

ONR TECHNICAL REPORT NO. 96
PROJECT: NR 056-378
CONTRACT: NONR 3357 (01)

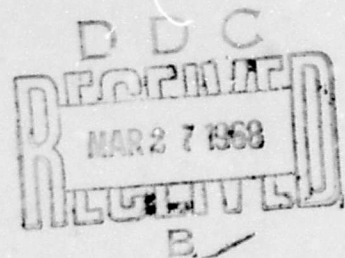
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TIME-DEPENDENCE OF CRYSTAL
ORIENTATION IN CRYSTALLINE POLYMERS

by

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November 1967



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Abstract

The results of two methods for studying molecular processes accompanying the deformation of polyethylene are described. The examination of spherulite deformation by observing light scattering patterns along with measurement of the birefringence, stress and strain during the rapid extension of polyethylene shows that this initial structural deformation is essentially instantaneous. Dynamic x-ray diffraction shows that this is followed by a slower relaxation involving change in the orientation of the crystals by two processes, the lower temperature one involving slipping of lamellae past each other and the higher temperature one involving viscoelastic flow of the crystals.

Introduction

In a previous publication¹, structural interpretations of mechanical properties were discussed. It was shown by combining the measurement of birefringence with that of stress, that the orientation of a crystalline polymer was time-dependent. For example, if a sample of high-density polyethylene is stretched, the birefringence does not immediately achieve its final value but continues to increase for more than 100 seconds after the sample reaches its final length. The interpretation of this observation is that the molecules required this amount of time to change from an unoriented state to an oriented one.

This orientation process in a crystalline polymer is complex in that the molecules reside partly in crystals and partly in amorphous regions. The crystals in turn are arranged in lamellae which participate in large superstructures such as spherulites. Consequently, the molecular orientation depends upon the participation of the molecules in the orientation of these structural elements of the polymer. It has been our objective to resolve molecular orientation into its constituent processes by employing a number of optical techniques².

It was concluded in these earlier studies that the large morphological units, the spherulites, deformed very rapidly, essentially simultaneously with the deformation of the sample. The crystals and amorphous units within the spherulites also underwent this rapid initial deformation. However, internal stresses result from this initial deformation process which are subsequently relieved by relaxation. This relaxation occurs within a longer time scale and is the process which results, for example, in the forementioned increase in birefringence with time. It occurs by means of a rearrangement of both the crystalline and amorphous regions within the deformed spherulite.

In this paper, additional studies which substantiate these processes are discussed. These involve (1) the observation of the time dependence of spherulite dimensions by light scattering during the rapid irreversible stretching of polyethylene films, along with the simultaneous measurement of local strain, stress and birefringence, and (2) the direct measurement of the time dependence of crystal orientation rates by the dynamic x-ray diffraction techniques.

High Speed Elongation Studies

These studies were principally carried out as part of a Ph.D. thesis by Dr. Peter Erhardt (Present Address: Xerox Corp., Webster, New York) and are described in detail elsewhere³. The samples were stretched from both ends at rates up to 4000 in/min using a pneumatic-hydraulic device which has been described^{3,4} and which is shown in the photograph of Fig. (1). The strain of the sample was monitored during the rapid extension by taking high speed motion pictures of lines ruled on the surface of the sample. Thickness was obtained from the initial thickness, and the measured change of length and width of the sample assuming constant volume. Stresses were measured using a modified BLH dynamic load cell with an output displayed on a cathode ray oscillograph.

Low angle photographic light scattering patterns were obtained simultaneously using a laser and second high speed motion picture camera as has been described^{3,5} and is seen in Fig. (1) and shown diagrammatically in Fig. (2).

Simultaneous measurement of birefringence is accomplished by determination of the transmittance of light when the stretched sample is placed between polaroids oriented at $\pm 45^\circ$ to the stretching direction. To do this, a portion of the laser beam used for the light scattering photography is reflected by a tilted partially reflecting glass plate into a photomultiplier tube as shown in Fig. (2).

A typical set of light scattering photographs enlarged from selected frames of the motion picture are presented in Fig. 3 for a compression-molded film of a Monsanto experimental medium-density polyethylene stretched between 0° and 90° crossed polaroids (designated I_+) at a rate of 1636 in/in/min. and photographed at 2000 frames/sec. The elongation ratios

in the stretching direction, α_x , and the times after stretching are indicated under the photographs. The deformation of the spherulite is characterized by the distortion of the scattering pattern. For purposes of characterizing this distortion, $1/2$ of the angle B is defined in Fig. 4. For the undeformed spherulite, $1/2 B = 45^\circ$. B increases toward 90° as the spherulite becomes deformed and changes from a sphere to an ellipsoid elongated in the stretching direction. $1/2 B$ may be quantitatively related to the axial ratio of the ellipsoid using a theory for the scattering from deformed spherulites proposed by the author and coworkers⁷⁻⁹ and in a more approximate but mathematically simpler manner by Samuels¹⁰.

