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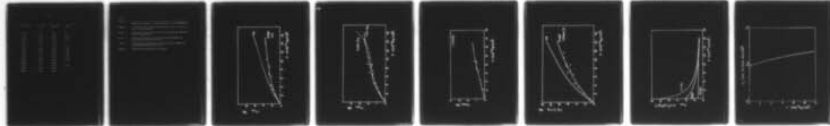
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) An x-ray diffraction study of poly(vinylidene fluoride) Phase II has been been carried out at pressures up to 14,000 kg/cm ² at room temperature. The crystal modification Phase II was found to be stable in this pressure range. The crystal lattice compressibility was studied at different pressures, and it was found that the variation of lattice strain with pressure was best represented by the Tait function. It was found that the linear compressi- bility in the chain direction is much greater than is the case for linear		

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polyethylene. The lattice bulk modulus was determined and found to increase with pressure according to the equation

$$K_B = (P+B_V) \left[\frac{1}{C_V} - \ln \left(1 + \frac{P}{B_V} \right) \right]$$

The Gruneisen constant was determined to be $\gamma_0 = 5.65$.

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A HIGH PRESSURE X-RAY STUDY OF POLY(VINYLLIDENE FLUORIDE)

PHASE II

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INTRODUCTION

The phenomenon of polymorphism in poly(vinylidene fluoride) has been observed by several authors. The crystal structure of the orthorhombic phase, Phase I, has been investigated in detail.^(1,2,3) The molecule assumes a planar zigzag conformation and there are two polymer chains per unit cell. On crystallization from the melt at atmospheric pressure, a second crystalline phase, Phase II, is produced. The crystal structure of Phase II has also been extensively studied.^(4,5,6) Doll and Lando proposed two possible crystal structures with space groups P2₁ and P1, each containing two chains per unit cell. The molecular conformation was found to be trans-gauche-trans-gauche (TG₂GTG). The existence of a third form has been suggested by various workers.^(7,8,9,10) The conditions of formation for the above three forms are complicated, and have been reported to be due to the kind of solvent, the content of head-h-head linkages, and high hydrostatic pressure.

The stability of the three polymorphic forms and the effect of high pressure has been investigated recently.⁽¹¹⁾ In this study poly(vinylidene fluoride) was subjected to various temperatures and pressures and subsequently examined upon release of high pressure. In such an investigation the possibility of reversible solid-solid transformations could not be studied. Such a phenomenon can only be investigated using the high pressure x-ray diamond cell method.

In this study a high pressure x-ray camera was used to obtain x-ray diffraction from poly(vinylidene fluoride) Phase II modification at pressures up to $14,000 \text{ kg/cm}^2$ at room temperature. A similar study of polyethylene has recently been made⁽¹²⁾ and it is interesting to compare the results obtained with the data obtained in this study. Of particular interest is the compressibility of the crystal lattice in the chain direction. Polyethylene assumes a zigzag conformation and distortions in the chain direction involve distortions of c-c-c bond angles and c-c bond lengths. Phase II with a TGTG conformation might be expected to show a larger compressibility in the chain direction.

EXPERIMENTAL

1. Sample Preparation

Thin films of poly(vinylidene fluoride) obtained from Kureha Corporation were melted and recrystallized by slow cooling. The samples obtained in this way exhibited the Phase II modification. These samples were then annealed at higher temperatures to increase the extent of crystallinity. Care was taken to avoid thermal degradation. If the annealing was carried out on a sample immersed in silicone oil at temperatures less than 150°C , for times less than two hours, no degradation of the sample was observed.

2. Apparatus

The high pressure x-ray camera described previously⁽¹²⁾ was used. A brass retaining ring with uniaxial aperture was used to contain the sample. The aperture was $1/32$ " in diameter and the retaining ring was $1/32$ " thick. The sample dimensions were a little smaller than these. Care was taken to insure that the sample was not in contact with the walls of the aperture or the diamond facets, so that the pressure applied was truly hydrostatic.

Following every application of pressure, an optical examination of the sample was made to insure that only hydrostatic pressure was applied to the sample. Hexamethylene tetramine (HMT) was used as an internal pressure standard

as described previously⁽¹³⁾, the accuracy being to within $\pm 200 \text{ kg/cm}^2$ throughout the entire pressure range. A Rigaku-Denki rotating anode generator, with a molybdenum target was used as an x-ray source. A zirconium filter was used to obtain Mo K α radiation.

