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A HIGH PRESSURE X-RAY STUDY OF NYLON 11.(U)
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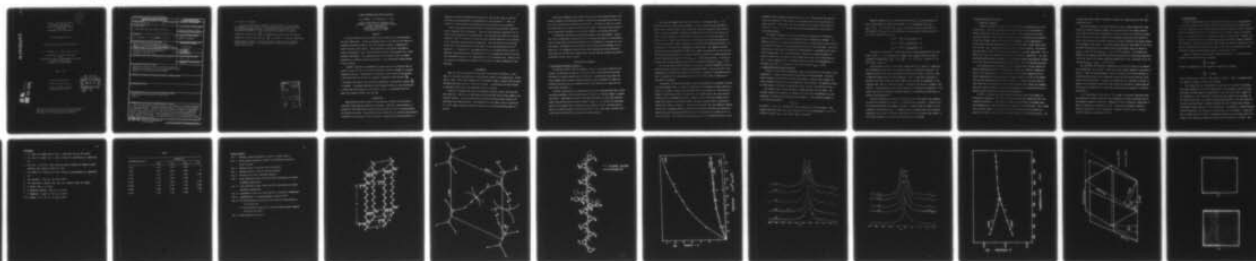
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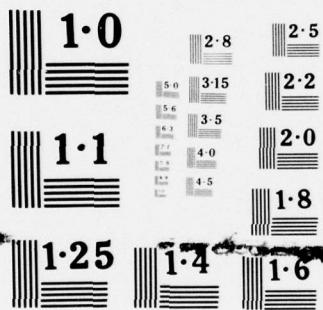
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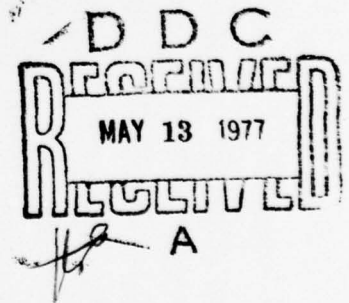
A HIGH PRESSURE X-RAY STUDY OF NYLON II

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and
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phase diagram for Nylon 11 was obtained and a triple point was observed at 310°C and 14.5 kbar. At pressures above 14.5 kbars the α -phase is stable until melting.

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A HIGH PRESSURE X-RAY STUDY OF NYLON 11

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ABSTRACT

An X-ray diffraction study of Nylon 11 was carried out at high pressures and high temperatures. Careful measurements made on both wet and dry samples at atmospheric pressure indicated that the structure of Nylon 11 suggested by Slichter was not quite correct. Some distortion of the planar conformation causes a shortening of the c repeat distance from the value required for a fully extended conformation. The compressibility of the crystal lattice at higher pressures up to 20kb was studied and related to the anisotropic bonding present in the structure.

A crystal transition at atmospheric pressure previously unreported was observed to occur at 95°C, the triclinic structure (α -phase) changing to a pseudo-hexagonal structure. The influence of pressure on this transition was studied. It was found that the increase in transition temperature with pressure $\frac{dT_t}{dP}$ (~15 K/kbar) was greater than the melting temperature increase with pressure $\frac{dT_m}{dP}$ (~9 K/kbar). A pressure-temperature phase diagram for Nylon 11 was obtained and a triple point was observed at 310°C and 14.5 kbar. At pressures above 14.5 kbars the α -phase is stable until melting.

INTRODUCTION

High pressure has been found to be an important variable in the study of structure, morphology and properties of polymers. Moreover, crystallization of polymers at high hydrostatic pressures has been shown to lead to new morphologies and crystal structures. High pressure X-ray diffraction is a technique particularly convenient for the study of crystal structure, morphology and crystallization of

polymers at elevated pressures and temperatures, and has been used to study the structure and crystallization of polyethylene at high pressures.^{1,2} Here, the results of a high pressure X-ray diffraction study of Nylon 11 are presented.

Nylon 11 was selected for study since it possesses some structural characteristics comparable with polyethylene. There are long paraffinic sequences with ten carbon atoms separated by the amide groups. The molecules pack with the α -crystal structure, that is, a structure in which both the hydrogen bonds and a close-packing of the paraffinic planar zigzags are important. This structure is non-centrosymmetric and it has been pointed out that Nylon 11 has interesting piezoelectric³ properties. A comparison of the compressibility of the α -phase crystal lattice in different directions with the compressibility of the polyethylene lattice would provide information related to the compressibility of the hydrogen bond. Finally there is a question concerning the stability of the α -phase at higher pressures and temperatures.

EXPERIMENTAL

Nylon 11, free from additives of any kind, was provided by Rilsan Co., Glen Rock, N.J. who also provided data on the molecular weight of the material $M_w = 20,000$ and $M_n = 8000$. Fibers were obtained by cold drawing a sample, quenched from the melt, and annealing under tension at 130°C for 12 hours. A crystalline film was obtained by quenching from the melt and annealing 130°C for 12 hours.

X-ray fiber diagrams were taken at atmospheric pressure using a flat film and $\text{CuK}\alpha$ radiation. The film to fiber distance was determined using silicon powder as an internal standard. The X-ray diffraction scans were recorded using a Norelco diffractometer with $\text{CuK}\alpha$ radiation. The temperature of the sample could be controlled to $\pm 0.1^\circ\text{C}$ using a resistance heater controlled by a Leeds and Northrup power controller.

X-ray fiber diagrams at high hydrostatic pressures were obtained using a high pressure apparatus described previously in conjunction with Rigaku Kenki 6kw rotating anode generator and molybdenum K_{α} radiation.¹ Pressures as high as 20 kbars and temperatures up to 350°C were used in this study. The pressure was determined using hexamethylene tetramine as an internal standard as described previously.⁴

At atmospheric pressure both wet and dry samples were investigated. Samples were dried by additional annealing at 60°C for several days prior to investigation. After pressurization in the high pressure cell, surrounded by a silicone oil pressure medium, the samples were essentially isolated from their environment and remained dry. At atmospheric pressure X-ray fiber diagrams and X-ray diffraction scans were also recorded from samples which had been immersed in water for periods exceeding 24 hours, prior to study.

RESULTS AND DISCUSSION

1. The Crystal Structure of Nylon 11.

No detailed crystal structure analysis of Nylon 11 has been carried out previously, but Slichter has pointed out that the X-ray fiber diffraction patterns from Nylon 11 closely resemble those of Nylon 66. Assuming that the chains are fully extended and a lateral packing described by Bunn and Garner⁶ for Nylon 66, Slichter calculated unit cell dimensions which were sufficient to index all the reflections from Nylon 11.

Slichter reported that the measured values of the c-spacing agreed with a value calculated assuming a fully extended chain to within 1%. We were unable to confirm this result. Measurements of layer line separations made on X-ray fiber patterns taken from both wet and dry fibers of Nylon 11 gave $c = 14.1 \pm 0.1 \text{ \AA}$, the calculated value for an extended chain conformation being taken as $14.9 \text{ \AA}$. An early study of Nylon 11 by Aelion⁷ showed a similar shortening of the c-axis repeat distance and a later study by Kinoshita⁸ also indicated the same feature.

