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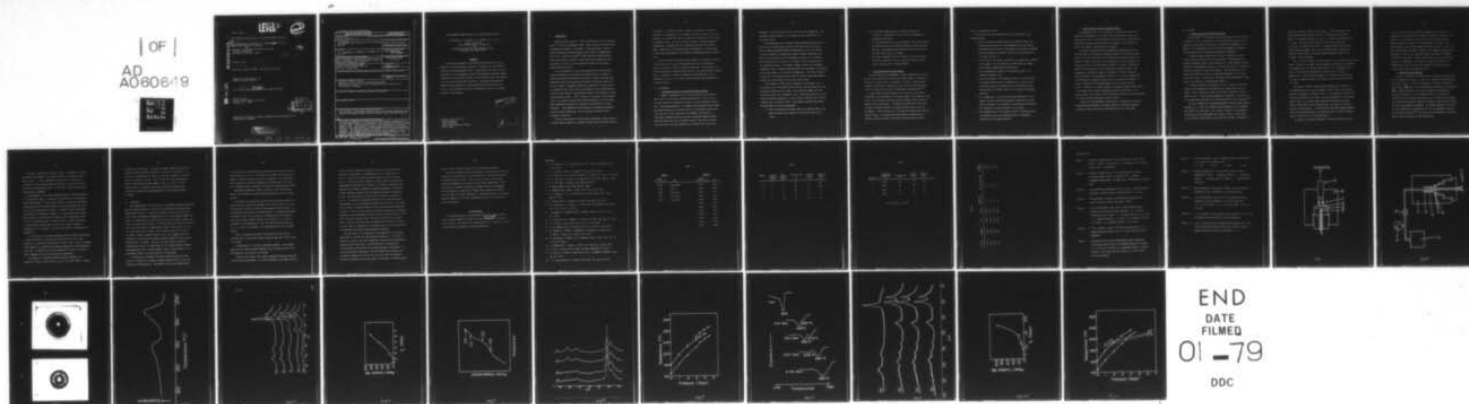
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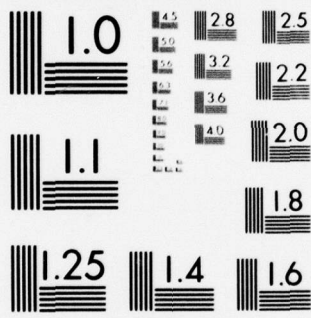
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HIGH PRESSURE CRYSTALLIZATION OF POLY(VINYLDENE FLUORIDE).

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HIGH PRESSURE CRYSTALLIZATION OF POLY(VINYLLIDENE FLUORIDE)

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ABSTRACT

The pressure dependence of the melting and crystallization temperatures of poly(vinylidene fluoride) is determined by high pressure differential thermal analysis (DTA). These results are used in the investigation of the polymorphic crystal form obtained by pressure quenching molten poly(vinylidene fluoride): The resulting crystal form depends on both the initial and final pressures. The pressure quenching experiments were performed in a high pressure piston-cylinder system and in a high pressure DTA system; a comparison is made of the results obtained by both methods.

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I. INTRODUCTION

Poly(vinylidene fluoride) (PVF_2) crystallizes in two (or possibly three)¹⁻⁵ different polymorphic forms. PVF_2 crystallizes from the melt at atmospheric pressure in the Phase II form and Phase I films are usually obtained by drawing Phase II films (~500%) at temperatures below -50°C . Kawai⁶ and others⁷⁻¹⁰ have shown that polarized PVF_2 films which contain the Phase I form exhibit high piezoelectric and pyroelectric activity; films containing the Phase II form exhibit greatly reduced activity.

In this laboratory, we have been studying the relation between crystal morphology and piezoelectric properties and as a means of producing different morphologies with Phase I crystal structures some experiments with high pressure crystallization have been carried out. Doll and Lando^{4,5}, Hasegawa, Kobayashi and Tadokoro¹¹, and Matsushige and Takemura¹² have shown that the polymorphic form and morphology obtained by high pressure crystallization depend on the pressure at which crystallization occurs. PVF_2 is known to be unstable at high temperatures. Our studies revealed very marked degradation at the extremely high temperatures required for isothermal crystallization at high pressures. This degradation may influence the resulting polymorphic form and crystal morphology. It may also affect electrical and mechanical properties.

During a high pressure crystallization experiment, using a piston-cylinder pressure vessel, an accident occurred which subjected a molten

PVF₂ sample to a sudden increase in pressure, equivalent to pressure quenching. An examination of the sample indicated that very little degradation had occurred and that the sample had crystallized in the Phase I polymorphic form. We then initiated a series of pressure quenching experiments to determine the best quenching conditions for producing Phase I samples with the minimum amount of degradation. We also hoped to gain some understanding of why pressure quenching produced the Phase I form.

We have recently constructed a high pressure DTA (capacity 10 kbar), which aside from its use in determining melting and crystallization points, could also be used for pressure quenching. This allowed us to obtain more accurate quenching data than with the piston-cylinder arrangement. A comparison is made to evaluate the advantages and the disadvantages in the use of the DTA and the piston-cylinder apparatus for quenching studies.

II. EXPERIMENTAL

1. Quenching Studies in the Piston-Cylinder Apparatus

A schematic representation of the high pressure piston-cylinder device used in the pressure quenching experiments is shown in Fig. 1. The high pressure was obtained by using a gas driven pressure intensifier. The pressure applied to the sample was calculated from the known gas pressure applied to the upper face of the intensifier piston, and the known ratio of the upper and lower (sample) piston areas. A PTFE-copper Bridgman type seal was used to maintain sample pressure. Some frictional force will be present in such a seal and, of course, the direction of that force depends on the direction of piston dis-

placement. The frictional force will also vary with temperature. The calculated pressure applied to the sample was not corrected for the frictional forces.

The thermocouple used to measure sample temperature was placed in a hole in the cylinder plug, just below the brass seal (see Fig. 1). With the sample separated from the thermocouple by ~0.5 cm of metal, it was not possible to measure any change in sample temperature produced by the application of the quenching pressure, or to determine when crystallization occurred, i.e. during or after the application of the quenching pressure. The change in sample volume with increasing temperature under a constant applied pressure was determined by measuring piston displacement as a function of temperature. The entire pressure vessel could be heated and cooled from the outside surface: The maximum heating rate being limited by the heater power output.

Pellet samples of PVF_2 (Kynar, supplied by the Pennwalt Corp.) were pressed into the pressure vessel, melted, and recrystallized under an applied pressure of ~0.35 kbar. The cylindrical sample was then sliced into discs with a thickness ~1 mm. These discs were used in the pressure quenching experiments. X-ray studies indicated that the discs contained only the Phase II form. The pressure quenching experiments were performed in the following manner:

- a) After the sample was inserted inside the pressure vessel, the applied pressure was increased to an initial value (P_1) of 1 kbar.

- b) As the sample temperature was increased (heating rate $1.9^{\circ}\text{C}/\text{min}$), a dilatometric curve of piston displacement vs. temperature was plotted.
- c) At a preselected point on the dilatometric curve after melting, the applied pressure was rapidly increased to some final pressure (P_f). The quenching was completed within three seconds. P_f varied from 3 kbar to 6.3 kbar.
- d) The sample temperature was then lowered to -80°C by blowing air over the pressure vessel, the pressure reduced to atmospheric pressure, and the sample removed.

2. Quenching Studies in DTA Apparatus

The high pressure DTA arrangement is shown schematically in Fig. 2. The cell was heated and cooled from the outside surface, limiting the heating and cooling rates to a maximum of $\sim 10^{\circ}\text{C}/\text{min}$. Chromel-Alumel (sheathed) thermocouples (Omega) were used, since the pressure dependence of the EMF for this type of thermocouple is negligible.^{13,14}

A small sample of PVF_2 was melted on a hot plate and the DTA thermocouple tip was embedded in the molten sample. The sample was then cooled. This procedure provided excellent thermal contact between the sample and the thermocouple. The sample was coated with a thin layer of epoxy to prevent diffusion of pressure medium (silicon oil) into the samples. After the epoxy set, the sample was placed inside the DTA pressure vessel. The melting and crystallization temperatures at various pressures were first determined using heating and cooling

rates of approximately $8^{\circ}\text{C}/\text{min}$.