3. Procedure

The diffraction patterns were recorded on flat film. The specimen to film distance could be determined accurately using the Debye-Scherrer rings obtained from the hexamethylene tetramine at atmospheric pressure.

Four reflections (020), (110), (021), and (002) from poly(vinylidene fluoride) Phase II were obtained on the film. However the (020) reflection from poly(vinylidene fluoride) overlapped the (110) reflection from HMT, so measurements were not made in the case of this reflection.

A series of exposures were made for the same sample corresponding to incremental increases in pressure up to $14,000 \text{ kg/cm}^2$. The interplanar spacings for (110), (021), and (002) planes were measured at each pressure, and the elastic strain on a given plane ϵ_{hkl} calculated from the relation

$$\epsilon_{hkl} = \frac{d_{hkl} - d_{hkl}^0}{d_{hkl}^0}$$

where d_{hkl} and d_{hkl}^0 are the lattice spacings at elevated pressure and atmospheric pressure respectively. The accuracy of each d-spacing measurement was estimated to be $\sim 0.005 \text{ \AA}$. The fractional error both in strain on sample and measured pressure is less than 10% for pressures above 2000 kg/cm^2 . All measurements were made at 25°C .

The entire experiment was repeated three times with different samples, to check for unsuspected systematic errors and reproducibility. Moreover this increased the statistical reliability of the conclusions.

RESULTS AND DISCUSSIONS

The Phase II modification of poly(vinylidene fluoride) was stable with increased pressure up to the highest pressure reached, 14,000 kg/cm².

In Table I the strains on the (110), (021), and (002) planes at different pressures are listed, and in Figures 1, 2, and 3 this data is shown in graphical form. The only other polymer for which this quantitative data exists is polyethylene⁽¹²⁾ and so the data obtained from polyethylene in the case of the (11) reflection is shown plotted in Figure 1. The lattice compressibility in a direction perpendicular to the chain axes is clearly less for the case of poly(vinylidene fluoride) than it is for polyethylene.

In previous studies, the pressure-lattice strain relationship could be empirically fitted to a polynomial series

$$- \delta_{hkl} = A_{hkl} p - B_{hkl} p^2 + C_{hkl} p^3 - \dots \text{ etc.}$$

For pressures up to 3000 kg/cm², a quadratic function sufficed⁽¹⁴⁾. For pressures up to 14,000 kg/cm² a cubic equation could be used. It was found impossible to adequately represent the data for the case of polyvinylidene fluoride using a polynomial expression, despite utilizing a computer least-squares fitting program to obtain the optimum parameters, unless the series was extended to an unacceptably large number of terms.

Tait proposed the following equation to represent the compressibility of sea-water,

$$1 - \frac{V}{V_0} = C_v \left(1 + \frac{P}{B_v(T)} \right)$$

where V and V_0 are the specific volumes at pressure P and atmospheric pressure respectively. The constant C_v was observed independent of temperature by a

number of investigators⁽¹⁵⁻²²⁾, and $B_v(T)$ is a constant depending on the temperature alone. The Tait equation was used to describe the compressibility of some liquid hydrocarbons⁽²³⁾ and some crystalline hydrocarbons⁽²⁴⁾.

If the Tait equation was used to fit the observed data, then an excellent agreement was obtained. In Figure 2 the strains on the (021) lattice planes are shown plotted at different pressures. The broken curve is a cubic function, the parameters optimized to fit the experimental data. The solid curve is the Tait function, the parameters are also optimized to obtain a best fit. Even though the Tait equation has only two variable parameters, it is clearly a better function to represent the data. It also seems likely that the Tait equation could be used for extrapolation to higher pressures, whereas this would certainly not be justified for a polynomial series.

In Figures 1, 2, and 3 the solid lines represent the Tait equation with parameters chosen to best fit the data. The equations are:

$$-\epsilon_{110} = 0.01383 \ln \left(\frac{P}{1.390 \times 10^3} + 1 \right)$$

$$-\epsilon_{021} = 0.01466 \ln \left(\frac{P}{3.513 \times 10^3} + 1 \right)$$

$$-\epsilon_{002} = 0.06450 \ln \left(\frac{P}{50.003 \times 10^3} + 1 \right)$$

Here the pressure P is in kg/cm^2 .

The strains shown in Fig. 3 represent lattice distortion parallel to the polymer chain axis. As compared with polyethylene these strains are large. This may arise from small rotations about c-c bands which lead to a decrease in (002) planes. The effect of such rotations would lead to a decrease in lateral

packing efficiency and a smaller lateral compressibility. This is in fact observed.