The variation of this value of $1/2 B$, the elongation ratio, α_x , the stress, σ , and the birefringence Δ during the elongation of such a polyethylene film are shown in Fig. (5). The rapid fall-off of stress at about 27 msec. is a consequence of sample breakage. It is seen that both the spherulite deformation and the birefringence increase rapidly and keeps pace with the sample deformation. Fig. (6) shows the results of a comparison of the spherulite elongation ratio calculated from the light scattering pattern (radius in stretch direction/original radius) and the sample elongation ratio. The two are approximately the same.

Similar results have been obtained by both light scattering and microscopic observation during slow stretching. Results on polybutene-1 from this laboratory have been published recently¹¹.

If the sample is held at constant elongated length following rapid stretching, the spherulite dimensions remain constant but the birefringence continues to increase at a slower rate for many seconds as previously discussed. Obviously, there must be a rearrangement of molecules within this deformed superstructure occurring by a different mechanism and with longer relaxation times. The nature of this structural rearrangement will next

be discussed.

Dynamic X-ray Diffraction Studies

It is believed that the birefringence increase is a consequence of delayed crystal orientation. The direct demonstration of this may be accomplished by the observation of the time-dependence of the x-ray diffraction by these crystals. The dynamic x-ray diffraction technique, developed in this laboratory, has been described briefly¹², and more complete descriptions are forthcoming^{13,14}.

The difficulty in following rapid changes in crystal orientation by the x-ray technique is that by ordinary techniques, diffracted x-ray intensities are sufficiently low that it is necessary to count individual quanta or else average over their rate of arrival for times of the order of seconds. To obtain a measurement of a fairly small change in crystal orientation, one must measure the intensity, itself, to a precision of the order of 1%. This would require the counting of several thousand diffracted quanta which would take several seconds using commonly available x-ray sources. Therefore, it is not feasible to follow directly crystal orientation changes occurring in times of the order of seconds or less.

An alternate approach for the determination of the time-dependence of crystal orientation is to observe x-ray intensities during cyclic deformation as in the dynamic birefringence measurement². While it is not possible to measure directly the cyclic variation of diffracted x-ray intensity with time during a single cycle, such information can be obtained by averaging the results over many cycles of sample deformation. The procedure has the disadvantage, however, that only reversible changes in orientation can be studied. The rearrangement of crystals within a deformed spherulite following stretching is not completely reversible, so that one does not learn the complete

story. However, the correspondence which has been observed¹⁵ between dynamic birefringence data obtained in cyclic experiments at small (0.1%) strain amplitude, relaxation experiments at 1% strain, and constant rate of strain experiments at up to 8% strain amplitude indicate, at least, that up to these strains, the same phenomena is seen by the various methods.

The principal of the dynamic x-ray technique is illustrated in Fig. (7) and a photograph of the essential parts of the apparatus is shown in Fig. (8). The sample is vibrated in tension at frequencies between 0.01 and 20 cycles/sec. at a controlled temperature with a dynamic strain amplitude of 2.5%. This is superposed on a static strain of about 20%, which is necessary in order to avoid the sample becoming slack during the vibration. In fact, for samples such as high density polyethylene at room temperature, measurements are not possible because of the low degree of recoverable elasticity.

A counter is set at a particular Bragg angle so as to receive diffracted intensity from a particular crystal plane. The amplified output of the counter is distributed to four counting channels (scalers) by a switching arrangement operating in synchronism with the sample vibration. (In the diagram, and photograph, this is shown as a rotating camshaft with microswitches. This has now been replaced by a more satisfactory "photoswitch" involving a rotating optical sector wheel with photocell operated gating circuits as described elsewhere¹³.) Each counting channel receives the signal during a particular interval of the strain cycle and does so repetitively during the same time interval over many cycles of sample vibration. In this respect, the apparatus acts as an "x-ray stroboscope."

By comparing the accumulated count in the different channels, it is possible to calculate (1) the amount by which the diffracted intensity changes in the course of sample vibration, ΔI , and (2) the phase angle, χ , between

intensity variation and strain. A typical result is shown in Fig. (9) for the amplitude of the change in diffracted intensity accompanying the cyclic straining of the sample for the (110) peak of medium-density polyethylene at 30°C. This is plotted as a function of the azimuthal angle of diffraction, ϕ , defined in Fig. (10). The parts of ΔI which are in phase ($\Delta I'$) and out-of-phase ($\Delta I''$) with strain are plotted.

The azimuthal angle at which a crystal diffracts depends upon its orientation. If there is random orientation of crystals, the intensity of diffraction will be independent of azimuthal angle. The degree of the dependence of intensity upon this azimuthal angle is a measure of the degree of crystal orientation.

When the strain of the sample is changed, the diffracted intensity at a particular set of angles may change for at least two reasons: (1) the amount of diffracting material may change, as might result, for example, from a change in the degree of crystallinity, or (2) the distribution of orientation of these crystals may change. These two possibilities can be distinguished by observing the dependence of the change of intensity upon azimuthal angle. If the intensity changes because of (1), the scattered intensity should either increase or decrease for all azimuthal angles; however, for an orientation change, (2), one should find the intensity increasing at some values of ϕ and decreasing at others, as in the case in Fig. (9). This represents an increase in the number of crystals oriented at some angles and a decrease at others; hence, a change in crystal orientation.

