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An X-ray study of polyethylene at pressures up to 14 000 kg cm^{-2} at 298 K

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The diamond piston–anvil method was used to make X-ray wide-angle diffraction studies of polyethylene at 298 K and at pressures up to 14 000 kg cm^{-2}. The data obtained were compared with the results of a study by Ito and Marui, and their observations (which were made at pressures up to 3000 kg cm^{-2}) were essentially confirmed. However, our data revealed that the linear compressibility in the [1 1 0] and [2 0 0] directions did not vary with pressure in a linear fashion over the entire range, and the empirical relation $-\epsilon_{hkl} = A_{hkl}p - B_{hkl}p^2$, where ϵ_{hkl} is the stress on hkl planes, was not found to be adequate for the planes (1 1 0) and (2 0 0) for pressures up to 14 000 kg cm^{-2}. With the addition of a third cubic term $C_{hkl}p^3$ to the relation, a better fit of the data could be achieved. By ignoring strains in the chain direction, the volumetric strains as a function of pressure were calculated, and the data agreed well with the equation of state derived by Pastine for the crystalline phase of polyethylene. A value for the Grüneisen constant γ_0 at atmospheric pressure and 298 K was calculated and a value $\gamma_0 = 3.64$ was obtained. This agrees well with values obtained by Ito and Marui. No phase transition was observed at 298° C for the pressure range reported.

1. Introduction

In recent years, investigations of the effects of crystallization and annealing treatments at high pressures on polymer structure and morphology have been carried out, and new morphologies [1–9] and crystal structures [10–17] have been found. In addition, many studies of the mechanical properties of polymers at high hydrostatic pressures have been made, and a number of interesting observations reported [18–23]. Also, important theoretical contributions to the understanding of the equation of state of polymer crystals have been published [24, 25].

On the other hand, the direct observation of polymers under conditions of high pressure has not been carried out in any systematic way. In particular, the number of X-ray diffraction studies of polymers at elevated pressures are very few. A high-pressure X-ray study of polytetrafluoroethylene was carried out by Flack [12]. A solid-state, reversible phase transition occurring at ~ 7 kbar was found, and the X-ray data included that the conformation of the polytetrafluoroethylene macromolecule had changed to the planar zigzag at the higher pressures. A study of polyethylene was made by Ito and Marui [26] for pressures up to 3000 kg cm^{-2}. No phase transition at room temperature was observed in this pressure range, although the crystal lattice deformations were extremely anisotropic. An empirical representation of the equation of state for the polyethylene lattice was derived and an estimate of the Grüneisen parameter calculated. Klemper and Karasz [27] also reported on a preliminary study of the compressibility of polyethylene in the pressure range of atomospheric to 9.3 kbar. A diamond-anvil cell was employed with NaCl for the pressure standard. Since no liquid was used in the cell for pressure-transmitting medium, it is doubtful that pure hydrostatic pressure was achieved. Furthermore, the use of NaCl as the pressure standard will introduce an error of at least 44% at 3 kbar in pressure calibration [28]. A study of polyethylene at elevated pressures and temperatures was made by Bassett *et al.* [29], who reported that polyethylene crystallizing from the melt at pressures in the range 3 to 4 kbar crystallized in a hexagonal phase which, as the temperature was reduced, transformed to the more usual orthorhombic phase. This phase transition appeared to be related to the extended-chain lamellae morphology produced in polyethylene by crystallizing or annealing in this pressure–temperature region.

The experimental problems implicit in reliable studies of this kind are considerable, and it was decided to improve experimental techniques and to carry out systematic studies of polymeric materials. Our results for a study of high-density linear polyethylene up to 14 000 kg cm^{-2} at 298 K are given here, together with a description of our experimental methods.