By combining lattice strains in different directions volumetric lattice strains can be computed at different pressures. These results are shown in Fig. 4, where the solid line is a best fit Tait equation

$$-\epsilon_v = 0.0791 \ln \left(\frac{P}{7.240 \times 10^3} + 1 \right).$$

In Fig. 4 the volumetric strains for the case of polyethylene are also shown. Despite the very different linear compressibilities the total lattice volume compressibility for the two polymers is not too different.

Linear compressibility K_{hkl} can be defined

$$K_{hkl} = - \frac{d\epsilon_{hkl}}{dp}$$

If we assume a Tait function we have:

$$K_{hkl} = \frac{C_{hkl}}{P+B_{hkl}}$$

Fig. 5 shows a plot of the linear compressibilities as a function of pressure. It is interesting to note that although at atmospheric pressure the linear compressibility in the [110] direction is several times greater than the linear compressibility in the chain direction, at higher pressures this anisotropy decreases and at 8000 kg/cm^2 the polymer compressibility is almost isotropic.

By using the Tait function for the volumetric strains, an expression for the bulk modulus K_B can be derived

$$K_B = (P+B_V) \left[\frac{1}{C_V} - \ln \left(1 + \frac{P}{B_V} \right) \right]$$

This function is shown plotted in Fig. 6.

Finally the Gruneisen parameter for Phase II poly(vinylidene fluoride) can be derived using Slater's formula

$$\gamma_0 = -\frac{2}{3} - \frac{1}{2} \frac{V(\partial^2 P / \partial V^2)_T}{(\partial P / \partial T)_T}$$

Using the same Tait function the value of γ_0 at atmospheric pressure is given by

$$\gamma_0 = -\frac{2}{3} + \frac{1}{2C_V}$$

We obtain $\gamma_0 = 5.65$.

CONCLUSIONS

1. Phase II of polyvinylidene fluoride is stable at atmospheric pressures up to $14,000 \text{ kg/cm}^2$ at room temperature.
2. The lattice linear compressibility in the chain direction is much greater than is the case of polyethylene.
3. The lattice strains, and lattice volumetric strains are better represented by a Tait function than a polynomial series.
4. The lattice linear compressibilities approach isotropy at higher pressures.
5. The lattice bulk modulus, reported here for the first time for poly(vinylidene fluoride), increases with pressure and can be represented by the function

$$K_B = (P+B_V) \left[\frac{1}{C_V} - \ln \left(1 + \frac{P}{B_V} \right) \right]$$

6. The Gruneisen parameter for poly(vinylidene fluoride) at atmospheric pressure was determined for the first time

$$\gamma_0 = 5.65$$

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TABLE I

P (10^2 kg/cm ²)	$-\epsilon_{110}$ (%)	$-\epsilon_{021}$ (%)	$-\epsilon_{002}$ (%)
0	0	0	0
0.6071	0.431	0.051	0.0
2.159	1.221	0.682	0.203
3.402	1.782	1.015	0.425
4.327	1.984	1.344	0.502
4.353	2.175	1.156	-
6.382	2.137	1.458	0.727
6.821	2.647	1.847	0.948
7.272	2.589	1.458	0.952
8.247	2.629	1.752	0.934
8.673	2.438	1.572	0.952
8.778	2.647	2.081	1.182
10.364	3.119	1.964	-
11.473	3.119	1.964	1.260
13.823	3.276	2.434	-
14.444	3.431	2.434	-

Legend

- Figure 1 Variation of (110) lattice strains with pressure for poly(vinylidene fluoride) Phase II and polyethylene, at room temperature.
- Figure 2 Variation of (021) lattice strains with pressure for poly(vinylidene fluoride) Phase II.
- Figure 3 Variation of (002) lattice strains with pressure for poly(vinylidene fluoride) Phase II.
- Figure 4 Variation of volumetric lattice strains with pressure for poly(vinylidene fluoride) Phase II.
- Figure 5 Variation of linear lattice compressibility with pressure for poly(vinylidene fluoride) Phase II.
- Figure 6 Variation of bulk modulus with pressure.