Now from the dependence of diffracted intensity upon azimuthal angle, it is possible to calculate a quantity called the orientation function designated by using procedures described elsewhere^{16,17}. An f may be associated with any crystal plane and has the following properties:

For random orientation, f is zero. If the normal to the crystal plane is parallel to a characteristic direction of a sample (the stretching direction), $f = +1$. If the normal to this plane is perpendicular to this direction, $f = -1/2$.

Similarly, it is possible to describe the change in orientation of a crystalline plane in terms of a change in the orientation function, Δf , which may be determined from the dependence of ΔI upon ϕ ^{13,18}. This is plotted as a function of temperature for the a, b, and c crystal axes in Fig. 11 obtained from the data of I. Kimura in my laboratory¹⁹. [Actually $\Delta f'$ is plotted which is the part of Δf which is in phase with strain and given by $(\Delta f) \cos \chi$]. It is seen that:

(1) Δf_c is positive while Δf_a and Δf_b are negative. This means that upon stretching, the c axis is turning toward the stretching direction while the a and b axes are turning away. This is reasonable since the c axis is the polymer chain axis which is expected to orient parallel to the stretching direction.

(2) In the lower temperature range (below 60°C), the amount of orientation change increases with increasing temperature. The increase in f_c is about equal to the decrease in f_a , with a smaller change in f_b . This would closely correspond to a rotation about the b axis, perhaps accompanied by some tilting of the c axis of the crystal within the lamellae. It is to be noted that the b axis normally lies in the radial direction of polyethylene spherulites. Consequently, it is suggested that this relaxation involves the twisting of the lamellae which lie along the radius, this occurring principally in the equatorial regions of the spherulite. Such twisting involves the sliding of lamellae over each other. This motion is expected to become easier with increasing temperature. The region between crystalline lamellae is probably occupied with irregular chain folds, tie chains and chain ends. The increasing

case of this intercrystalline motion is probably associated with the increasing mobility of these types of chains.

(3) At higher temperature (above 70°C) Δf_c decreases with increasing temperature (becomes less positive) while Δf_a becomes less negative. Δf_b is found to become more negative. It is suggested that in this region motion begins and the crystals become viscoelastic, in that the crystal lamellae no longer preserves its identity and molecules within the crystal move with respect to each other. This may occur as motion of dislocations within the crystal lattice or even by a melting and recrystallization. In fact, the increase in perpendicular b-axis orientation with stretching in this region is reminiscent of the formation of row-oriented crystals observed upon heating drawn polyethylene samples at temperatures somewhat below their melting points.

In previous studies of the dynamic birefringence, the strain-optical coefficient, K' , was observed to pass through a maximum with increasing temperature as shown in Fig. (12). The present experiments demonstrate that this maximum in K' is a consequence of a maximum in the orientability of the crystals.

Conclusions

The present experiments further demonstrate that the orientation of a crystalline polymer is at least a three-stop process involving (1) an instantaneous deformation of the superstructure and its constituent parts, (2) a slower slipping of lamellae past each other within the deformed superstructure, and (3) a still slower viscoelastic flow of molecules within the crystal. The relative contribution of these processes to the mechanical properties of the polymer depend upon the time scale of the experiment and the temperature, and are dependent upon the crystallinity and morphology.

The relaxation of polyethylene in this temperature region of 40 - 90°C has been called the α relaxation process. Some explanations of this process have been concerned with the motion of the chain folds. This, for example, has been proposed by Sinnott on the basis of his studies of this relaxation of single crystal mats of differing fold period²⁰. Other workers such as Takayanagi²¹ have postulated an intercrystalline mechanism and have pointed out that this relaxation occurs at temperatures where the rate of increase in the a-axis dimension of the unit cell is observed to become greater.

We feel that our data conclusively demonstrate that both of these mechanisms contribute to the alpha relaxation, the former at lower temperatures and the latter at high. There has been some discussion as to whether the alpha relaxation is a crystalline or an amorphous process. The present experiments show that these contributions cannot always be clearly distinguished in that the low temperature mechanism involves the onset of motion of the crystallites because of the onset of motion of the amorphous surface layers.

Future Work

The postulated origin of the alpha loss peak in terms of the two mechanisms suggested here points to several additional experiments:

(1) To what extent do the alpha loss mechanisms involve changes in the amorphous orientation? This might be studied by:

(a) Quantitative comparison of the observed strain-optical coefficient with that calculated for the crystalline contribution from the dynamic x-ray diffraction data. The difference must arise from orientational changes of amorphous regions. Preliminary experiments¹⁸ have indicated that crystalline orientational changes are the largest contributor, but more precise experiments are in progress.

(b) Direct study of the dynamic x-ray scattering from the

amorphous halo of polyethylene. The quantitative relationship between the azimuthal distribution of the intensity of amorphous scattering and the amorphous chain orientation is not clear-cut, but it is apparent that the azimuthal dependence of ΔI in this region should be related to the change in $\Delta f_{\text{amorph.}}$. Preliminary measurements¹³ indicate that $\Delta I_{\text{amorph.}}$ is small and does not differ much in phase from the strain.