2. Experimental

2.1. Apparatus

Two different types of X-ray high-pressure diffraction cameras have been used in the study of polymeric materials. The camera used by Ito and Marui [26], was based on a design developed by Kabalkina and Vereshchagin [30]. The sample is placed in an axial circular hole drilled in the beryllium window of a high-pressure cell of a piston-cylinder type. Water can be used as the pressure medium, and pressures up to 5000 kg cm^{-2} can be obtained by use of a 20 ton hydraulic press. The pressure generated can be measured using a conventional high-pressure gauge. The particular advantage of this camera is that the pressure can be controlled and measured quite accurately. The disadvantage is that the hydrostatic pressures reached are rather low, lower than the pressures involved in the many interesting phenomena [1–23] which it would be desirable to study.

A second design capable, in principle, of reaching much higher pressures was used by Flack [12] and Bassett *et al.* [29]. This is the diamond-anvil pressure cell first reported in 1959 [31] and used extensively in the study of minerals, ionic compounds, and metallic materials at high pressures. Schematic diagrams are shown in Figs. 1 and 2. The high pressures are produced by compressing materials between two opposed diamond-anvils. A hole drilled in a metal gasket filled with some pressure medium contains the sample, and when this system is compressed, the sample is subjected to a truly hydrostatic pressure, provided that pressure medium does not solidify. The pressured volume is usually assumed to be a right circular cylinder (0.25 mm diameter and 0.15 mm thick). The metal gasket flows in such a way as to decrease the volume, that is, to increase the pressure on the sample. The advantage of this method is that very high pressures can be reached. The disadvantage is that some method of ascertaining the pressure must be found. Moreover, the X-ray beam must traverse both diamonds in addition to the gasketed sample. The sample is small, and for polymeric materials it is generally much smaller than the

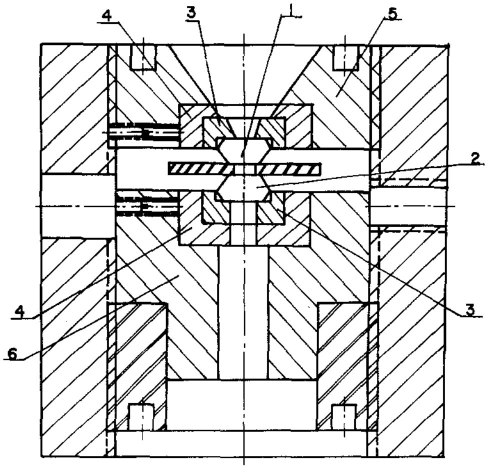

Figure 1 Schematic diagram of the diamond-anvil, high-pressure X-ray diffraction camera.

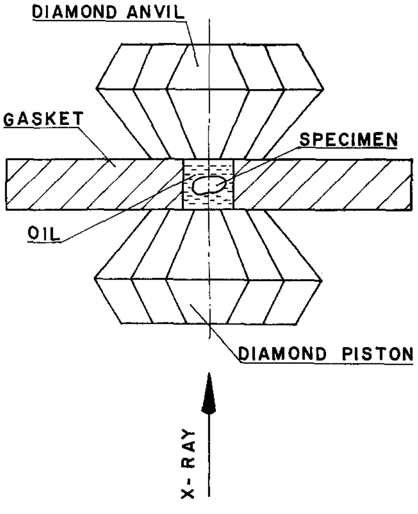

Figure 2 Schematic details of the arrangement of diamonds, gasket and specimen.

X-ray optimum thickness. This fact, combined with incoherent scatter from the diamonds, implies weak diffracted intensities on a high background, with extremely long exposure times, if conventional X-ray equipment is used.

It was felt that the advantages of reaching the higher pressures attainable, using this latter technique, outweighed these disadvantages, and in this study an X-ray camera based on the diamond-anvil pressure cell was used. The compressibility of linear, high-density polyethylene was studied as a function of pressure up to 14 000 kg cm^{-2}. A similar study of Ito and Marui [26] was limited by a maximum pressure of 3000 kg cm^{-2}. Since the design of the high-pressure X-ray camera they used was entirely different from the one used in this investigation, it was felt that a direct comparison with their study would be an important confirmation of the reliability of both techniques.