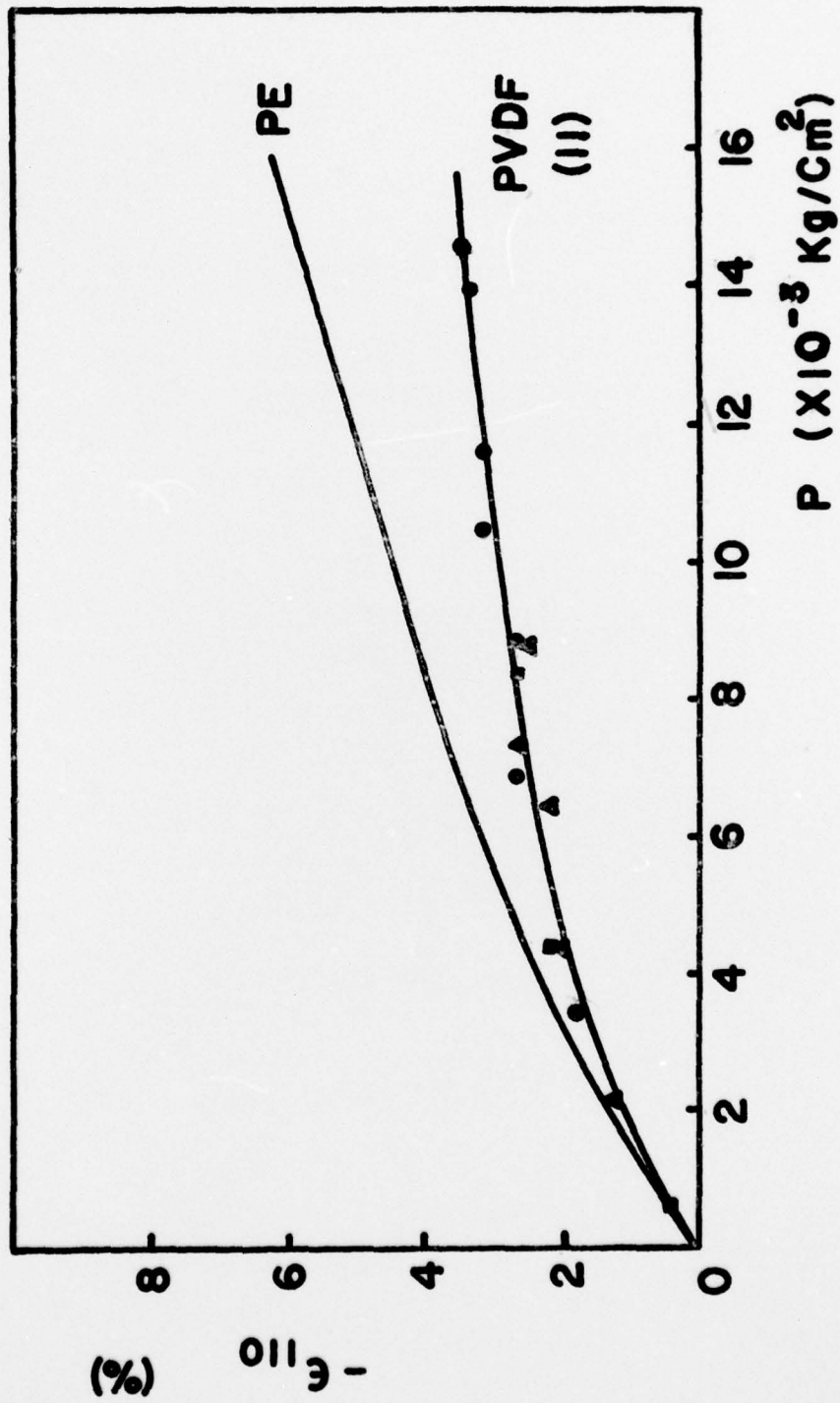


Fig. 1