The pressure quenching experiments were then performed in the following manner:

- a) After the sample was sealed inside the pressure vessel, the pressure was increased to a predetermined value less than P_i , the desired initial value of the pressure for pressure quenching. The valve between the pressure vessel and the intensifier was left open (see Fig. 2).
- b) As the DTA cell was heated, the EMF of the thermocouple embedded in the sample, and the difference in EMF between the sample and reference thermocouples were recorded.
- c) As the temperature increased (to the melting point), the pressure increased to P_i .
- d) Just before melting of the sample occurred, the valve between the pressure vessel and the intensifier was closed, and the intensifier pressure was pumped up to a predetermined value greater than P_f , the final value of the pressure for pressure quenching.
- e) At a temperature $\sim 10^{\circ}\text{C}$ above the melting temperature of the sample, the valve between the pressure vessel and the intensifier was opened. The pressure in the system then reached P_f . The increase in pressure occurred in ~ 0.1 second.
- f) The temperature was then lowered to -80°C by blowing air over the pressure vessel, the pressure reduced to atmospheric pressure, and the samples removed.

3. X-Ray Studies of Pressure Quenched Samples

The polymorphic form of the crystals in the pressure quenched PVF₂ samples was determined by wide angle x-ray diffractometer scans; CuK α radiation was used. The diffractometer scans were used to quantitatively determine the percent crystallinity of the samples and the percent of Phase I and Phase II forms present in a sample.

The percent crystallinity was determined by taking the ratio of the area under the crystalline diffraction peaks (of the diffractometer scan) to the total area under the crystalline and amorphous peaks. The percent of Phase I and Phase II was determined in a similar manner, by taking the ratio of the area under the Phase I or Phase II diffraction peaks, to the area under all the crystalline diffraction peaks. The assignment of diffraction peaks to the Phase I or Phase II form was based on previous crystallographic studies.¹⁻⁵ It is not supposed that the crystalline to amorphous ratios and the volume ratios of Phase I to Phase II obtained by those measurements provide accurate absolute values. However, as a relative measure for comparing samples crystallized in different ways the data obtained are considered sufficient. The Miller indices of the Phase I and II diffraction peaks and the corresponding 2θ values for CuK α radiation are given in Table 1.

Because of the approximation method used in determining the percent crystallinity and because of the small amount of diffracted intensity at high 2θ values, only those reflections with $2\theta < 50^\circ$ were used.

III. RESULTS

1. Quenching in Piston-Cylinder Apparatus

Previous work^{5,15,16} has shown that crystallization by slow cooling ($-10^{\circ}\text{C}/\text{min}$) of PVF_2 at pressures ≥ 3.5 kbar produces the Phase I form; however, we found that this resulted in significant degradation of the samples. Not surprisingly, we also found that degradation increased as the crystallization pressure and temperature increased.

To minimize sample degradation, we first determined the lowest initial pressure necessary for producing Phase I crystallization by pressure quenching, using a final pressure of 6.3 kbar; samples pressure quenched from atmospheric pressure to 6.3 kbar were found to be Phase II. An initial pressure ~ 1 kbar was necessary. X-ray diffraction photographs taken before and after the quenching experiment ($1 \rightarrow 6.3$ kbar) are shown in Fig. 3. The pressure quenching produced samples with mostly Phase I but apparently containing some Phase II.

To further establish the presence of the two distinct crystalline phases, a DSC experiment was performed using a small piece of this sample. Phase II melted at -160°C , while Phase I melted at -190°C as shown in Fig. 4. These melting temperatures correspond to the peaks of the DSC endotherms and agree with values available in the literature.^{5,16}

We then continued the quenching experiments using the same initial pressure ($P_i = 1$ kbar) but different final pressures (P_f) to determine what effect this would have on the content of Phase I in the samples. The results of these experiments are listed in Table 2, which gives P_i , P_f , percent crystallinity, and the percent of Phase I and Phase II

crystalline material present in each sample. The corresponding x-ray diffractometer scans are shown in Fig. 5. Sample a was a reference sample, not pressure quenched, $P_i = P_f$, i.e., melted and recrystallized at 1 kbar. The heating rate of all the test runs was identical ($1.9^\circ\text{C}/\text{min}$). As can be seen in Fig. 5, sample a exhibits only Phase II x-ray diffraction peaks. Fig. 5 also shows that as P_f increases the intensity of the Phase II diffraction peaks decreases, while that of the Phase I peaks increases.

Fig. 6, a plot of Phase I content versus P_f ($P_i = 1$ kbar) shows that the percent of Phase I increases with increasing P_f (>2 kbar), and approaches (the maximum value of) 100% at higher values of P_f . Although we were unable to continue the experiments to values of $P_f > 6.3$ kbar, it appears that a final quenching pressure of ~ 8 kbar would be sufficient to produce a sample containing $\sim 100\%$ Phase I using an initial pressure of 1 kbar.

The percent of Phase I present after quenching also depended on the temperature point on the dilatometric curve at which the quenching pressure was applied. Referring to Fig. 7, we arbitrarily selected the four points marked a, b, c, and d: Point a corresponds to a premelting region, point b to a region where significant melting has occurred, point c $\sim 5^\circ\text{C}$ above the end of melting point, and point d $\sim 30^\circ\text{C}$ above the end of melting point. In the previously discussed quenching experiments, the quenching pressure was applied at point c, when the samples were 5°C above their end of melting points.

The results of pressure quenching at these four point are listed

in Table 3, which gives the quenching temperature, the percent of crystallinity, and the percent of Phase I and Phase II present in the samples. All the samples listed in Table 3 were quenched from an initial pressure of 1 kbar to a final pressure of 6.3 kbar. The diffractometer scans of these samples are shown in Fig. 8. As can be seen from the data, the Phase I content of the samples increases as the temperature (at which the quenching pressure was applied) increases. The sample crystallinity, however, varies very little with quenching pressure or temperature. This behavior, previously discussed by Nakagawa and Ishida,¹⁷ results from secondary crystallization which occurs during cooling and depressurization.

2. Quenching in DTA Apparatus

In order to establish a reference base, the melting and crystallization temperatures of PVF_2 as a function of pressure were determined and are shown in Fig. 9. The rate of increase of the melting temperature with pressure ($\frac{dT_m}{dp}$) and of the crystallization temperature with pressure ($\frac{dT_c}{dp}$) is nearly identical with those of Matsushige and Takemura.¹⁶ One major difference is a 15°C downward shift in our melting and crystallization curves resulting from the use of different PVF_2 samples: We used Kynar PVF_2 samples (supplied by Pennwalt) whereas Kureha polymer was used by Matsushige and Takemura. The sample dependence of the melting and crystallization temperatures of PVF_2 (at atmospheric pressure) was previously discussed¹⁸⁻²⁰ and results from differences in molecular weight, chain branching, and stereo-regularity.

The Phase I melting points shown in Fig. 9 correspond to a second endotherm which appears if the sample is melted at pressures greater than -3 kbar. It first appears as a small peak at 3.1 kbar, but increases in size at higher pressures (see Fig. 10) while the size of the Phase II endotherm decreases. At 4.5 kbar, only the second endothermic peak is observed.

The assignment of the second endothermic peak at various pressures to the melting of Phase I is based on the previous work of Matsushige, Nagata and Takemura.¹⁶ These authors observe on heating an endotherm, corresponding to the melting of Phase II, an exotherm which they associate with crystallization of Phase I, followed by another endotherm corresponding to the melting of Phase I. In experiments using Kureha films as well as the Kynar film we observe the two endothermic peaks but not the exothermic peak. We were not able to extend the melting or crystallization curves past 4.5 kbar due to rapid (explosive) decomposition of the samples. This was also observed by Matsushige and Takemura.¹²

As in the case of the piston-cylinder pressure quenching experiments, we were interested in determining the minimum value of the initial pressure, P_i , necessary for producing the Phase I form. Since the maximum final pressure, P_f , available for pressure quenching on the DTA apparatus was 7 kbar, we decided to use final pressures -6.3 kbar to allow for better comparison with the piston-cylinder experiments.

The results of these DTA pressure quenching experiments are presented in Table 4, which lists P_i , P_f , T_i , T_f , $\Delta T/\Delta P$, Phase I content,

and percent crystallinity. The change in sample temperature produced by pressure quenching averaged $7^{\circ}\text{C}/\text{kbar}$, and was due to two factors: The work done in compressing the sample, and the heat released by crystallization or enthalpy of fusion. Fig. 11 shows the x-ray diffractometer scans of the pressure quenched samples. Fig. 12, a plot of Phase I content versus P_i , indicates that an initial pressure greater than 1.45 kbar is necessary for producing Phase I if the final pressure is -6.3 kbar.