The use of the diamond-anvil pressure cell raised the three problems already discussed: measurement of pressure, low contrast of the diffracted intensities, and extremely long exposure times. The latter problem was solved by the use of a 6 kW Rigaku–Denki rotating anode X-ray generator utilizing molybdenum radiation with a zirconium filter. Using 60 kV and 100 mA, exposure times of under 4 h were practicable. The problem of low contrast could be solved most directly by the increase of sample size, the optimum thickness of polyethylene for molybdenum radiation being ~ 17 mm. Since the sample size is limited by the size of the pressurized volume, which depends critically on the type of gasket used, some initial experimentation was carried out with different types and thicknesses of gaskets. The effect of increasing the hold diameter was also studied.

2.2. Gaskets

Very simply, the maximum pressure attainable depends on the normal and frictional forces developed between the faces of the diamond-anvils and the faces of the gaskets. These forces of reaction prevent blow-out, and their maximum values depend on the strength of the material. In order to produce high pressures, the pressurized volume must decrease by as much as 30 to 40%, and this can only be achieved by considerable deformation of the gasket. The gasket must then be ductile but also work-harden to provide sufficient strength to prevent blow-outs. In order to produce extremely high pressures, the gasket should be very thin, so that even small deformations result in large fractional decreases in volume, and thus high pressures. If the thickness of the gasket is increased, greater deformation is required to reach the same pressure. After some experimentation, brass gaskets with thicknesses of up to ~ 1 mm were found suitable provided pressures of 20 000 kg cm^{-2} were not exceeded. Larger diameter holes (~ 1 mm) could be used with the thicker gaskets. This entailed the use of very large diamonds (0.5 carat), so that the ratio of surface area compressed to surface area of the hole remained approximately the same.

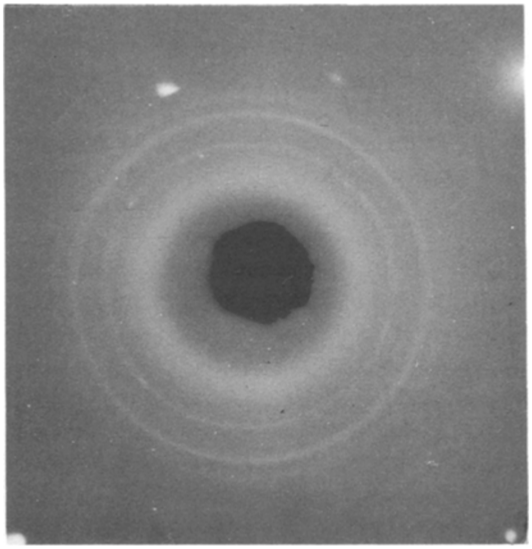

Figure 3 Typical X-ray diffraction picture of polyethylene with hexamethylene tetramine.

The pressurized volume being thus increased, much larger samples could be used, and quite good contrast was obtained for the two most intense reflections from polyethylene, the (2 0 0) and (1 1 0). Using 60 kV and 100 mA, X-ray photographs could be obtained in only 4 h. A typical example is shown in Fig. 3. In addition to the polyethylene (2 0 0) and (1 1 0) reflections, some lines from the gasket material and, also, spots from the diamond single crystals can be observed. It was found that the sample should occupy not more than approximately 75% of the original pressurized volume. At higher fractions than this, during the compression the faces of the diamonds might begin to bear directly on the sample, thus introducing non-hydrostatic stress components. This could be detected by broadening and distortion of the diffracted lines. Similar observations were reported by Flack which he attributed to twinning and shearing processes. One advantage of the camera used by us was that the sample could be observed directly under pressure, using a low-power microscope. Any distortion of the sample could then be observed directly. Provided at least 25% of the pressurized volume was occupied by the pressure medium, this phenomenon did not occur at pressures up to 14 000 kg cm^{-2}. Fig. 4 shows a sample pressurized at 14 000 kg cm^{-2}, the sample having been observed to deform isotropically up to this pressure. Silicone oil was used as a pressure medium.

