Ch. 13, 14
22 Kijima, T., Koga, K., Yoshizumi, T., Imada, K. and Takayanagi, M. *Proc. 4th Int. Conf. High Pressure, Kyoto, 1974*, p. 78
23 Iohara, K., Imada, K. and Takayanagi, M. *Polym. J.* 1972, **3**, 357