IV. DISCUSSION

Some understanding of the results of the pressure quenching experiments may be obtained from Fig. 13, a plot of the melting and crystallization temperatures of PVF_2 as a function of pressure on which the initial and final states of pressure and temperature of the (DTA) quenched samples are shown. By connecting the initial and the final states with straight line paths, we observe that the path 1-1' entirely misses the Phase I crystallization curve, the path 2-2' approaches the curve, and the path 3-3' and 4-4' cross deep into the curve. We also observe that as this occurs, the Phase I content increases from 0% to 95%. This suggests that the polymorphic form obtained by pressure quenching depends on which crystallization curve is crossed. That is, if a path crosses the Phase II crystallization curve, we obtain Phase II; if a path crosses the Phase I crystallization curve, we obtain Phase I; and if a path crosses in the intermediate region, we obtain a mixture of both phases.

In connecting the straight line paths between initial and final states, we included the increase in sample temperature due to the heat released by crystallization. This means that the actual temperatures

at which most of the crystallization occurred were slightly lower than those indicated in Fig. 13. The result of including this error was to produce a slightly steeper path for all the samples. Any corrections would reinforce the previous suggestion by bringing path 3-3' closer to the boundary between the Phase I and Phase II crystallization curves.

The results presented in Table 2 and Fig. 6 show that the polymorphic form obtained by pressure quenching depends also on the final pressure.

The pressure quenching data obtained from the piston-cylinder experiments are in qualitative agreement with the DTA results, i.e. for a final pressure ~6.3 kbar, there is some minimum initial pressure, P_i , and temperature necessary for producing Phase I. The major quantitative differences occurs in the value of P_i obtained from the two methods: The piston-cylinder results indicate that a value of $P_i \sim 1$ kbar is necessary for producing Phase I, while the DTA results indicate that a $P_i > 1.45$ kbar is necessary. The difference may be due to several factors.

First, the unknown frictional force between the seal and the cylinder wall of the piston-cylinder pressure vessel may be quite large (~0.5 kbar).

A second factor is the rate of pressure quenching. The pressure quench on the piston-cylinder apparatus took ~3 seconds, while on the DTA apparatus, the time was ~0.1 seconds.

A third factor results from a major difference between the DTA and piston-cylinder experiments. In the DTA experiment, the sample was sub-

jected to purely hydrostatic pressure, while in the piston-cylinder experiment, the pressure is nonhydrostatic and the sample was subjected to significant shearing stresses during the pressure quench. Since it is known that PVF_2 undergoes a stress induced crystal-crystal transformation from Phase II to Phase I,¹ we further investigated the possibility that Phase I produced by pressure quenching in the piston-cylinder apparatus resulted from the shearing of Phase II crystals or nuclei. This possibility was ruled out on the basis of the data in Table 3. We applied the quenching pressure at four different points (temperatures) on the dilatometric melting curve (see Fig. 7) and found that the Phase I content increased as the initial quenching temperature increased. Since the initial Phase II content decreases with increasing temperature (due to melting) and should be zero at point d which is 30°C above the Phase II melting point (and which resulted in the highest Phase I content) we decided that the shearing of the Phase II crystals or nuclei was not responsible for producing Phase I. This was proven by the subsequent DTA studies using hydrostatic pressure.

The last factor to be discussed is the measurement of the sample temperature in the DTA and piston-cylinder apparatus. In the DTA, we were able to monitor the entire temperature history and the temperature measured was the actual one. We were also able to observe that crystallization occurred after the quenching pressure was applied. In the piston-cylinder experiments, the only thermal data available was the sample temperature, within $\pm 3^\circ\text{C}$, up to the time the quenching pressure was applied, and we were unable to determine if crystallization

occurred during or after application of the quenching pressure.

The Phase I samples produced by pressure quenching exhibit much less degradation (discoloration) than those obtained by melt crystallization at pressures above 3.5 kbar. This is due to the fact that the melt crystallized samples are subjected to much higher temperatures. This will allow us to study the effects of different Phase I morphologies on the piezoelectric properties of PVF_2 without significant concern with the effects of sample degradation. The morphologies of the pressure quenched samples are now being investigated and will be discussed in a future publication.

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TABLE 1

<u>PHASE I</u>		<u>PHASE II</u>	
Peak Position (2θ)	hkl	Peak Position (2θ)	hkl
20.83	(110),(200)	17.74	(100)
35.06	(001)	18.43	(020)
36.55	(020),(310)	20.04	(110)
37.32	(040),(210)	25.78	(120)
41.14	(111),(201)	26.72	(021)
		27.97	(111)
		32.28	(121)
		33.15	(130)
		36.07	(200)
		38.66	(131)
		39.00	(002)
		45.59	(221)

TABLE 2

Sample	Initial Pressure (Kbar)	Final Pressure (Kbar)	Crystallinity (%)	Phase I Content (%)	Phase II Content (%)
a	1	1	57	0	100
b	1	3	55	14	86
c	1	4	52	30	70
d	1	5	53	53	47
e	1	6.3	52	81	79

TABLE 3

Sample No.	Quenching Temperature (°C)	Crystallinity (%)	Phase I Content (%)	Phase II Content (%)
a	177°C	52	51	49
b	193°C	50	66	34
c	208°C	52	81	19
d	234°C	55	85	15

$$\Delta P = (6.3-1) = 5.3 \text{ kbar}$$

TABLE 4

P_i (kbar)	P_f (kbar)	T_i (°C)	T_f (°C)	Phase I Content (%)	Crystallinity (%)	$\Delta T/\Delta P$ (°C/kbar)
0.93	6.25	213.1	254.4	4	51	7.76
1.15	6.38	217.3	255.6	12	50	7.32
1.45	6.21	225.8	257.3	19	52	6.62
1.80	6.4	231.9	261.0	95	60	6.33

FIGURE CAPTIONS

- Figure 1 - Schematic representation of the high pressure piston-cylinder device: A-piston, B-pressure cell, C-Bridgman seal, D-sample, E-brass plate, F-thermocouple.
- Figure 2 - Schematic representation of the high pressure DTA device: A-pressure gauge, B-valve, C-pressure cell, D-sample, E-sheathed thermocouple, F-copper seals, G-PTFE seal, H-intensifier.
- Figure 3 - X-ray diffraction photographs (CuK α) of PVF₂: A-before pressure quenching, B-after pressure quenching from 1 to 6.3 kbar.
- Figure 4 - DSC measurement of pressure quenched PVF₂ showing melting points of Phase II (160°C) and Phase I (190°C).
- Figure 5 - X-ray diffractometer scans (CuK α) of PVF₂ samples pressure quenched in the piston-cylinder apparatus: (a) - isobaric crystallization at 1 kbar, (b) - pressure quenched, 1 to 3 kbar, (c) - pressure quenched, 1 to 4 kbar, (d) - pressure quenched, 1 to 5 kbar, (e) - pressure quenched, 1 to 6.3 kbar.
- Figure 6 - A plot of Phase I content (%) versus final pressure, P_f , for samples pressure quenched from 1 to P_f kbar (piston-cylinder apparatus).
- Figure 7 - Dilatometric curve (piston displacement versus temperature) showing the points at which the quenching pressure was applied ($P_i = 1$ kar, $P_f = 6.3$ kbar) (a)- premelting region, (b)-during melting, (c)-5°C above the end of melting, (d)-30°C above the end of melting.

Figure 8 - X-ray diffractometer scans of samples pressure quenched from 1 to 6.3 kbar at a temperature of:

(a) 177°C (b) 193°C (c) 208°C (d) 234°C

Figure 9 - Pressure dependence of the melting and crystallization temperatures of PVF_2 : -melting of Phase II, -melting of Phase I, -crystallization of Phase II, -crystallization of Phase I.

Figure 10 - DTA thermograms of the melting of PVF_2 at several pressures. Temperatures shown correspond to the endotherm peaks.

Figure 11 - X-ray diffractometer scans (Cuka) of PVF_2 samples pressure quenched in the DTA apparatus: (a) 0.93 to 6.25 kbar, (b) 1.15 to 6.38 kbar, (c) 1.45 to 6.21 kbar, (d) 1.6 to 6.4 kbar.