The structure suggested by Slichter for Nylon 11 is shown in Fig. 1. The molecular chain is in the c-axis direction. It has a planar zig-zag conformation with a repeat distance equal to the theoretical distance assuming a fully extended chain. The axes of chains connected by hydrogen bonds lie in the (010) planes and form a layered structure. The direction of the a-axis is given by the mutual disposition of the chains in the sheet, and is defined by the structural requirements of the hydrogen bond. These requirements are correct bond distances and angles, and coplanarity of the four atoms comprising the amide group. The oxygen to nitrogen distance should be approximately $2.8\text{\AA}$ and the oxygen atom should lie on the N-H axis. The magnitude and direction of the a-axis required to fulfill all these requirements can be calculated, an angle $\beta = 77^\circ$ and $a_{\text{calc}} = 4.94\text{\AA}$ being obtained. It should be noticed that the experimental value for the a-parameters obtained is $a_{\text{exp}} = 4.78\text{\AA}$.

We conclude that a careful analysis of the model structure proposed by Slichter, reveals that the structure, although approximately correct, does not fit all of the experimental data within the limitation of accuracy. Moreover it should be noticed that the packing of the hydrocarbon sections in the (010) planes is very poor if this model is assumed.

Accordingly, we explored alternative chain conformations in an attempt to better fit the experiment data. In order to establish the conformation actually adopted by Nylon 11, a complete crystal structure would have to be carried out, and since the number of reflections obtained is very few, it is unlikely that even this analysis would provide an unambiguous solution. However, such a structure analysis has already been carried out by Bunn and Garner for Nylon 66, which gives a diffraction pattern very similar to Nylon 11. We noted with interest that this analysis revealed that the best agreement between observed and calculated intensities was obtained by placing the planar zig-zag paraffin sections of the molecule at an angle of 20° to the (010) planes. The distance between hydrogen atoms in neighboring chains at this

orientation can be simply calculated and found to be $2.55\text{\AA}$ (based on the observed chain axis separation $4.78\text{\AA}$), which is a reasonable value for a van der Waals hydrogen diameter. Furthermore, the close packing of such layers yields the value $3.7\text{\AA}$ with $\alpha = 63.5^\circ$. Fig. 2 shows the projection perpendicular to the c-axis of the packing proposed.

The problem remaining is that the structural requirements for the hydrogen bond can no longer be met if a fully extended chain conformation is assumed. The simplest solution is to assume that rotations about C-C bonds occur in such a way as to re-orient the plane of the poly-amide group back into the (010) plane. That such a distortion in the chain conformation is indeed present is confirmed by the experimental observations. The structure analysis carried out by Bunn and Garner for Nylon 66 showed that the oxygen atom was pushed back nearly to the [100] direction. Fig. 3 shows a suggested chain conformation which would meet the experimental requirements and lead to a shortened c-axis repeat distance $c_{\text{calc}} = 14.2\text{\AA}$.

2. Compressibility at Room Temperature

A series of X-ray fiber diagrams were taken at pressures up to 19.5 kbar at room temperature. No phase transformation was observed at these pressures. The interplanar spacings of the (100), (010) and (001) planes, as well as the c-repeat distance determined from the layer line separation, were measured. The measured strains on these planes at different pressures are listed in Table 1 and plotted in Fig. 4.

The change in the c-repeat distance at higher pressures is very small. The c-repeat distance can change by the adoption of a new chain conformation or by the straining of covalent bond distances and bond angles. If we assume the change in c is linear with pressure

$$\frac{\Delta c}{c} = k p$$

we obtain $k = 1.81 \times 10^{-7} \text{ cm}^2/\text{kg}$, for a least squares best fit of the data. This compares reasonably well with a value obtained by Ito for polyethylene $k = 3.0 \times 10^{-7} \text{ cm}^2/\text{kg}$ (0-3 kbars) over a very limited range of pressures.

Empirical equations for the stress-strain relations in other directions can also be established but these are not linear. If a logarithmic form $-\epsilon_{hkl} = A_{hkl} \ln \left(\frac{p}{p_0} + 1 \right)$ is assumed, where ϵ_{hkl} is the observed elastic strain and p is the pressure, and A_{hkl} and p_0 are constants to be determined, then we obtain for the (100), (010) and (001) planes

$$-\epsilon_{100} \% = 0.804 \ln \left[\frac{p}{0.297 \times 10^4} + 1 \right]$$

$$-\epsilon_{010} \% = 8.89 \ln \left[\frac{p}{0.352 \times 10^4} + 1 \right]$$

$$-\epsilon_{001} \% = 0.506 \ln \left[\frac{p}{0.108 \times 10^4} + 1 \right]$$

The units of p are kg/cm^2 . These functions are shown represented by the solid lines in Fig. 4. It is interesting to compare these equations with the equations obtained for polyethylene $A_{110}^{\text{P.E.}} = 4.80$, $A_{200}^{\text{P.E.}} = 3.09$, $p_0^{\text{P.E.}}(110) = 0.639 \times 10^4$ and $p_0^{\text{P.E.}}(200) = 0.290 \times 10^4$.

The anisotropic nature of the linear compressibilities of Nylon 11 complicates the deformation of the unit cell, even when subject to hydrostatic pressure. The changes observed in the chain direction and [100] direction are at least one order of magnitude smaller than the [010] direction. Fig. 5 shows that a reduction in spacing on the (001) planes and (100) planes can be achieved by compression of the hydrogen bond, that is a reduction of N-H ...O distance, and also by a change in the angle β . A closer packing of the (100) planes can be produced by increasing β . This cannot take place at atmospheric pressure owing to the geometrical restrictions imposed by the hydrogen bond.

From the simultaneous strains on the (001) and the (100) planes, the change in β , $\Delta\beta$ and the deformation in the N-H ...O distance can be measured. A value of $\Delta\beta = 3.5^\circ$ was obtained while the change in the N-H ...O distance was too small to be determined at the pressures used. It appears that the hydrogen bond can be regarded essentially as a rigid link between chains which can rotate slightly with respect to each chain changing β and therefore the (001) and (100) spacings.

3. Crystal Transition in Nylon 11

a) Atmospheric Pressure

A number of diffraction scans were taken at various temperatures up to the melting point. The most interesting observation was that this study revealed a crystal transition occurring in nylon 11 at 95°C. This transition has not been previously reported. Figs. 6 and 7 show the effect of temperature on the position of the two strongest peaks from (010) and (100) planes. As the temperature increases these two peaks approach each other and at 95°C only a single sharp reflection is seen. Fig. 7 shows the reverse process to occur on cooling. This phenomenon was found to occur in both wet and dry samples at the same temperature. Fig. 8 shows the a, and b cell parameters plotted as a function of temperature. The (010) spacing increases steadily, whereas the (100) spacing remains approximately constant up to ~50°C and then decreases quite sharply until at 95°C both spacings are equal.