(c) Direct study of crystalline and amorphous orientational changes by dynamic infrared dichroism. Earlier static measurements²² and more recent measurements by B. Read in this laboratory²³ have demonstrated the potential of the infrared dichroism technique for resolving crystalline and amorphous orientation. More recently time dependence studies^{24,25,26} have shown that at longer times, there is not much change observed in crystal orientation. We are presently instrumenting the high-speed elongation apparatus for obtaining dynamic infrared (and ultraviolet) dichroism measurements in short times.

(d) Direct study of the orientation of crystalline lamellae has been made, for example, by Hay and Keller²⁷ by low-angle x-ray scattering. The extension of this approach to time-dependence studies is desirable. The study in correlation of orientation of lamellae over distances in the thousand Angstrom range by wide angle light scattering has received preliminary attention^{6,28-30} and is currently under study in this laboratory.

(e) The extension of the rheo-optical methods to lower temperatures is desirable where molecular processes associated with the beta and gamma processes might be examined.

ACKNOWLEDGMENT

The work reported here was partly supported by a contract with the Office of Naval Research and by grants from the Army Research Office (Durham), the National Science Foundation and the Petroleum Research Fund of the American Chemical Society. The contributions of Dr. Peter F. Erhardt in the high-speed elongation light scattering studies, and those of Dr. T. Kawaguchi and Mr. I. Kimura in the dynamic x-ray diffraction work and the valuable assistance of Mr. Daniel Keedy in the difficult instrumentation problems in this work is gratefully acknowledged.

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FIGURES

1. A photograph of the high-speed stretching apparatus with laser and high-speed motion picture camera in place for recording low-angle light scattering patterns.
2. A schematic diagram of the instrumentation for simultaneously recording stress, strain, birefringence and light scattering for a sample subjected to rapid deformation; CYL is hydraulic cylinder, LC is load cell, FC are Fastex high-speed motion picture cameras, TD is a time delay circuit, L is a He-Ne gas laser, F. is a filter, A and E are diaphragms, B is a partially reflecting glass plate, P is a photomultiplier, T is a microswitch trigger, SL is a strobe light, BA is an amplifier, and CRO is a cathode ray storage oscilloscope.
3. A series of enlarged frames from the high-speed motion picture of the I_+ scattering pattern obtained during the rapid stretching of a Monsanto medium-density polyethylene film.
4. The angle B used as an index of the spherulite deformation.
5. The variation of the angle, $1/2 B$, the stress, σ , the elongation ratio, α_x , and the birefringence, Δ , during the rapid elongation of a medium-density polyethylene film.
6. The variation of the spherulite elongation ratio, α_s , calculated from light scattering with the measured sample elongation ratio during the rapid elongation of a medium-density polyethylene film.
7. A diagrammatic sketch of the dynamic diffractometer.
8. A photograph of the dynamic diffractometer.
9. The variation in ΔI , the amplitude of the cyclic change in diffracted intensity of the $\{110\}$ peak of medium-density polyethylene upon cyclically straining at various frequencies at 30°C plotted as a function of the azimuthal angle of diffraction.

FIGURES-2

10. The Bragg and azimuthal diffraction angles, θ and ϕ .
11. The variation of $\Delta f'$ for the a, b, and c crystal axes of medium-density polyethylene as a function of temperature for measurements at 1 c.p.s.
12. The variation of the dynamic strain-optical coefficient, K' , at 1 c.p.s. with temperature for medium-density polyethylene.