Figure 12 - A plot of Phase I content versus initial pressure ($P_i = 6.4$ kbar) for samples pressure quenched in the DTA apparatus.

Figure 13 - A plot of the melting and crystallization temperatures of PVF_2 with the initial and final states of the pressure quenched samples connected by straight line paths (- - -).

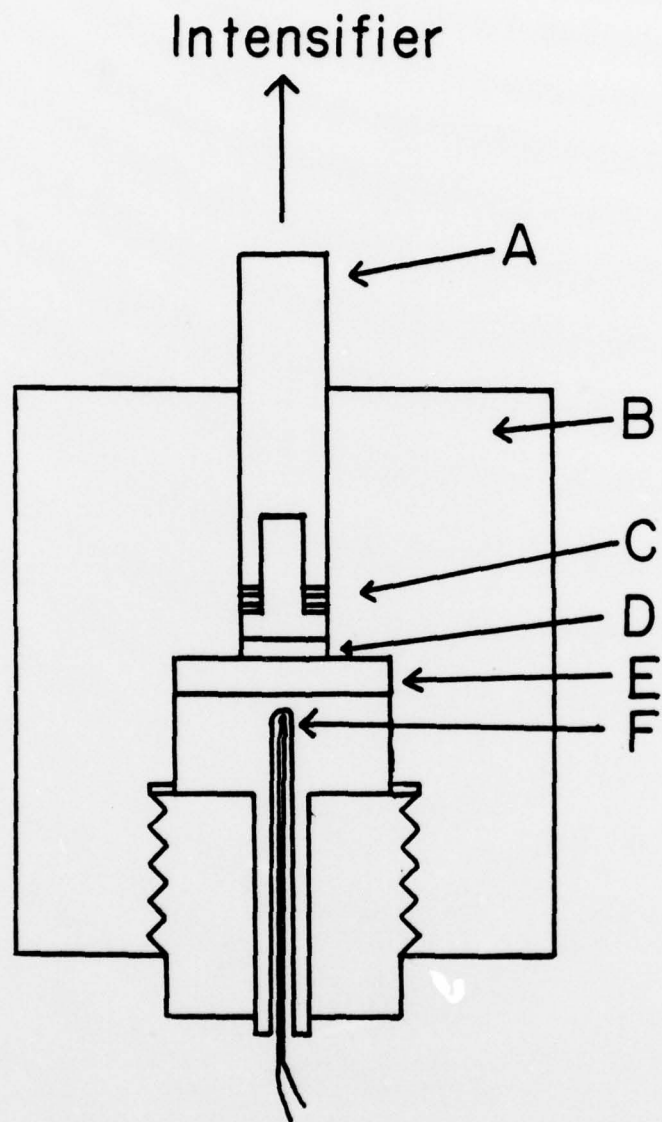


Fig 1

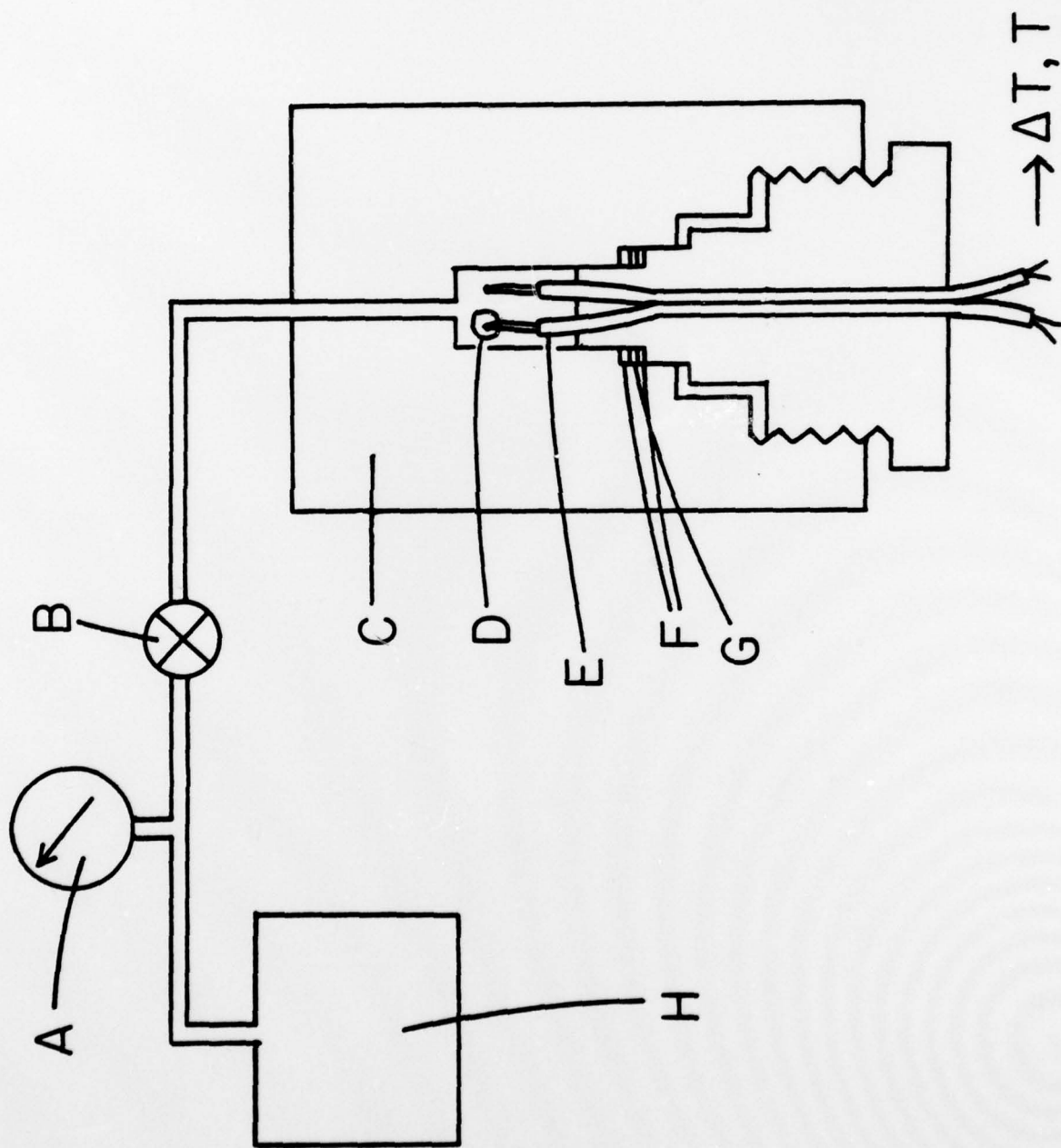
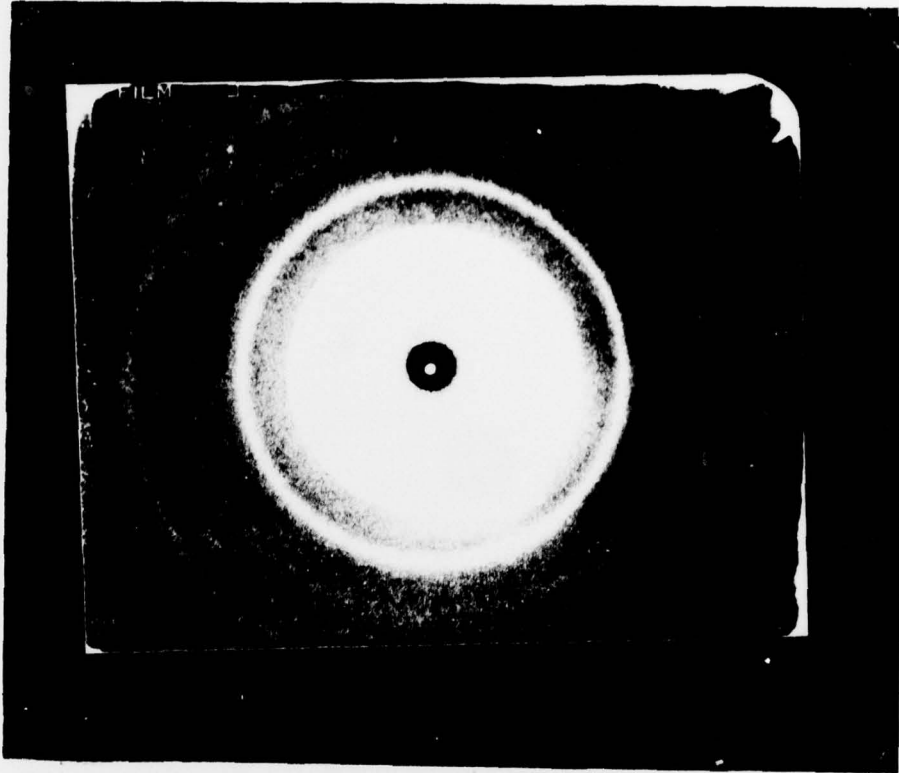