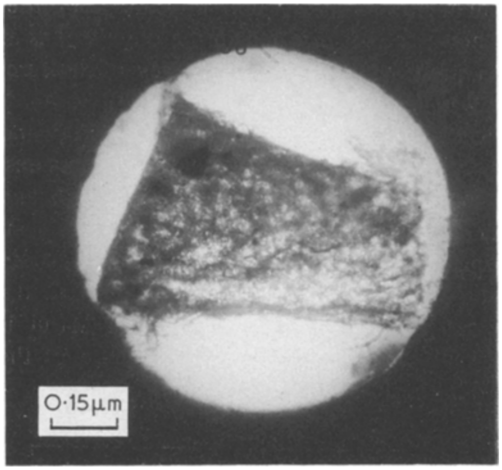

Figure 4 Optical microscopic picture of polyethylene specimen inside gasket under high pressure (14 000 kg cm^{-2}).

2.3. Pressure measurements

The problem remained of the accurate measurement of the pressure. The study carried out by Bassett *et al.* [29] involved higher temperatures, the polyethylene being crystallized from the melt. Of course, the melting point of polyethylene does depend on the pressure, and therefore a knowledge of the melting point can be used to estimate the pressure. In principle, the pressure can be determined by raising the temperature and measuring the melting point of the polymer. This is to assume that the pressurized volume remained constant with temperature. Since this assumption has not been verified up to the present time, this method was not used.

The method used by Flack [12] was to mix a small amount of NaCl with his sample. Measurements of the interplanar spacings of NaCl can be made and the pressure determined using the equation of state of Dekker [32]. This method is not reallly accurate at the low pressures of interest, however, since the compressibility of NaCl is quite low and the change in interplanar spacings very small. Molecular crystals generally have much higher compressibilities and make a more suitable standard. A separate experiment was carried out to determine the pressure–volume relationship for hexamethylene tetramine (HMT) at 298 K, and the results of this study are published separately. Using HMT as a standard, the pressure could be determined quite easily, with an accuracy of about 200 kg cm^{-2} at 10 000 kg cm^{-2} pressure.

2.4. Sample

A linear, high-density polyethylene, Marlex 6009, was used for these studies. The melting point of HMT exceeds that of polyethylene, and so it was found possible to mold a very small sample filled with finely ground HMT. The HMT crystals were embedded in a matrix of polymer, and it was assumed that the pressure exerted on the HMT crystals (measured by the change in interplanar spacing) was identical with the hydrostatic pressure exerted on the sample. This is to assume that the pressure is transmitted uniformly through the sample, which at the high pressures used seems reasonable. In addition, this technique entailed that the specimen-to-X-ray film distance was identical for both polyethylene and HMT. After solidification, the composite specimen was annealed at 110° C for 3 h to increase the degree of crystallinity.

3. Experimental procedure

A Rigaku–Denki rotating anode 6 kW generator was used with a molybdenum target. The radiation was filtered using a zirconium filter. The diffraction patterns were recorded on flat film, the exposure time being about 4 h for 60 kV and 100 mA. In this investigation, only the (2 0 0) and (1 1 0) reflections were studied. In general, the X-ray photographs showed Debye–Scherrer rings originating from polyethylene, HMT, and the gasket material and, in addition, Laue spots from the diamond-anvils. It so happended that reflections from planes which were not parallel to the *c*-direction were eclipsed by reflections originating from the metal gasket. The lattice parameter at atmospheric pressure being known for HMT [28], the sample-to-film distance could be determined with high accuracy from the diameter of HMT (1 1 0) Debye–Scherrer rings (averaged over several different patterns taken at atmospheric pressure).

By comparison of the results obtained by repeated pressure application and releases on the same specimen up to 14 000 kg cm^{-2}, it was found that the effects of previous pressure applications on the crystal lattice of polyethylene were negligible. This was not true, of course, in those cases when too large a sample was used, when the application of non-hydrostatic stresses produced plastic deformations. As described previously, care was taken to avoid this situation by using a sufficiently small sample.

Several photographs taken over a period of several days showed that no viscoelastic effects occurred. The pressure was found to be constant over a prolonged time period, providing the temperature was constant.