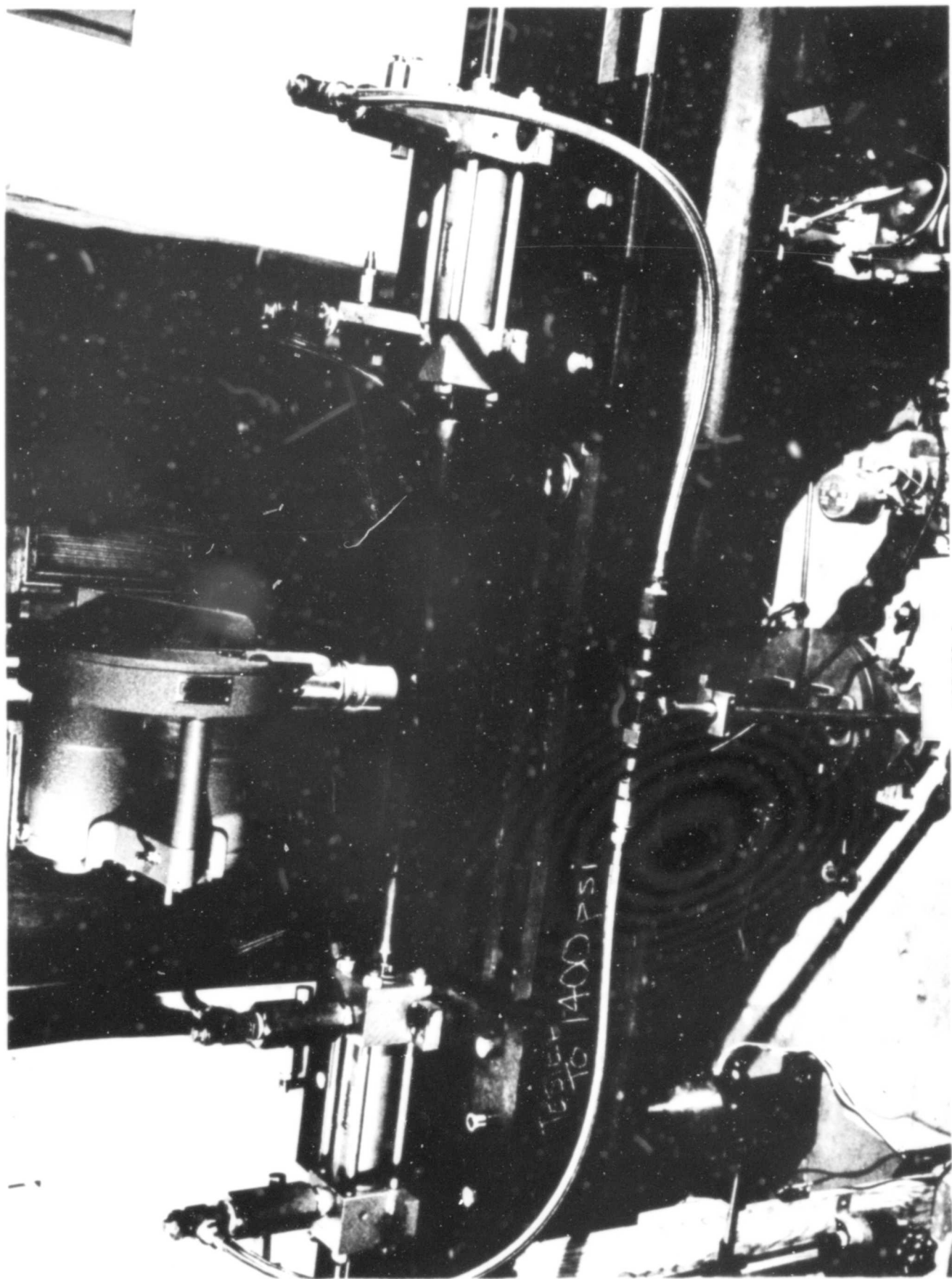


FIGURE 1

TEST 1400 PSI

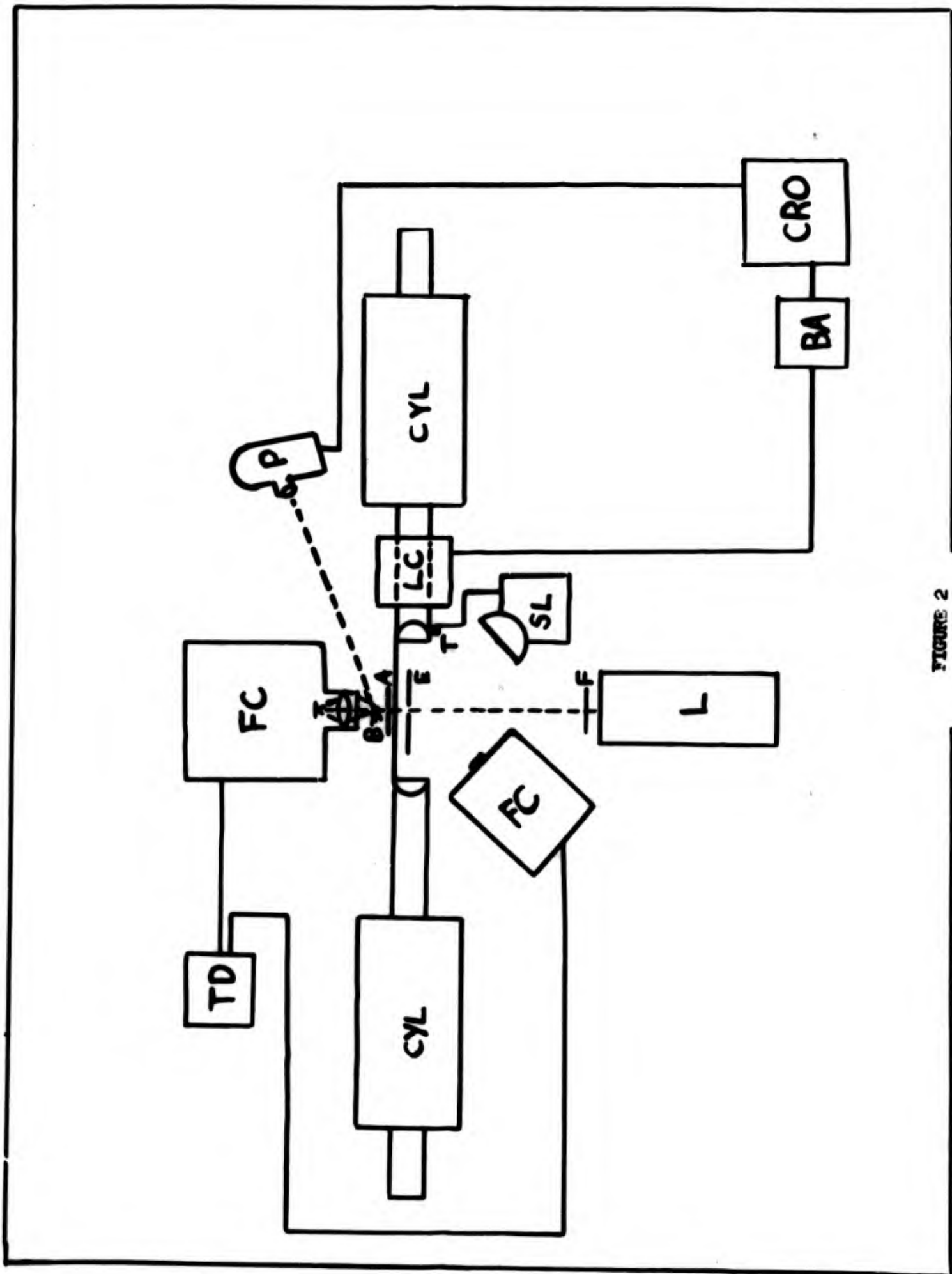


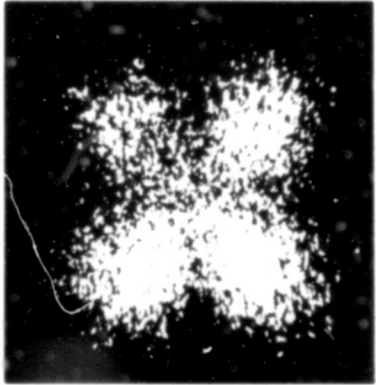
FIGURE 2



$\alpha_x = 1.00; t = 0$



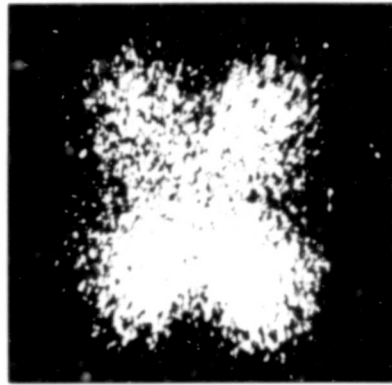
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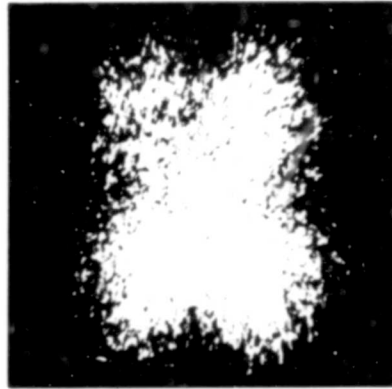
$\alpha_x = 1.19; t = 10.3 \text{ msec}$



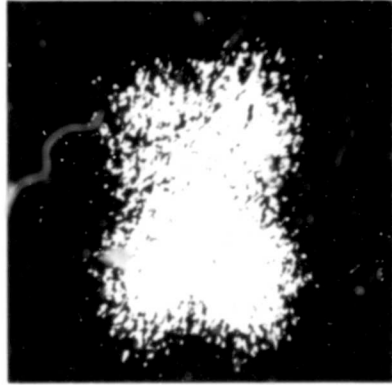
$\alpha_x = 1.30; t = 15.9 \text{ msec}$