The c-spacing was also measured at various temperatures, and was observed to remain approximately constant at temperatures through the transition temperature and up to the melting point. In the vicinity of the melting temperature and at higher temperatures the c-spacing shows a sudden decrease to 12.9⁰Å but we assumed that this was associated with the melting process. In view of the fact that the [001] direction is not parallel to the c-axis we assume that although the symmetry about the c-axis is hexagonal, the hexagonal symmetry is not possible and for this reason we term the new crystal phase as pseudohexagonal.

In Fig. 8, it can be seen that whereas the spacing of the (010) planes increased with temperature, the (100) d-spacings decrease with temperature up to the transition temperature. This does not suggest the contraction of hydrogen bonds with temperature but rather the anisotropic character of the structure. Fig. 9 shows that a gradual change to a lattice with hexagonal symmetry can be achieved by a change in the angle γ and by a normal thermal expansion in the [010] direction. The

hydrogen bond length remains essentially constant with temperature over this small temperature range.

The pseudo-hexagonal structure involves more than a simple geometrical change produced by thermal expansion however since we observe that the thermal expansion is isotropic in directions perpendicular to the c-axis above the transition temperature. For this to be true a change in the hydrogen bonding must have occurred so that in the new phase the hydrogen bonds are no longer confined to the planes defined by the original (010) planes. The linear thermal expansion coefficients in the [100] and [010] directions can be calculated from the experimental data, and values of $\alpha_{[100]} = 3.59 \times 10^{-5}/^{\circ}\text{C}$ and $\alpha_{[010]} = 1.15 \times 10^{-3}/^{\circ}\text{C}$ obtained. If we assume that above 95°C the hydrogen bonds are distributed isotropically in directions perpendicular to the c-axis, the thermal expansion perpendicular to the c-direction can be calculated as $\alpha_{[100]} = \alpha_{[010]} = 2.26 \times 10^{-4}/^{\circ}\text{C}$.

The relatively low transition temperature for the case of nylon 11 as compared with polyethylene we attribute to this very uneven thermal expansion in the case of nylon 11. When the pseudo-hexagonal lattice is reached, the lattice potentials in the different directions are in degenerate states and the hydrogen bond can easily form in the new directions. However, in polyethylene the difference in thermal expansion in the different direction is much smaller and therefore a pseudo-hexagonal lattice can be achieved only at quite high temperatures and pressures (~ 5 kbar and above 200°C).

It is interesting to note that at $\sim 95^{\circ}\text{C}$ changes in molecular relaxations have been observed by several authors and such phenomena are usually attributed only to the amorphous regions of the solid. Kawaguchi's⁹ data on mechanical relaxations in Nylon 11 indicate an α -relaxation at 90°C . Dielectric measurements indicate a molecular relaxation³ at this temperature. Moreover recently a D.T.A. study by Gordon¹⁰ revealed a transition at $\sim 90^{\circ}\text{C}$.

b) High Pressures

A number of observations of the transition were carried out at high pressures. The sample was initially pressurized and then the temperature was increased until both the temperature of the transition and the melting temperature could be observed. During the temperature increase, the pressure did not remain constant but increased also. This phenomenon has been discussed in a previous publication.² However, the pressure was determined for each temperature using the internal standard, hexamethylene tetramine. Typical high pressure X-ray diffraction patterns obtained at 7.13 kb and 24°C showing the triclinic form as shown in Fig. 10(a) and obtained at 9.79 kb and 250°C showing the new hexagonal phase as shown in Fig. 10(b).

Figure 11 shows the resulting phase diagram for Nylon 11. As the pressure increases the melting temperature increases,

$$\frac{dT_M}{dP} \sim 9^\circ\text{C/kbar}$$

However the temperature of the transition increases more rapidly,

$$\frac{dT_t}{dP} \sim 15^\circ\text{C/kbar}$$

until at 310°C and 14.5 kbars a triple point is reached. Thus, at pressures above 14.5 kbars the α -phase is stable until melting.

If we assume that the transformation occurs when the (100) and (010) planes have equal spacings and that this equalization of the spacings is due to the very anisotropic thermal expansion perpendicular to the main chain, then a reason for the suppression of the transition at higher pressures suggests the following: As we observed previously, the compressibilities perpendicular to the chain direction are also very anisotropic, at higher pressures the (010) spacing being reduced a considerable degree relative to the (100) spacing. Accordingly, at higher pressures greater temperatures are required for equalizations of the spacings. A rough estimate of this effect can be made at atmospheric pressure and the initial rate of increase of the transition temperature dT_t/dP can be calculated as $\sim 4^\circ/\text{kbar}$. From

the phase diagram, Fig. 10, dT_t/dP at atmospheric pressure can be estimated to $\sim 6^\circ/\text{kbar}$, showing that this effect is certainly a major contribution. The thermal expansion coefficients at higher pressures will decrease and this will have the effect of further increasing the temperature of the transition. If the pressure is sufficiently high, equalization of spacings will be impossible at temperatures lower than the melting point and thus the α -phase will be stable.