fig 2

Fig 3

A



B

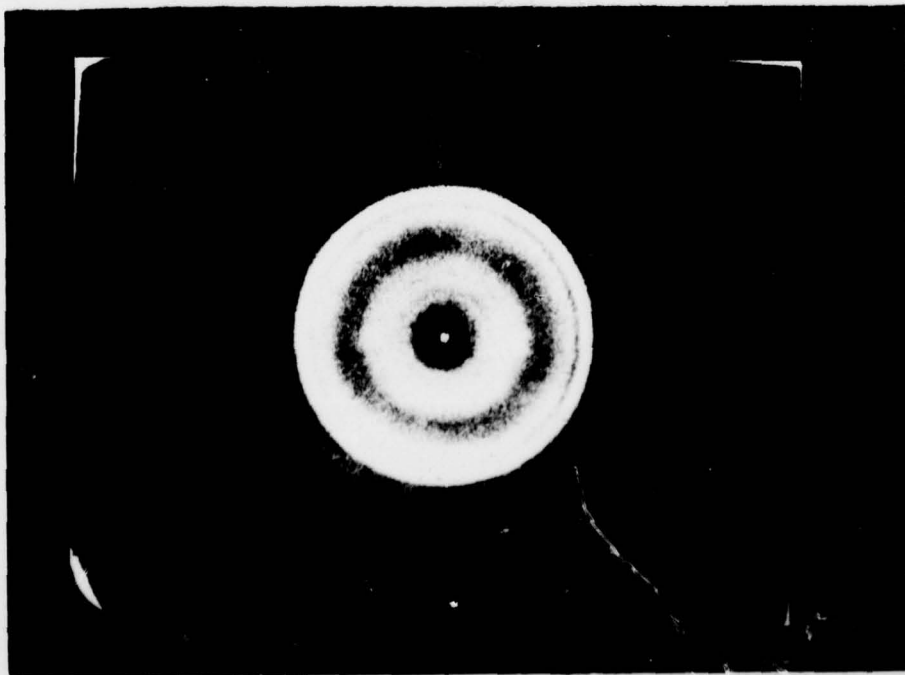
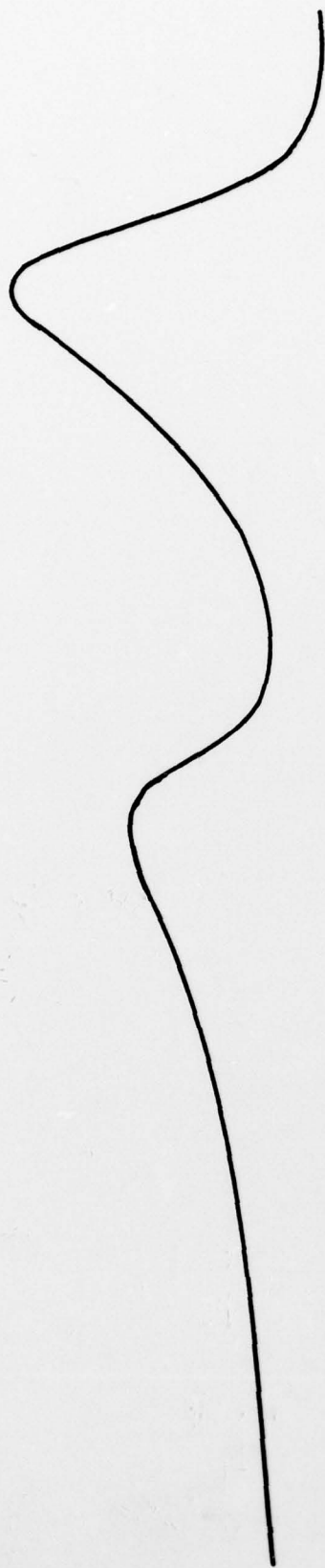


Fig 3

Endotherm



120 140 160 180 200

Temperature (°C)

Fig 4

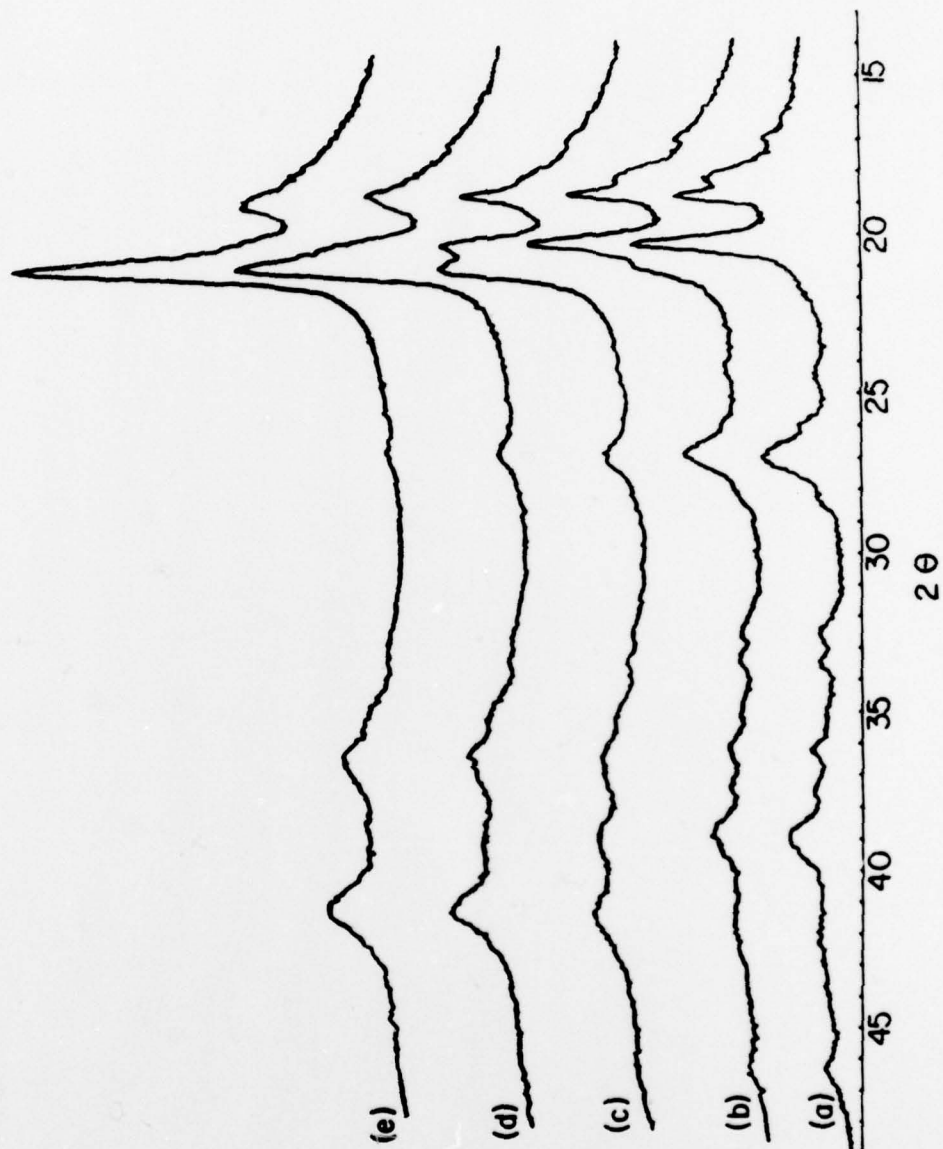
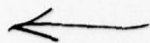