4. Results and discussion

The interplanar spacings of the (1 1 0) and (2 0 0) planes in the polyethylene lattice were measured at a number of different pressures up to 14 000 kg cm^{-2}. All the measurements were made on the same sample by increasing the pressure in small increments up to the maximum pressure. The equation $\epsilon_{hkl} = [d_{hkl} - (d_{hkl})_0]/(d_{hkl})_0$ is used to calculate the strains in [1 1 0] and [2 0 0] directions, where d_{hkl} is the d-spacing at an elevated pressure and $(d_{hkl})_0$ at atmospheric pressure. The results of the calculation are tabulated in Table I. The limit of accuracy of measurement of each d-spacing was estimated to be within ~ 0.005 Å, which implies the strains are accurate to about ± 0.002. However, the fractional error in the strains is not better than ~ 10% until pressures greater than 2000 kg cm^{-2} are reached. This problem is compounded in that the pressures are also determined by the measured strains of the HMT lattice. It was estimated that the pressure measurements are in error by ± 200 kg cm^{-2} throughout the entire range. The fractional error in the pressures, then, is not less than 10% until pressures greater than 2000 kg cm^{-2}. It was precisely for this reason that HMT was used rather than sodium chloride, but even so it is clear that the data obtained at the lower pressures are less reliable.

TABLE I

p (10^3 kg cm^{-2})	$-\epsilon_{110}$ (%)	$-\epsilon_{200}$ (%)
0	0	0
0.4733	0.34	0.45
1.0937	0.68	1.20
1.7775	1.18	1.64
2.4820	1.68	2.08
4.0198	2.33	2.66
4.8537	2.65	2.95
5.7285	3.13	3.23
6.6440	3.45	3.51
7.6018	3.77	3.80
9.6467	4.39	4.49
11.8751	5.01	5.18
14.0055	5.62	5.58

Of course, more refined techniques of measurement of the d-spacing are possible to improve measurements of these lower pressures. Our interest, however, was directed to the observations at higher pressures, where the accuracy of measurement was sufficient.

Figs. 5 and 6 show the strains of the (1 1 0) and (2 0 0) planes, respectively, at different pressures. For comparison, the data obtained by Ito and Marui [26] are also shown on both plots. Considering the possible errors in the pressure–strain measurements in the low-pressure region, the agreement with the data of Ito and Marui is remarkably good, especially for the case of the (2 0 0) lattice planes.

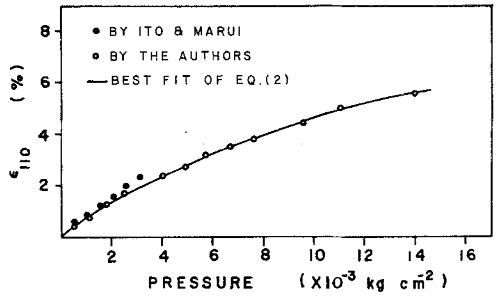

Figure 5 Strain versus pressure curve for (1 1 0) plane of polyethylene.

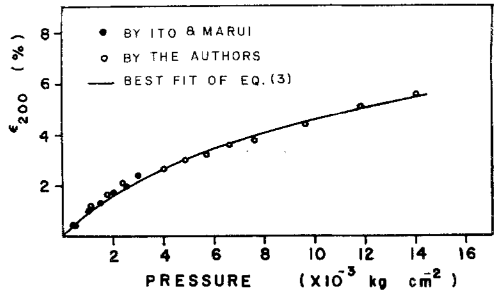

Figure 6 Strain versus pressure curve for (2 0 0) plane of polyethylene.

TABLE II

Reference	Plane	Empirical relation
Ito and Marui	(1 1 0)	$-\epsilon_{110} = 8.68 \times 10^{-6}p - 0.0379 \times 10^{-8}p^2$
	(2 0 0)	$-\epsilon_{200} = 11.5 \times 10^{-6}p - 0.120 \times 10^{-8}p^2$
This work	(1 1 0)	$-\epsilon_{110} = 7.390 \times 10^{-6}p - 0.03828 \times 10^{-8}p^2$
	(2 0 0)	$-\epsilon_{200} = 11.872 \times 10^{-6}p - 0.1410 \times 10^{-8}p^2$