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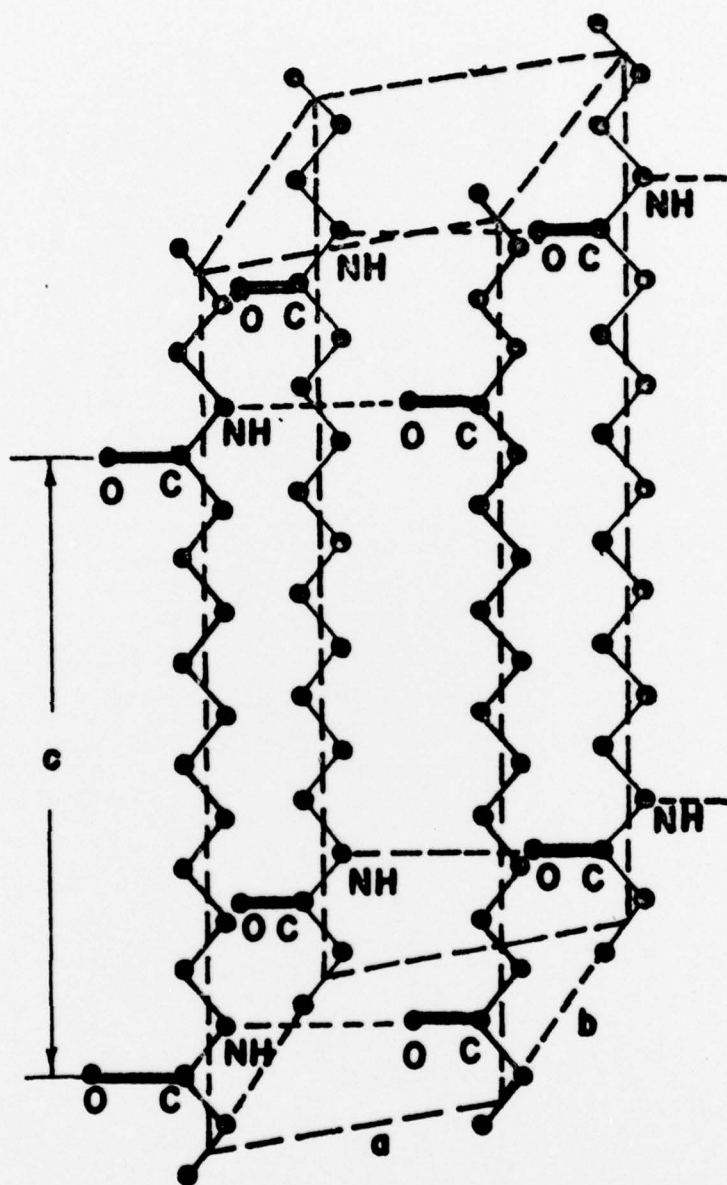
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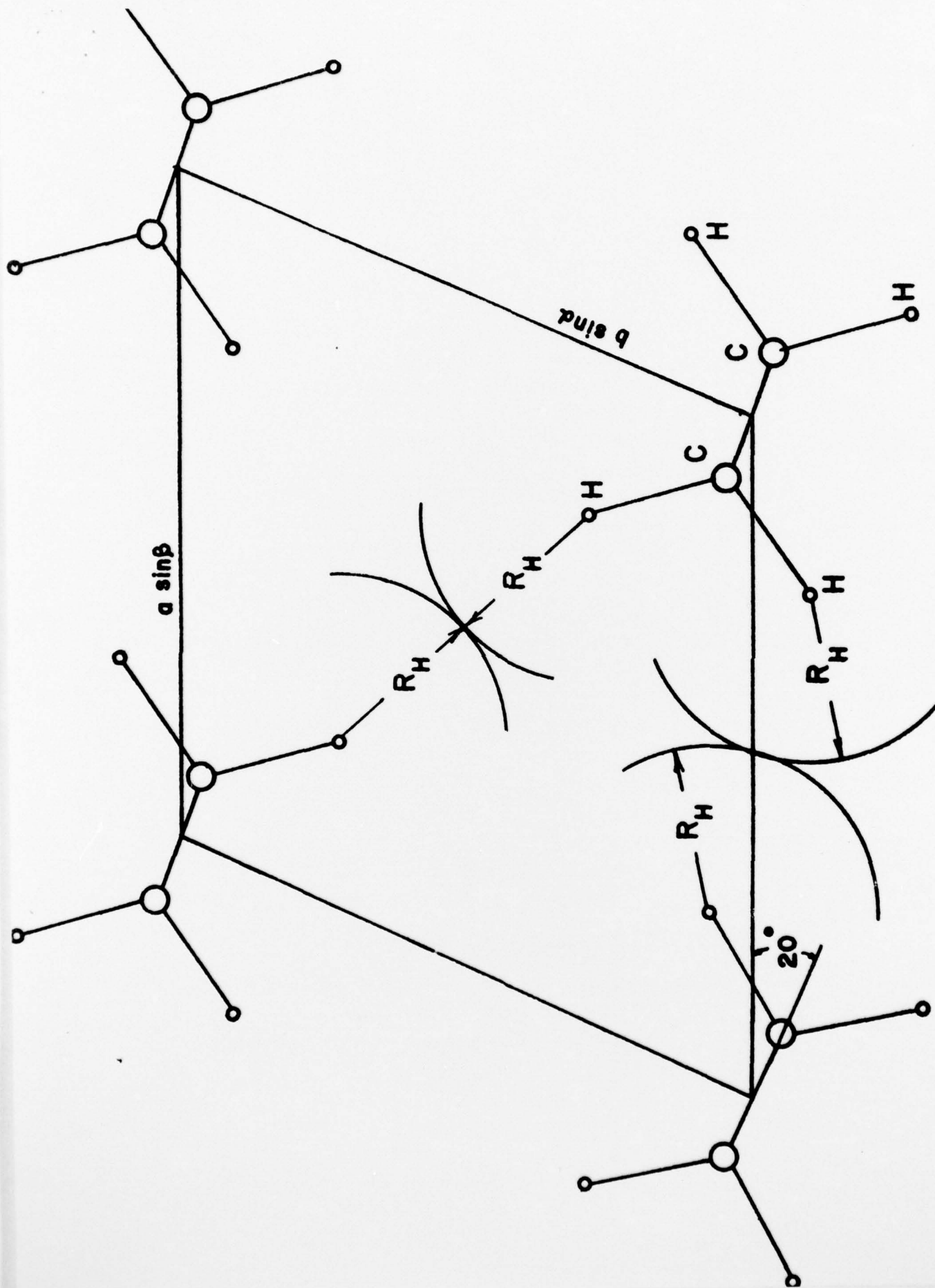
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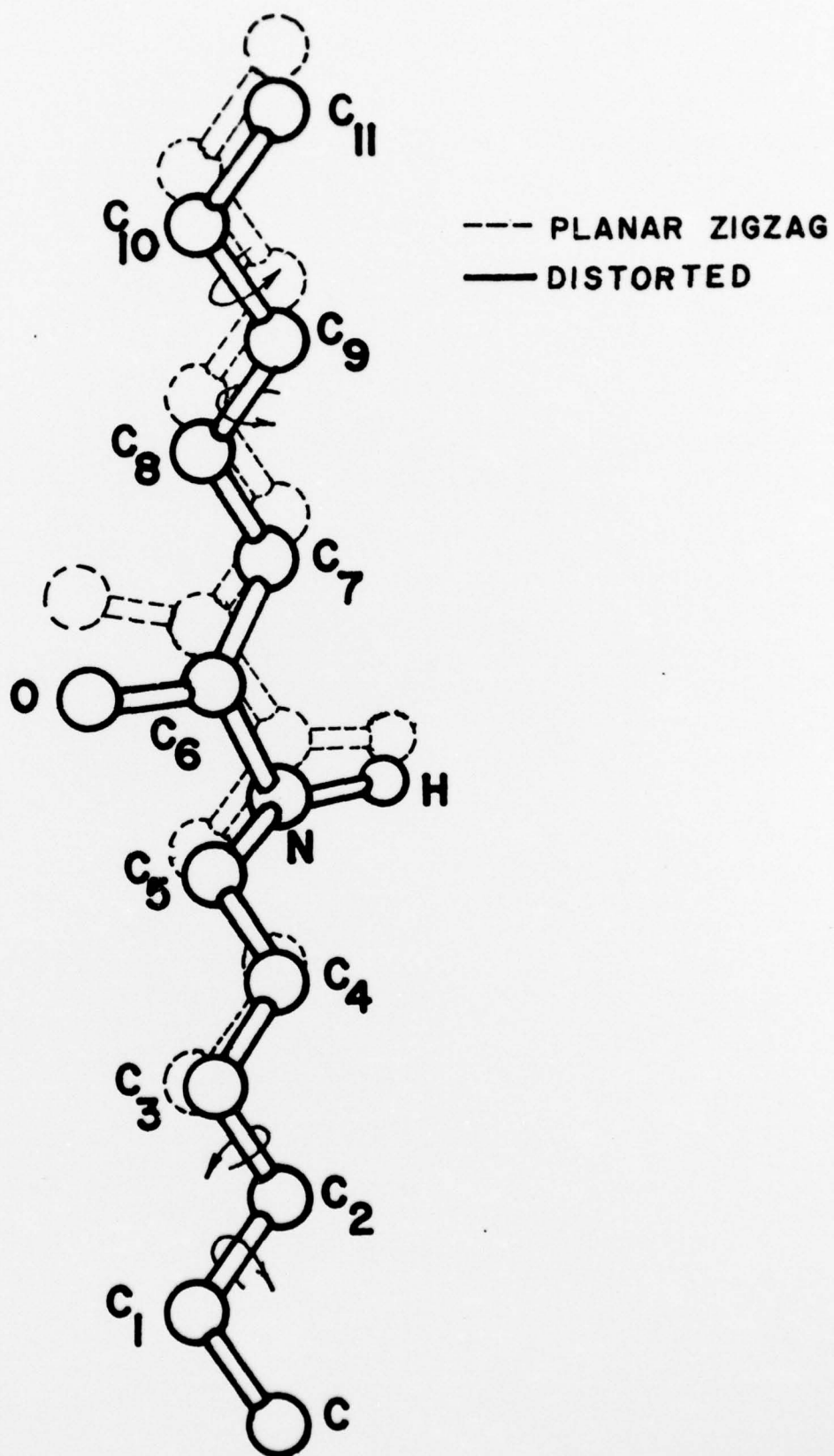
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	$-\epsilon_{100}$	$-\epsilon_{010}$	$-\epsilon_{001}$	$-\epsilon_c$
2.967	0.366	2.294	0.650	0
7.236	1.067	4.448	1.206	0
9.220	1.278	4.972	1.060	0.336
11.610	1.383	5.831	0.972	0
13.234	1.383	5.900	1.262	0.336
16.081	1.488	6.759	1.342	0.336
17.962	1.488	7.009	1.439	0.336
19.274	1.592	7.257	1.609	0