Fig 5



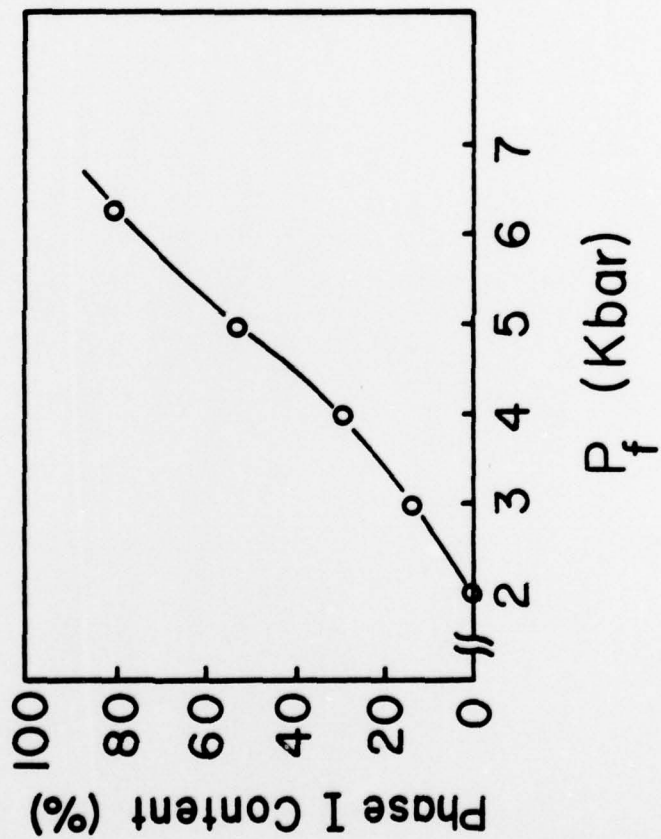


fig 6

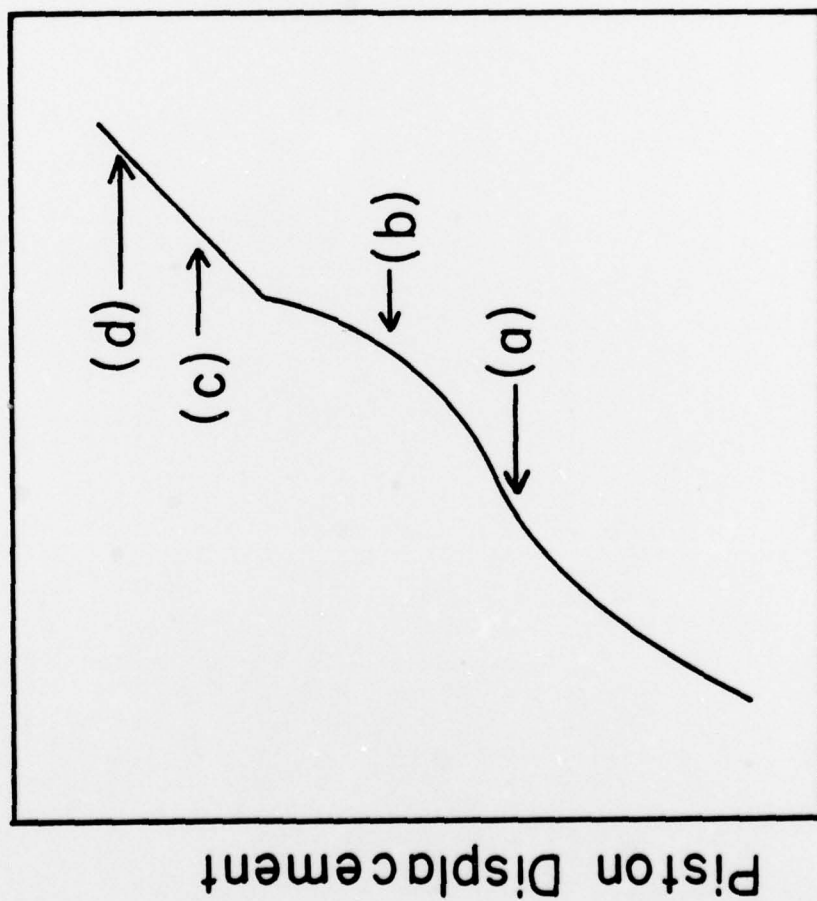


Fig 7

Fig 7 ↑

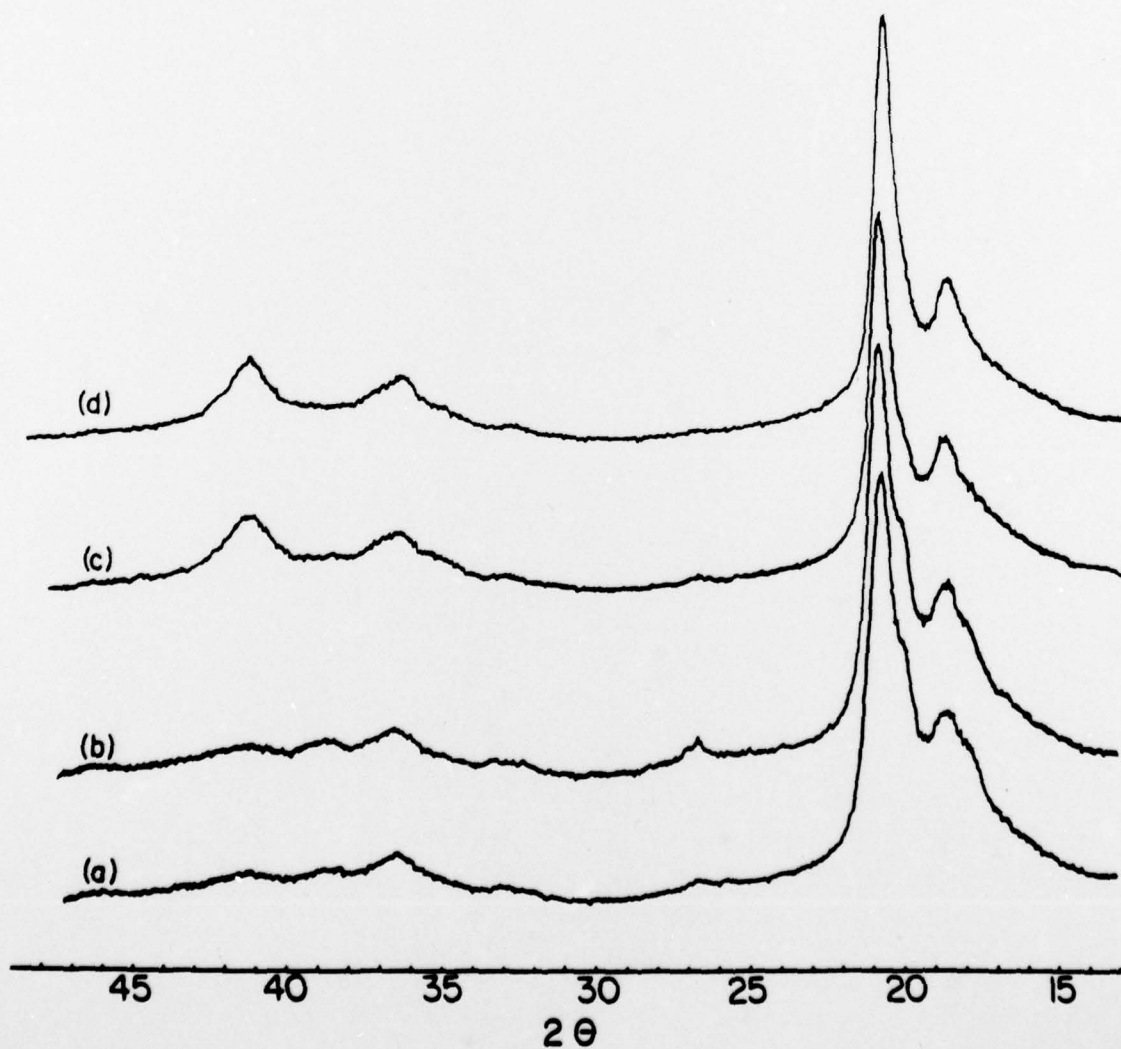