Pressure range: 0 to 3000 kg cm^{-2}
The least-squares fits for empirical equation: $-\epsilon_{hkl} = A_{hkl}p - B_{hkl}p^2$

Ito and Marui suggested that the pressure–strain plot could be represented by the function

$$-\epsilon = Ap - Bp^2 \quad \text{or} \quad -\frac{d\epsilon}{dp} = A - 2Bp \quad (1)$$

and fitted their data by a least-squares method to this function. In order to further compare our observations with those of Ito and Marui, we also carried out this least-squares fit to the data. Of course, the function is only empirical and implies a linear decrease in the linear compressibility $K_{hkl} = d\epsilon_{hkl}/dp$ of the lattice planes (hkl). This would certainly not be a valid assumption for higher pressures. For this reason, in addition to fitting the data over the entire pressure range (0 to 14 000 kg cm^{-2}), we carried out a separate fit of the data over a low-pressure range (0 to 3000 kg cm^{-2}). The best-fit parameters A and B obtained for this low-pressure range are shown in Table II.

Clearly, the agreement with Ito and Marui is quite good providing only the low-pressure data are considered. However, the empirical fit cannot be extrapolated to higher pressures. It was found impossible to fit the strain–pressure data satisfactorily using Equation 1 over the entire pressure range 0 to 14 000 kg cm^{-2}. Actually, Equation 1 is the approximation for small pressures of a general polynomial series $-\epsilon_{hkl} = A_{hkl}p - B_{hkl}p^2 + C_{hkl}p^3 + \ldots$. By extension of Equation 1 to the third term $C_{hkl}p^3$, we were able to obtain a better fit of our data using the least-squares method. The following empirical equations were found:

$$-\epsilon_{110} = 7.25 \times 10^{-6}p - 0.0386 \times 10^{-8}p^2 + 0.111 \times 10^{-13}p^3 \quad (2)$$

$$-\epsilon_{200} = 8.46 \times 10^{-6}p - 0.0532 \times 10^{-8}p^2 + 0.147 \times 10^{-13}p^3. \quad (3)$$

These empirical equations are valid only for the pressure range 0 to 14 000 kg cm^{-2}, and extrapolation to higher pressures should not be made. The fit of Equations 2 and 3 to the measured data is shown in Figs. 5 and 6, where the data of Ito and Marui are also shown. For the case of the (1 1 0) planes, Equation 2 represents a good fit of the data over the entire pressure range. For the case of the (2 0 0) planes, Equation 3 represents a good fit of the data for pressures greater than 4000 kg cm^{-2}. At the lower pressures, some systematic discrepancies exist.

When the linear compressibilities K_{110} and K_{200} are considered, it is more evident that a function with the form of Equations 2 and 3 is more reasonable than Equation 1. If Equations 2 and 3 are used, then

$$K_{hkl} = \frac{d\epsilon_{hkl}}{dp} = A_{hkl} + 2B_{hkl}p + 3C_{hkl}p^2. \quad (4)$$

Comparing the linear compressibility with pressure of the planes (1 1 0) and (2 0 0), it is obvious from Fig. 7 that at lower pressures (0 to 2000 kg cm^{-2}) the rate of change of K_{200} is much greater than that of K_{110}. However, at higher pressures the rate of change of K_{110} and K_{200} is rather close.

Volumetric strain can be obtained by addition of the linear strains of the three orthorhombic axes ϵ_{200}, ϵ_{020}, and ϵ_{002}. The strains in the c-direction ϵ_{002} were not observed, but accord-

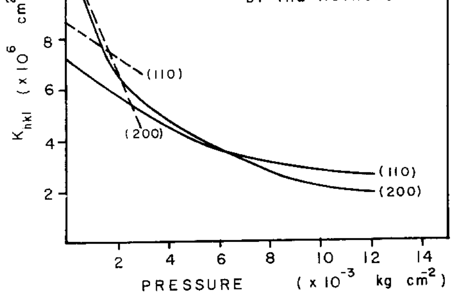

Figure 7 Linear compressibility versus pressure curves for (1 1 0) and (2 0 0) planes of polyethylene.

ing to Ito and Marui, these strains are smaller than ϵ_{200} and ϵ_{020} by at least an order of magnitude. If these strains are neglected, the volumetric strains $\Delta V/V$ can be obtained from the data available. We have the relation

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

where a, b, and c are the edges of the orthorhombic unit cell of polyethylene.