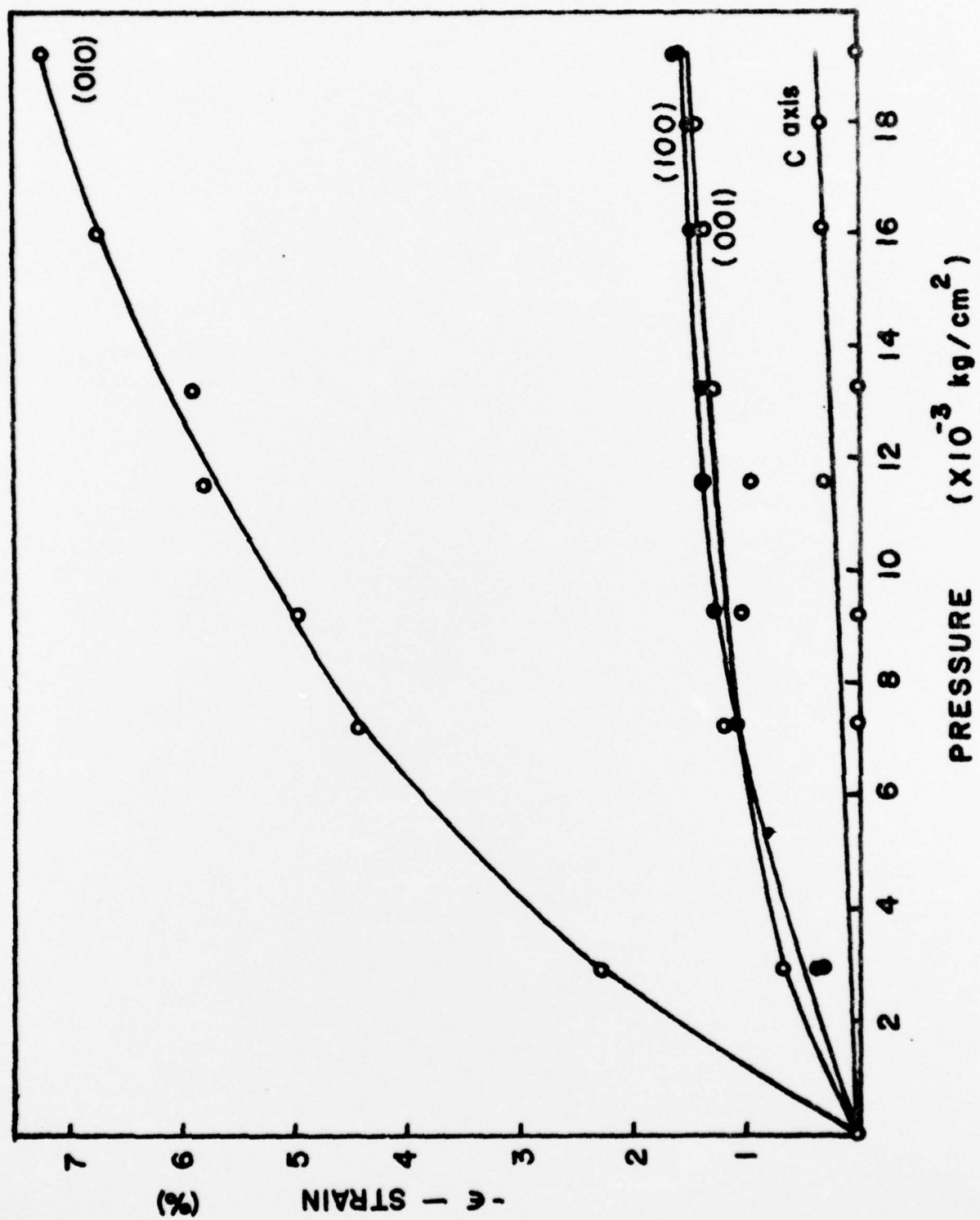
Figure Captions.