Fig 8

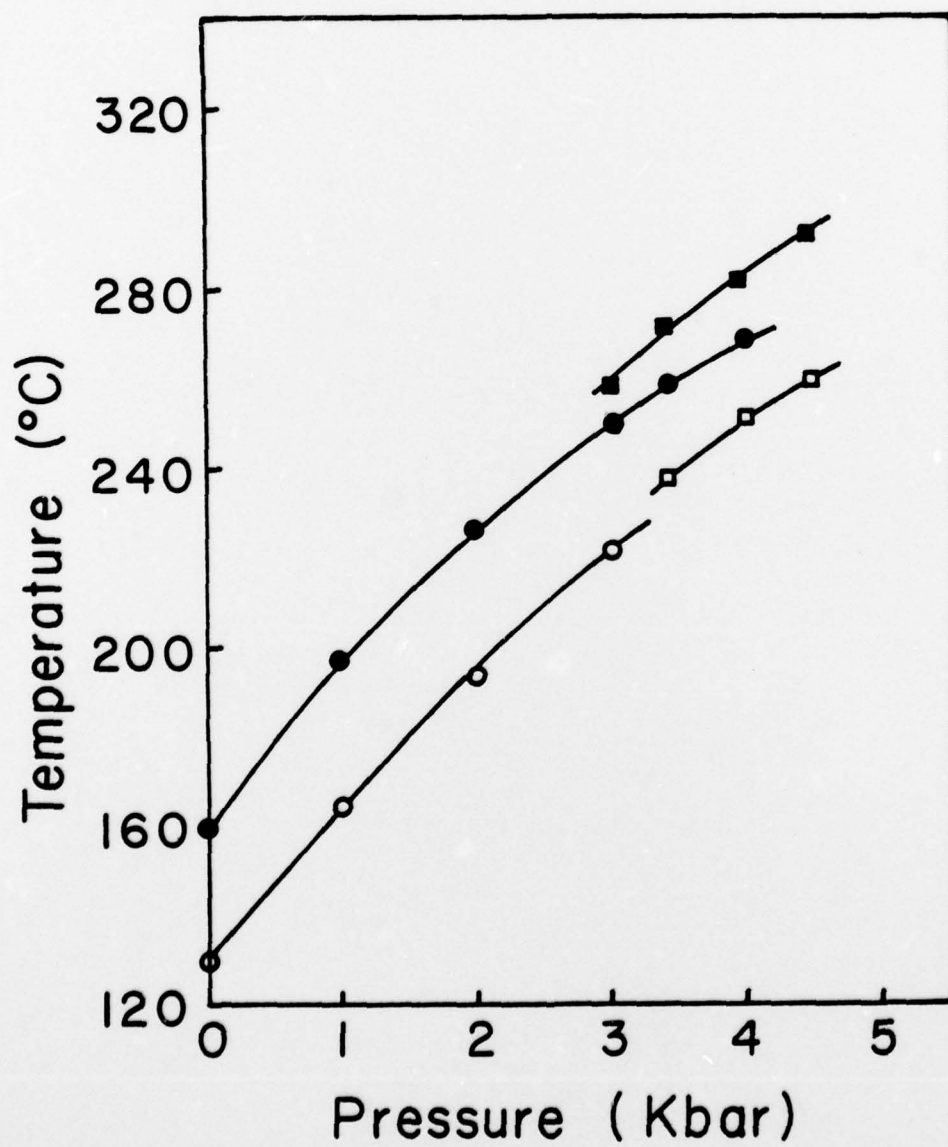


Fig 9

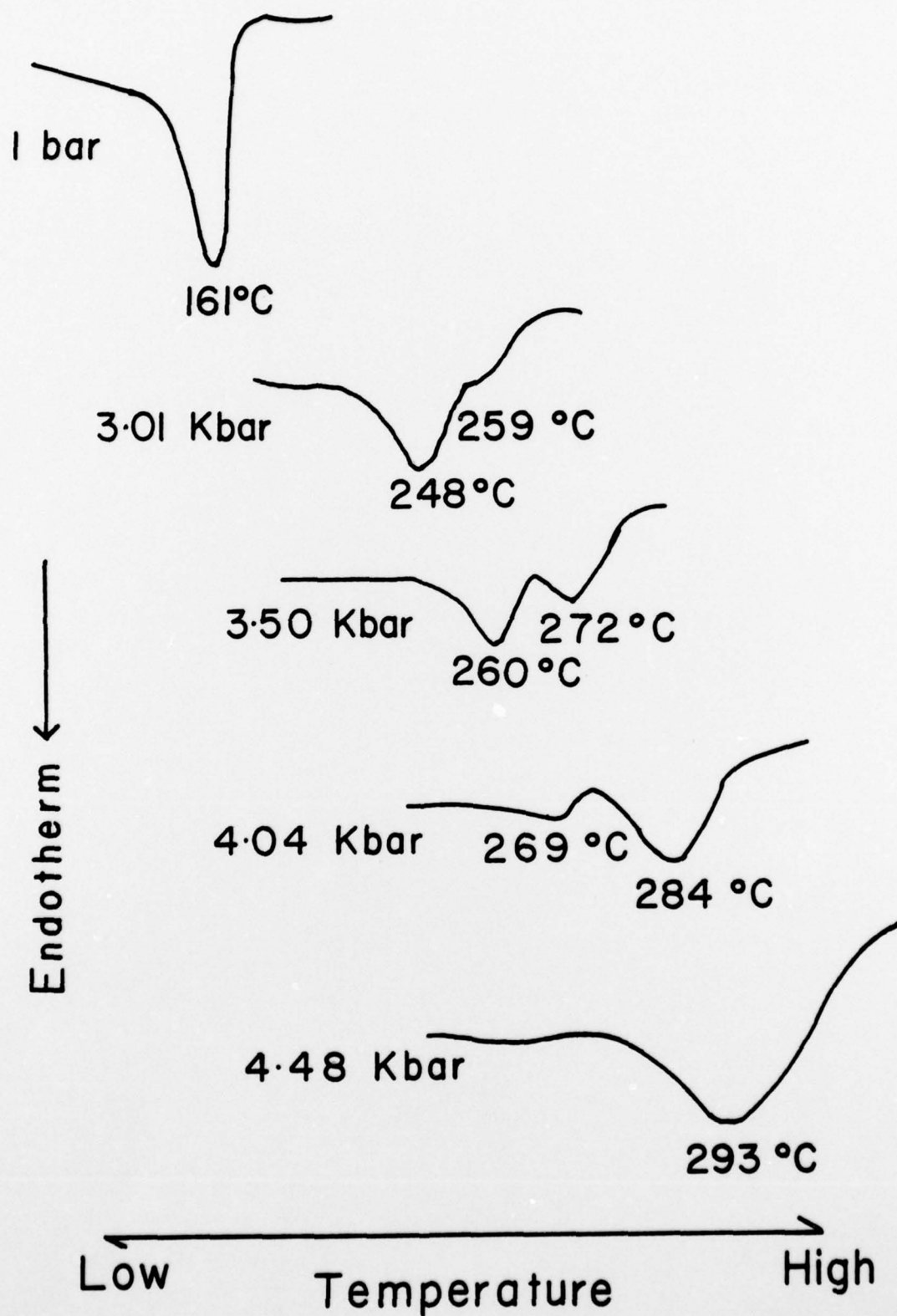


Fig 10