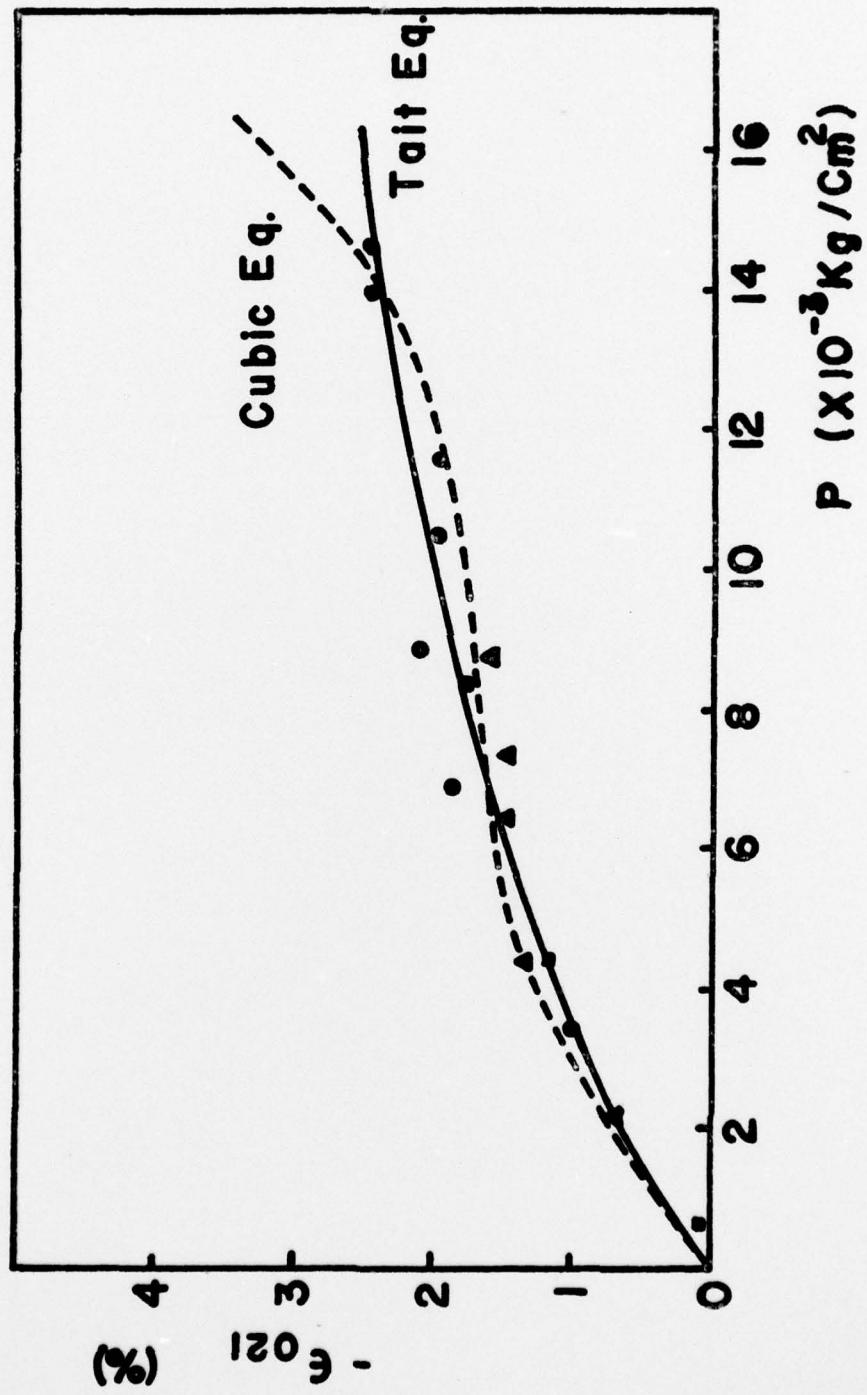
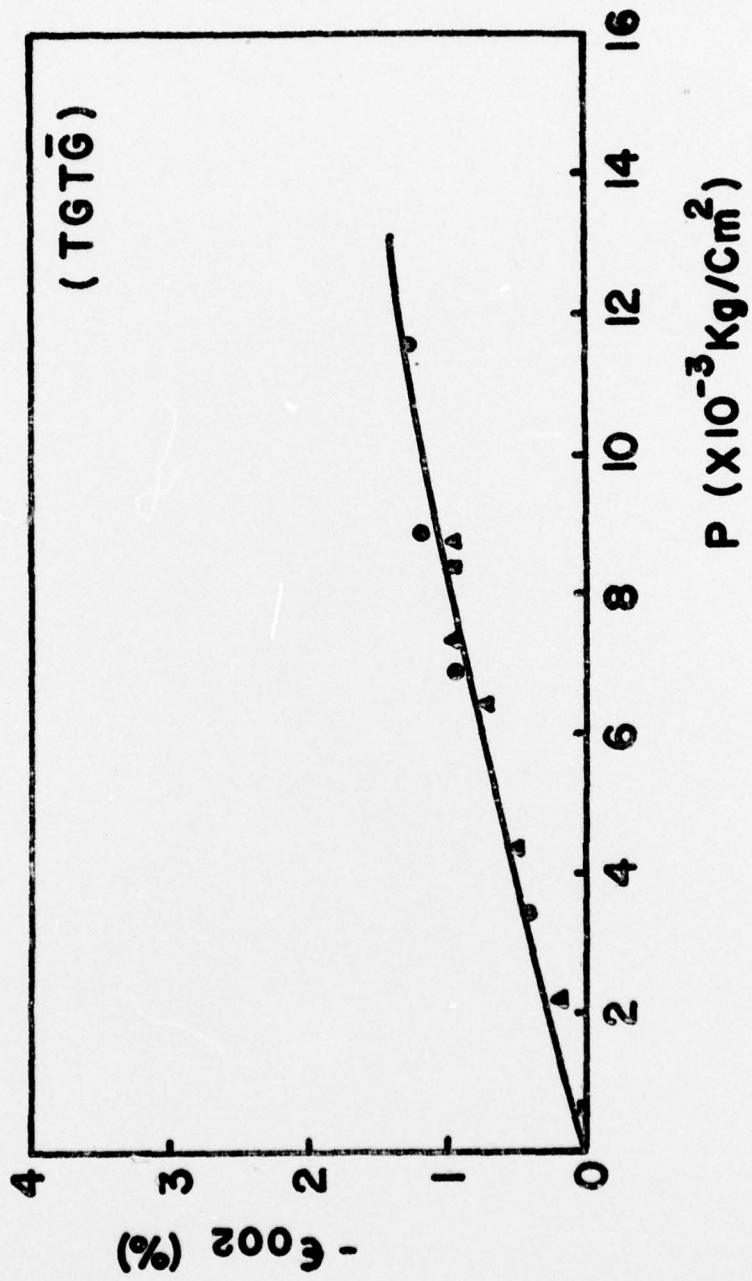