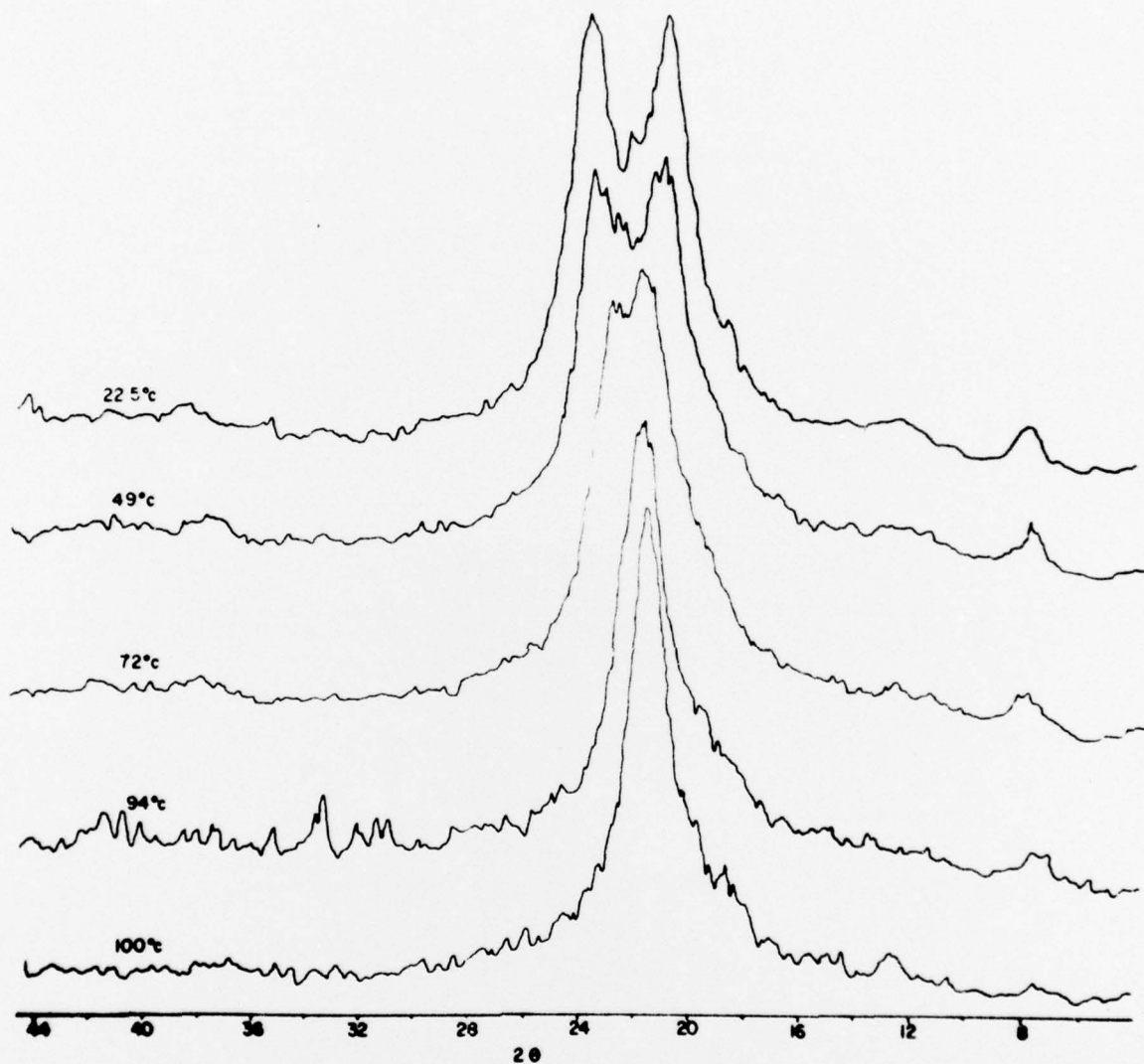
- Fig. 1. Hydrogen bonding arrangement in nylon 11 crystal lattice.
- Fig. 2. Close packing arrangement proposed for paraffinic sections of nylon 11 chains.
- Fig. 3. Proposed nylon 11 distorted chain conformation.
- Fig. 4. Measured elastic strains at various pressures.
- Fig. 5. Distortion of β with increasing pressure.
- Fig. 6. X-ray diffraction scans ((100) and (010) reflections) at various increasing temperatures.
- Fig. 7. X-ray diffraction scans ((100) and (010) reflections) at various decreasing temperatures.
- Fig. 8. d-spacings of (010) and (100) planes as a function of temperature.
- Fig. 9. Transformation to a pseudo-hexagonal lattice at 95°C.
- Fig. 10. (a) X-ray diffraction pattern of the triclinic form obtained at 7.13 kb and 24°C.
(b) X-ray diffraction pattern of the new hexagonal phase obtained at 9.79 kb and 250°C.
- Fig. 11. Phase diagram for nylon 11.