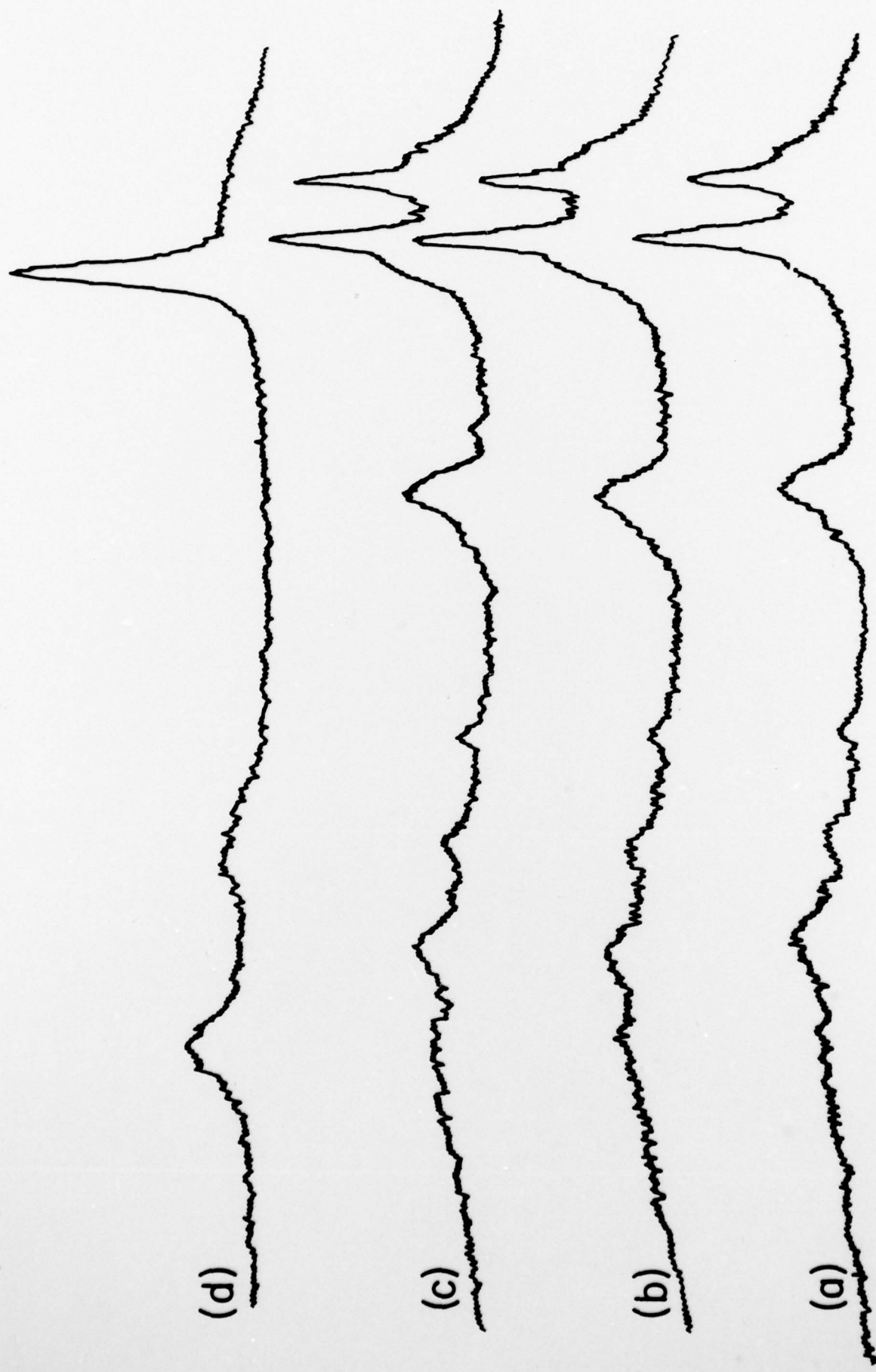


Fig 11

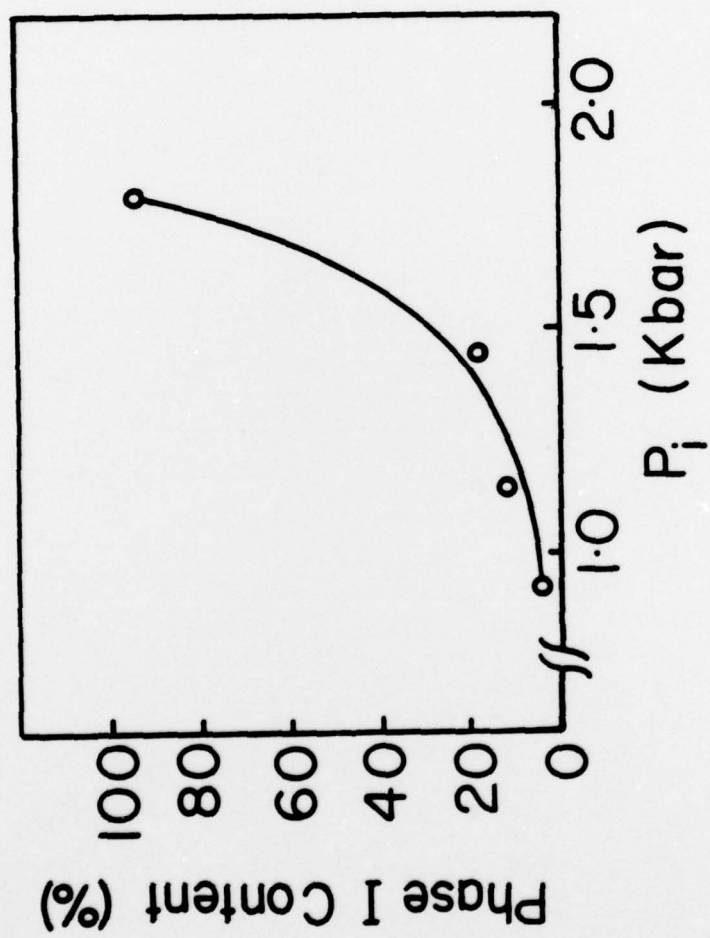


Fig 12

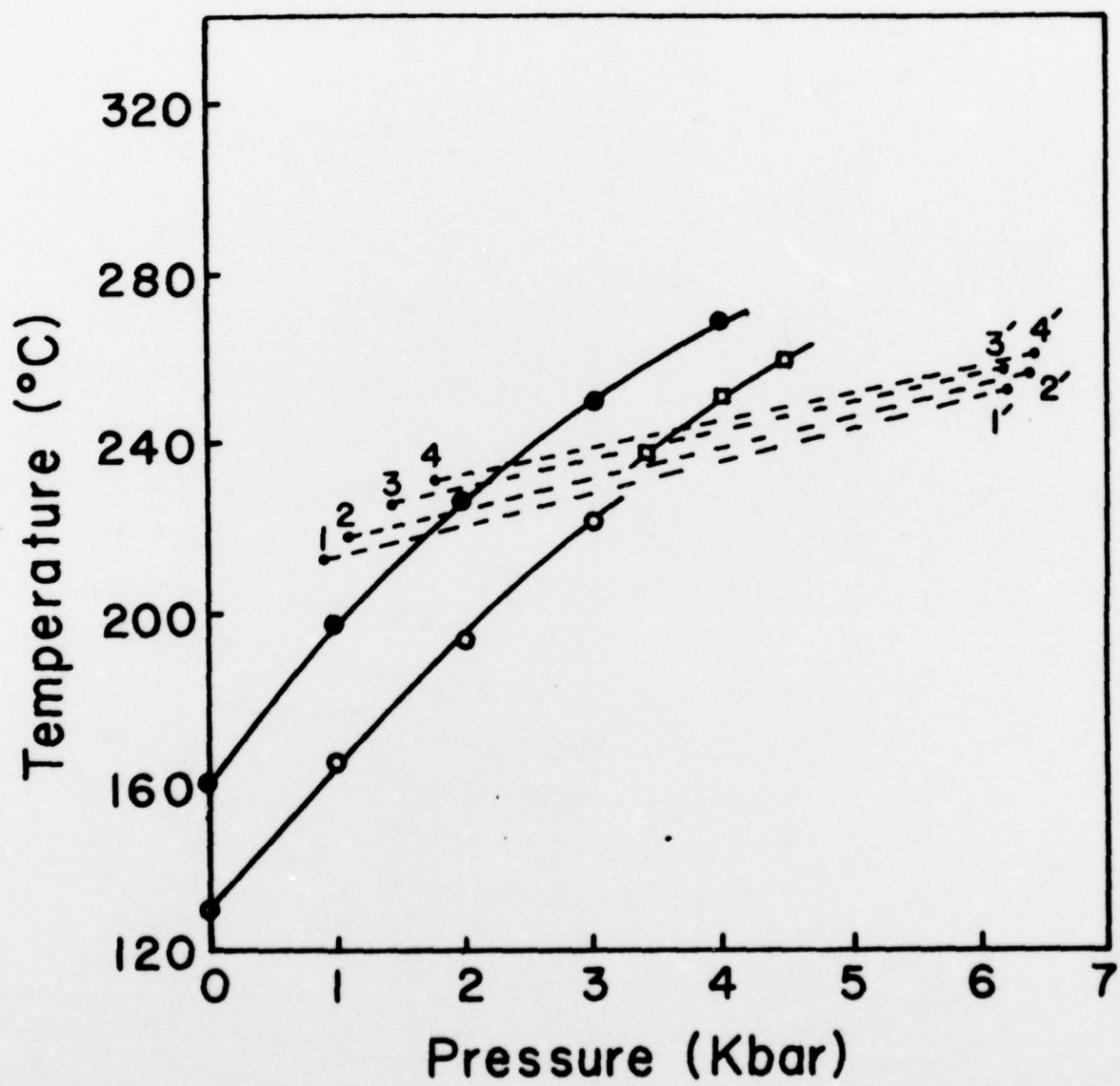


Fig 13