Fig. 2



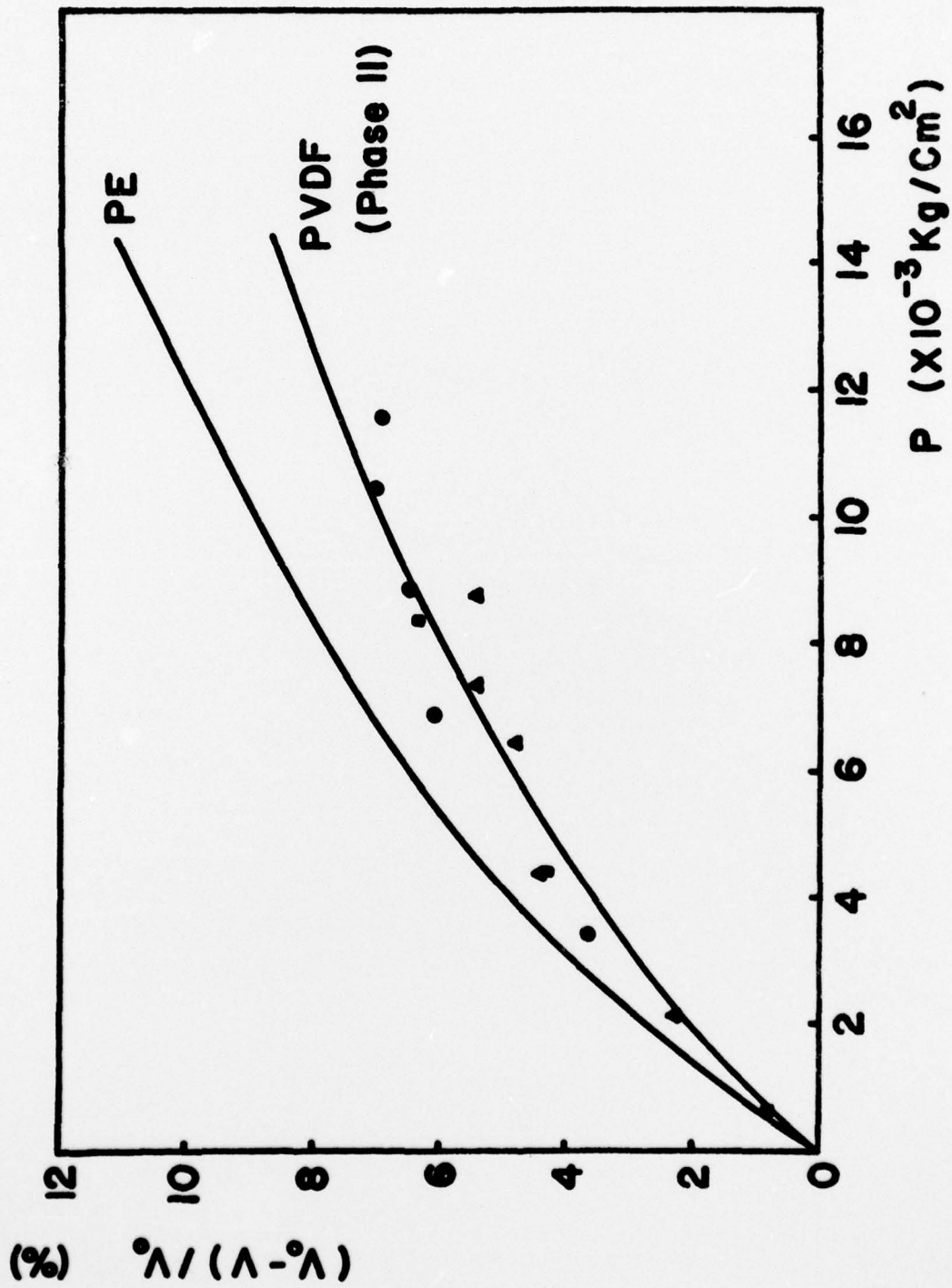