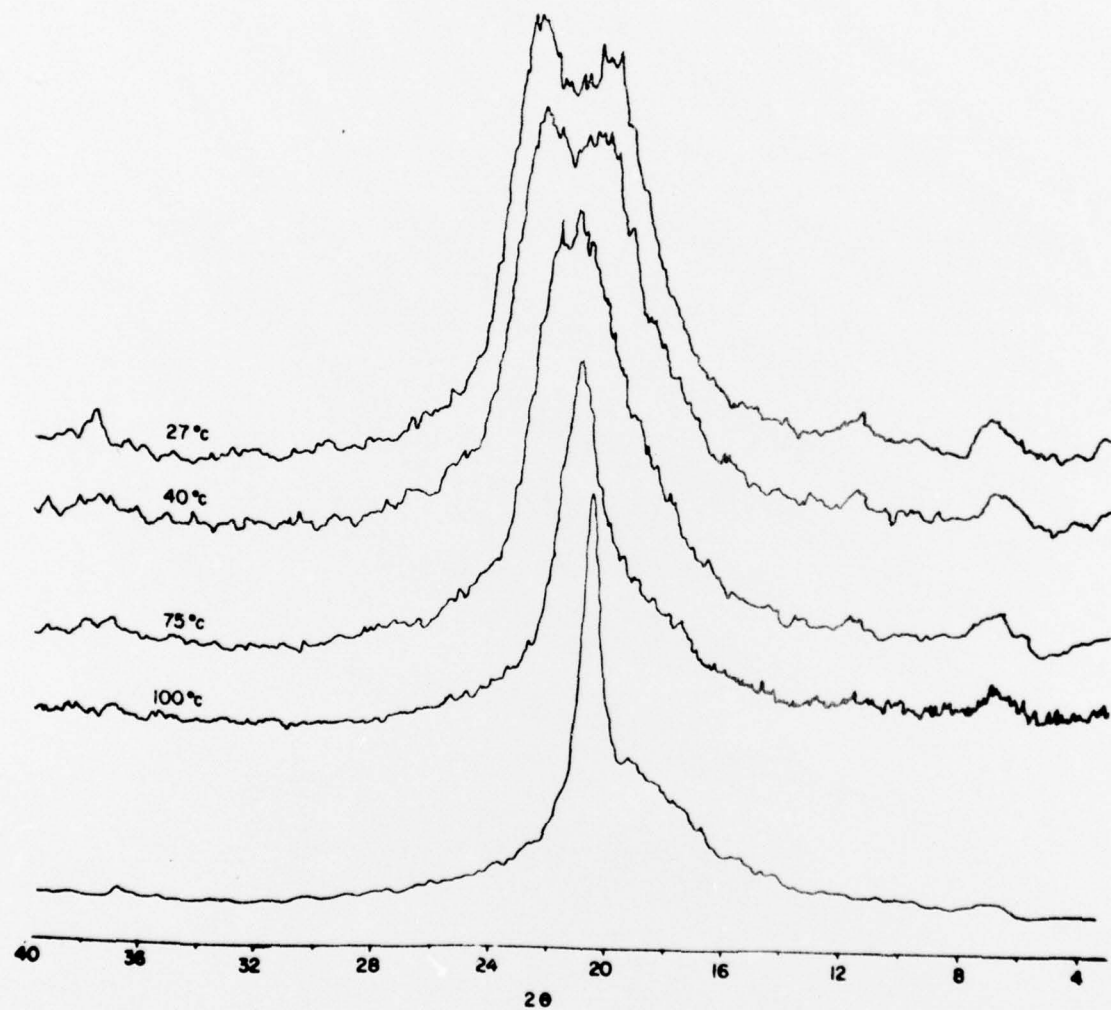


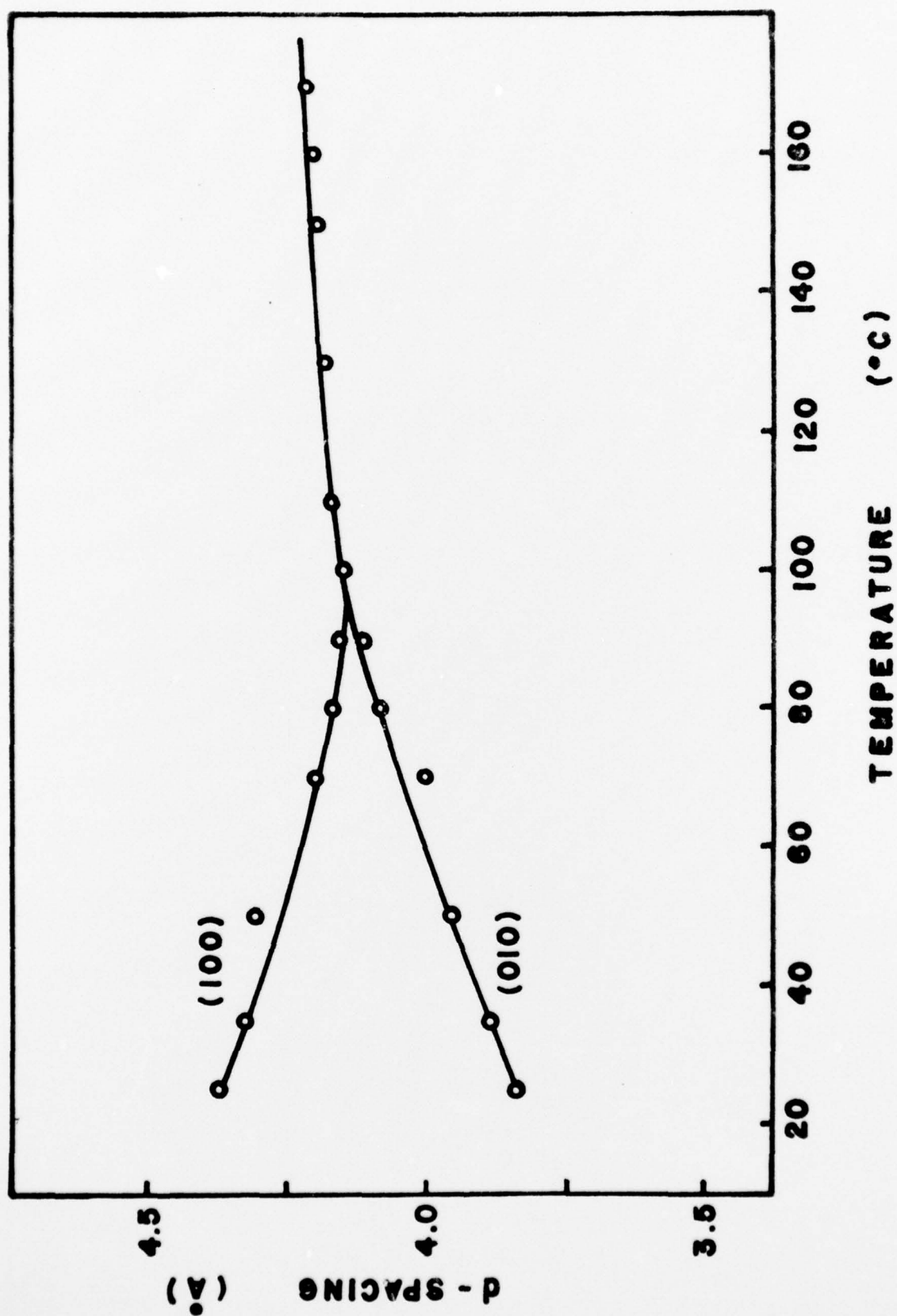


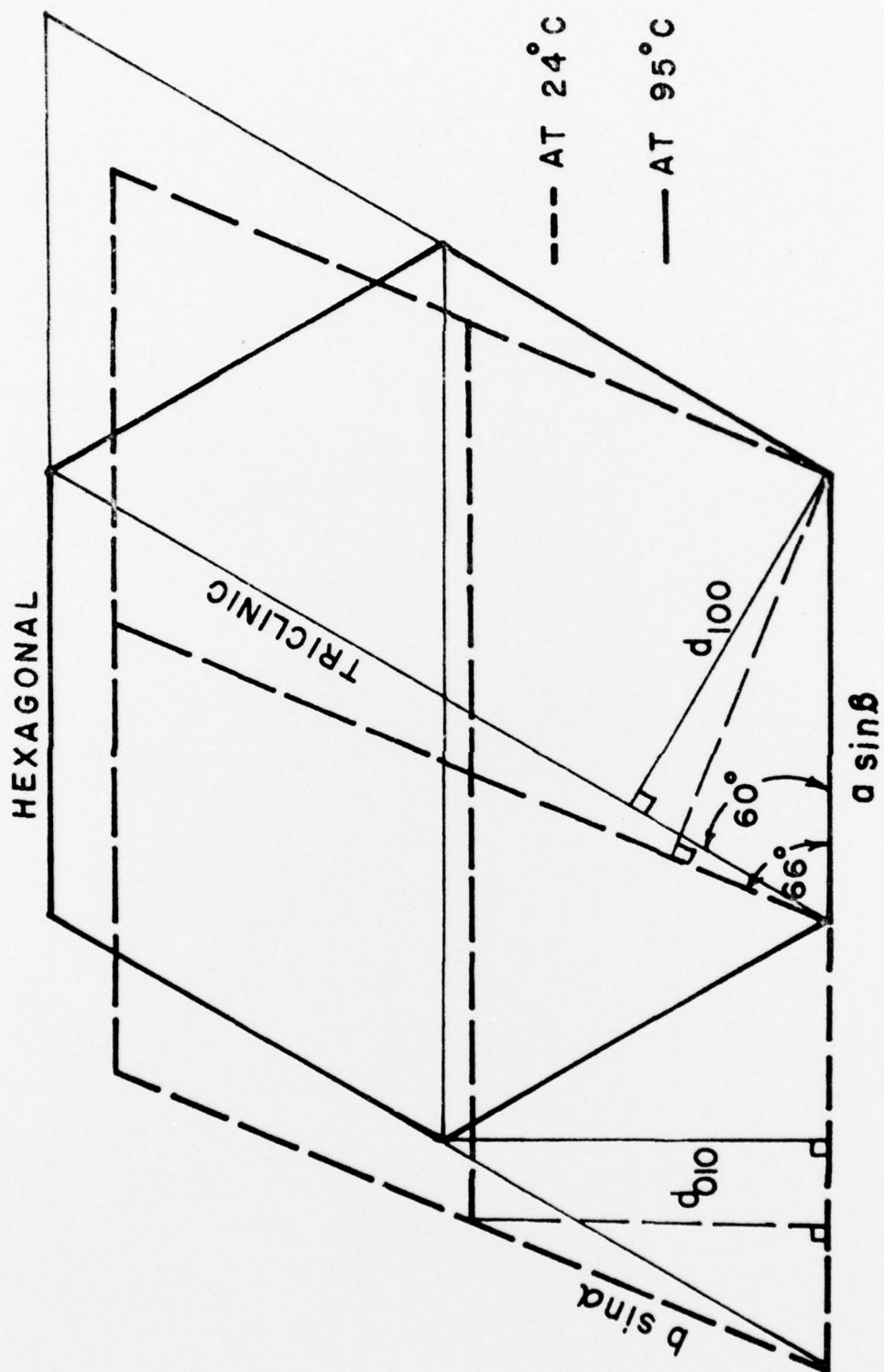