If ϵ_{hkl}, ϵ_a, ϵ_b, and ϵ_c are the infinitesimal strains in the direction of (hkl), a, b, and c, respectively, one can write [26], by neglecting higher-order terms,

$$\frac{1}{d_{hkl}^2}\epsilon_{hkl} = \frac{h^2}{a^2}\epsilon_a + \frac{k^2}{b^2}\epsilon_b + \frac{l^2}{c^2}\epsilon_c. \qquad (5)$$

From Equation 5, we acquire values of ϵ_{020} from the measured values of ϵ_{110} and ϵ_{200} as

$$\epsilon_{020} = 1.447(\epsilon_{110} - 0.309\epsilon_{200}) \qquad (6)$$

where $a = 7.41$ Å and $b = 4.95$ Å are used. Finally,

$$\begin{aligned}\frac{\Delta V}{V} &= \epsilon_{020} + \epsilon_{200} \\ &= 1.447(\epsilon_{110} + 0.382\epsilon_{200}).\end{aligned} \qquad (7)$$

It is interesting to compare these data with the theoretical results calculated by Pastine [24] for purely crystalline polyethylene at 298 K. The values obtained from our data can be compared with Pastine's theoretical function by reference to Fig. 8. The agreement is remarkable considering the fundamental character of Pastine's theory, and indeed gives confidence that such a theoretical approach is well justified.

An empirical equation of the form of a polynomial can be used to represent the pressure and volumetric strain relation

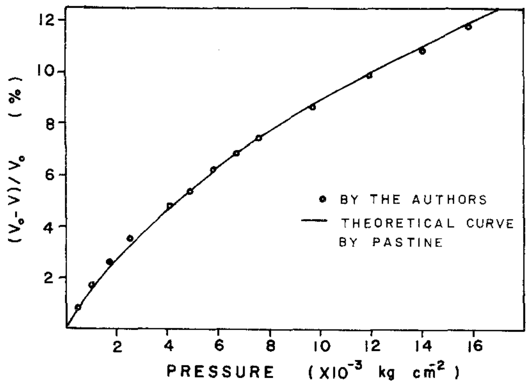

Figure 8 Per cent volume change $(1 - V/V_0)$ versus pressure plot for polyethylene.

$$-\epsilon_v = -\frac{\Delta V}{V_0} = A_v p - B_v p^2 + C_v p^3 + \ldots. \qquad (8)$$

Using the method of least squares, the parameters A_v, B_v, and C_v have been determined for polyethylene, and Equation 8 becomes

$$\begin{aligned}-\epsilon_v = {} & 15.57 \times 10^{-6}p - 0.1003 \times 10^{-8}p^2 \\ & + 0.323 \times 10^{-13}p^3.\end{aligned} \qquad (9)$$

The Grüneisen parameter, γ_0, of crystalline polyethylene at atmospheric pressure is obtained from Pastine's modified Slater's equation [24] as

$$\gamma_0 = -\frac{1}{2} + \frac{B_v}{A_v}. \qquad (10)$$

Substituting the values of A_v and B_v from Equation 9, the value of γ_0 is 3.64. It is rather close to the value of 3.4 calculated by Ito and Marui [26].

5. Conclusions

Polymer samples can be studied at pressures up to 14 000 kg cm^{-2} using the diamond-cell technique, and the interplanar spacings of the crystalline phase measured accurately. To obtain meaningful data, it should be emphasized that the use of a liquid medium to transmit the pressure is mandatory, since otherwise excessive pressure gradients can lead to gross distortion of the sample. The pressure can be measured accurately using HMT as a pressure standard. The linear compressibilities of polyethylene in the [200] and [110] directions decrease with pressure, but not in a linear fashion. The pressure-volume data at 298 K for the crystalline phase were obtained and were found to agree well with the theoretical predictions of Pastine.

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