Fig. 4

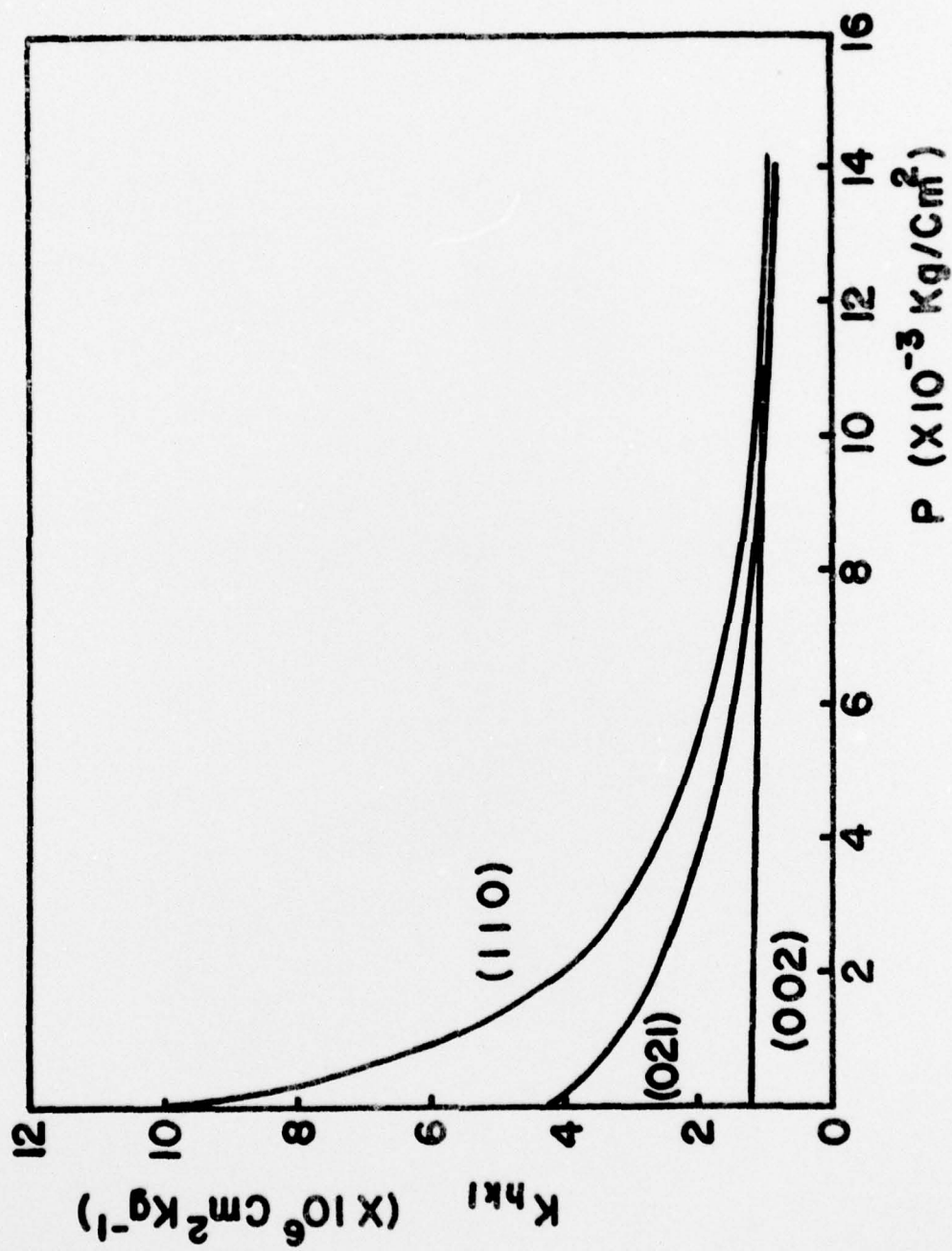