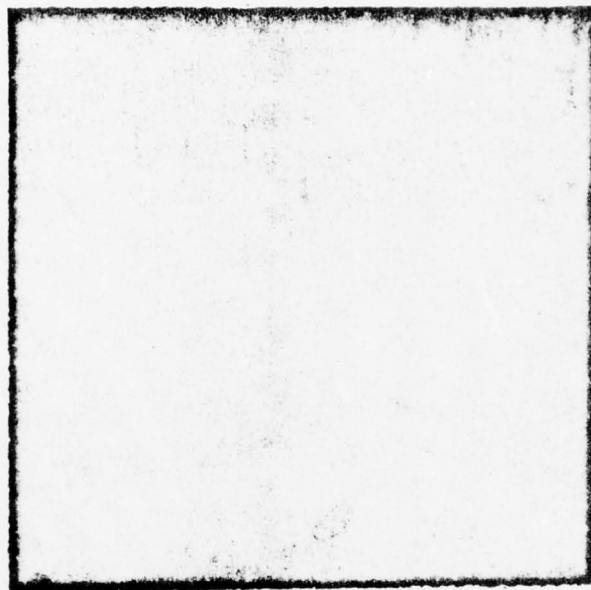




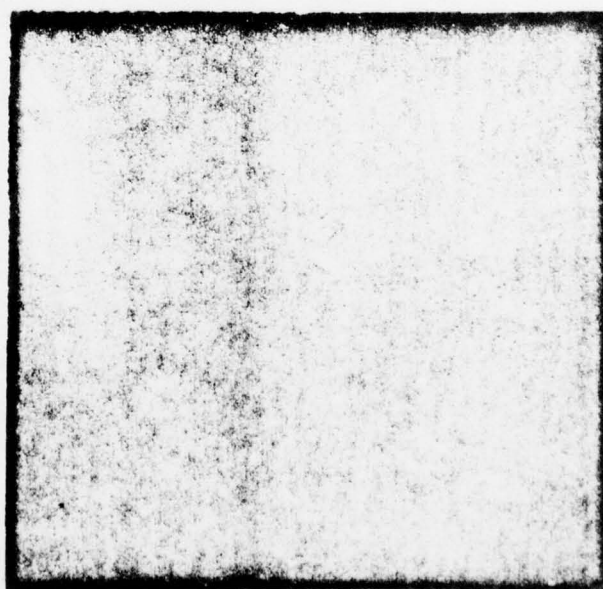








(a)



(b)

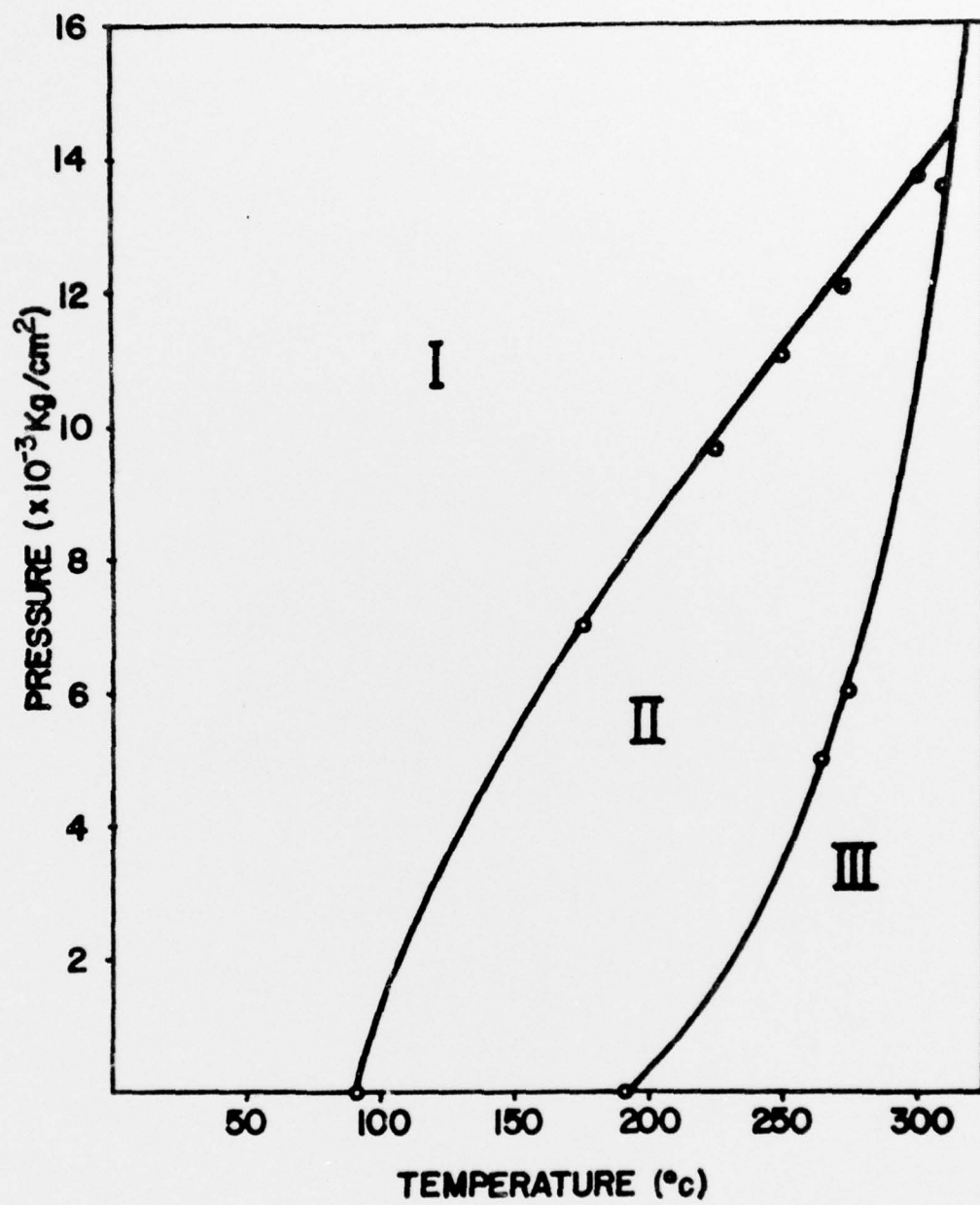


Fig 14