Fig. 5

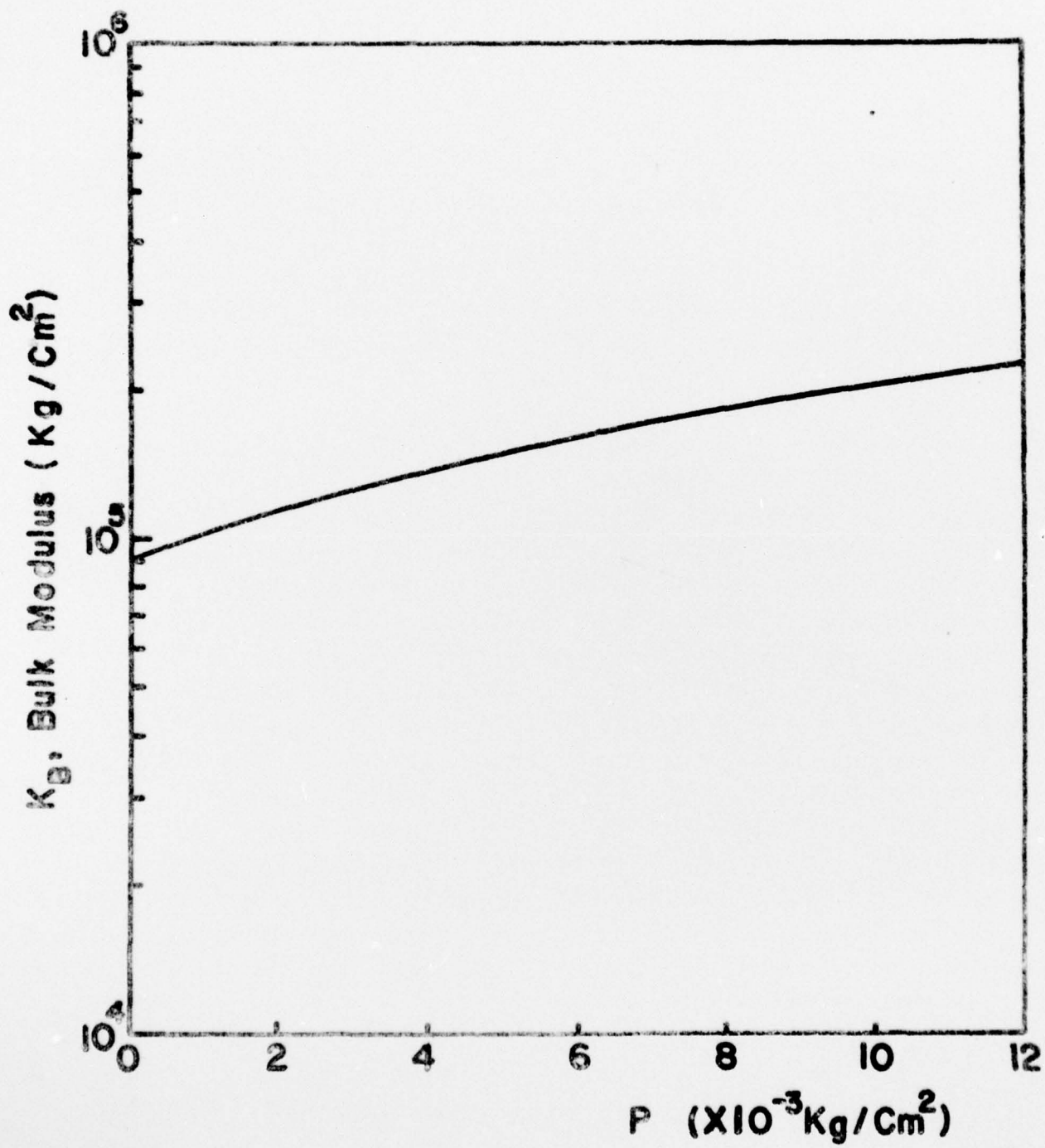


Fig 6