$\alpha_x = 1.35; t = 20.2 \text{ msec}$



$\alpha_x = 1.44; t = 27.0 \text{ msec}$



$\alpha_x = 1.49; t = 31.7 \text{ msec}$



$\alpha_x = 1.50; t = 38.0 \text{ msec}$

FIGURE 3

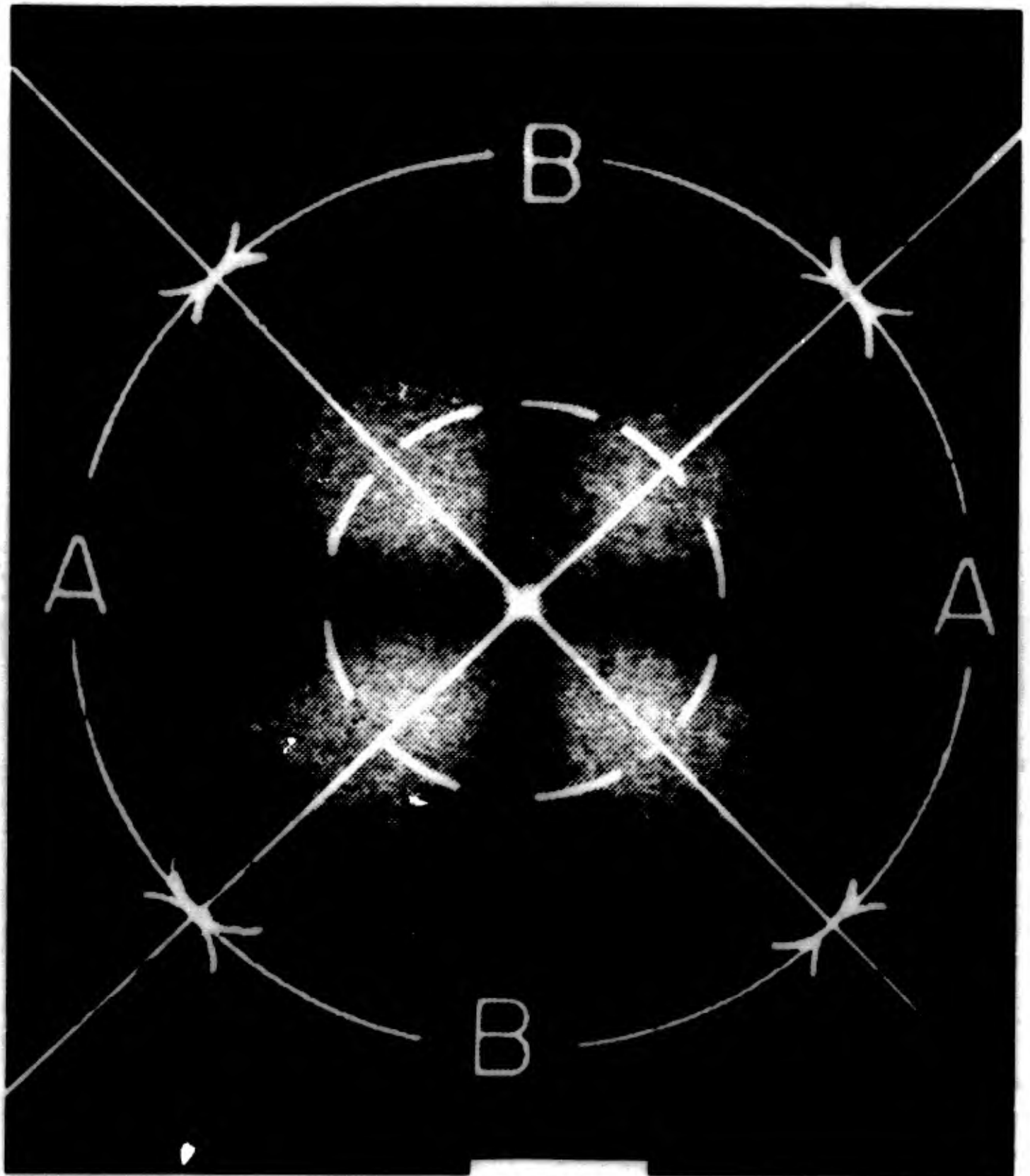


FIGURE 4

Polyethylene

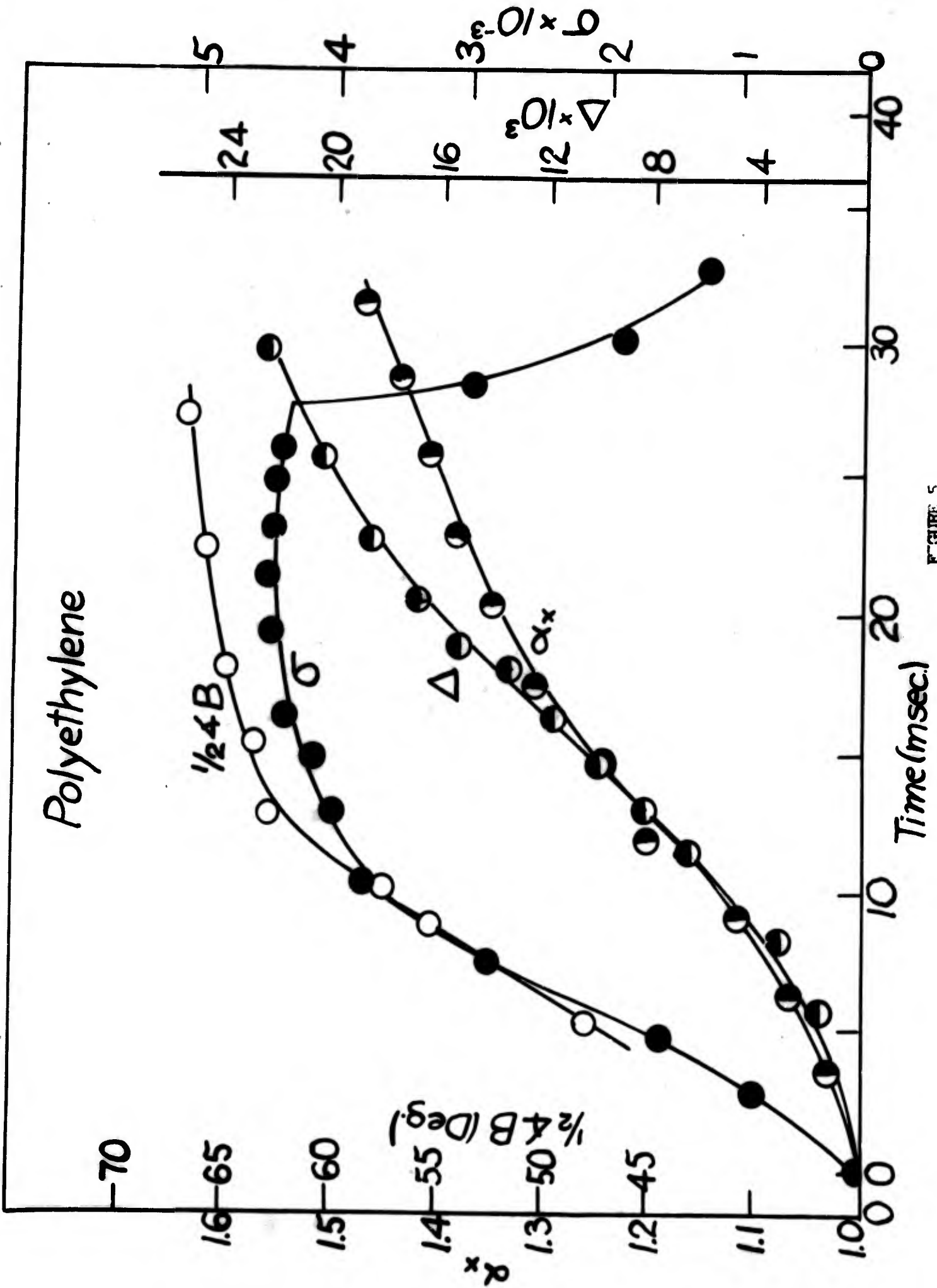


FIGURE 5

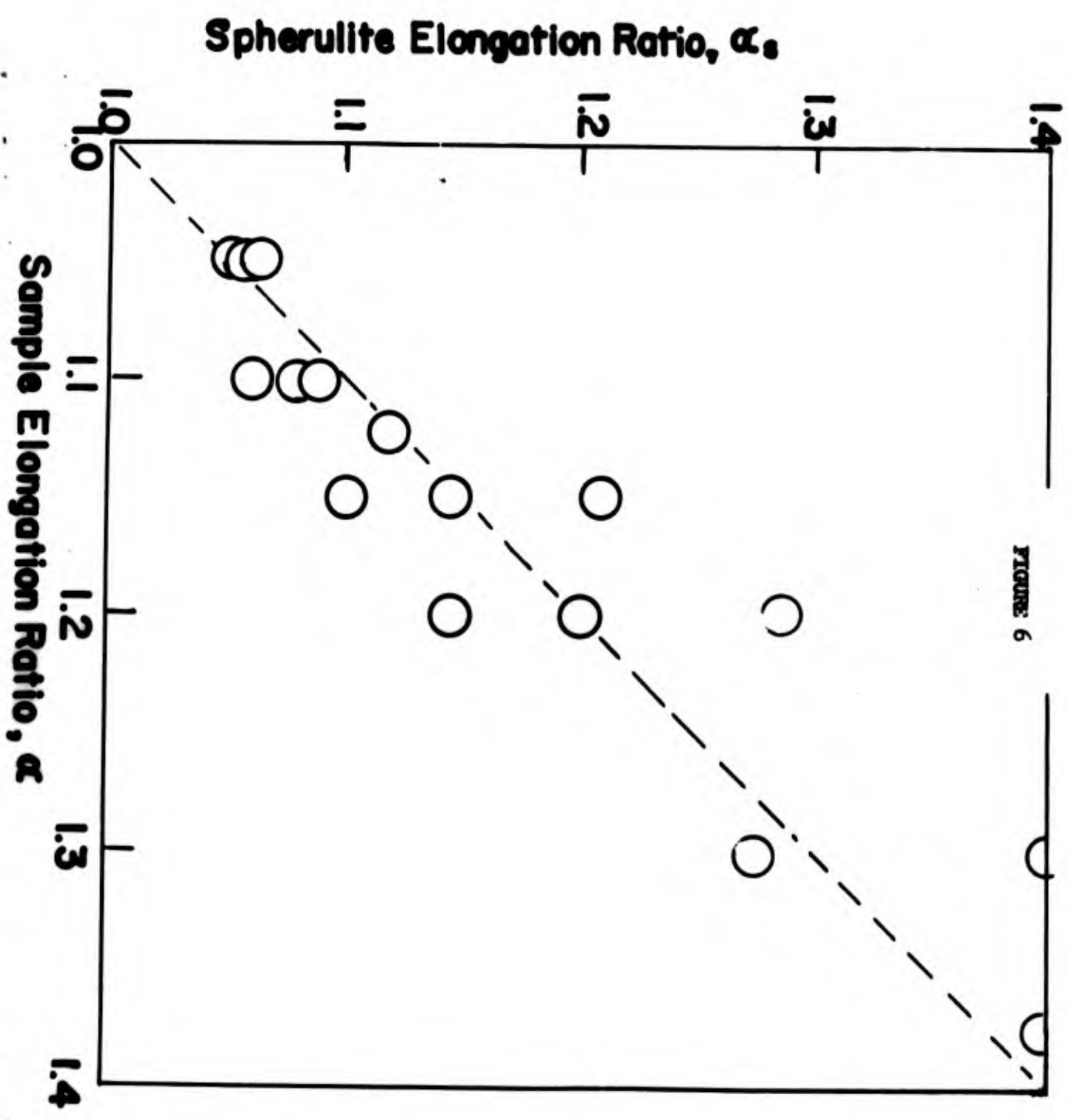


FIGURE 6

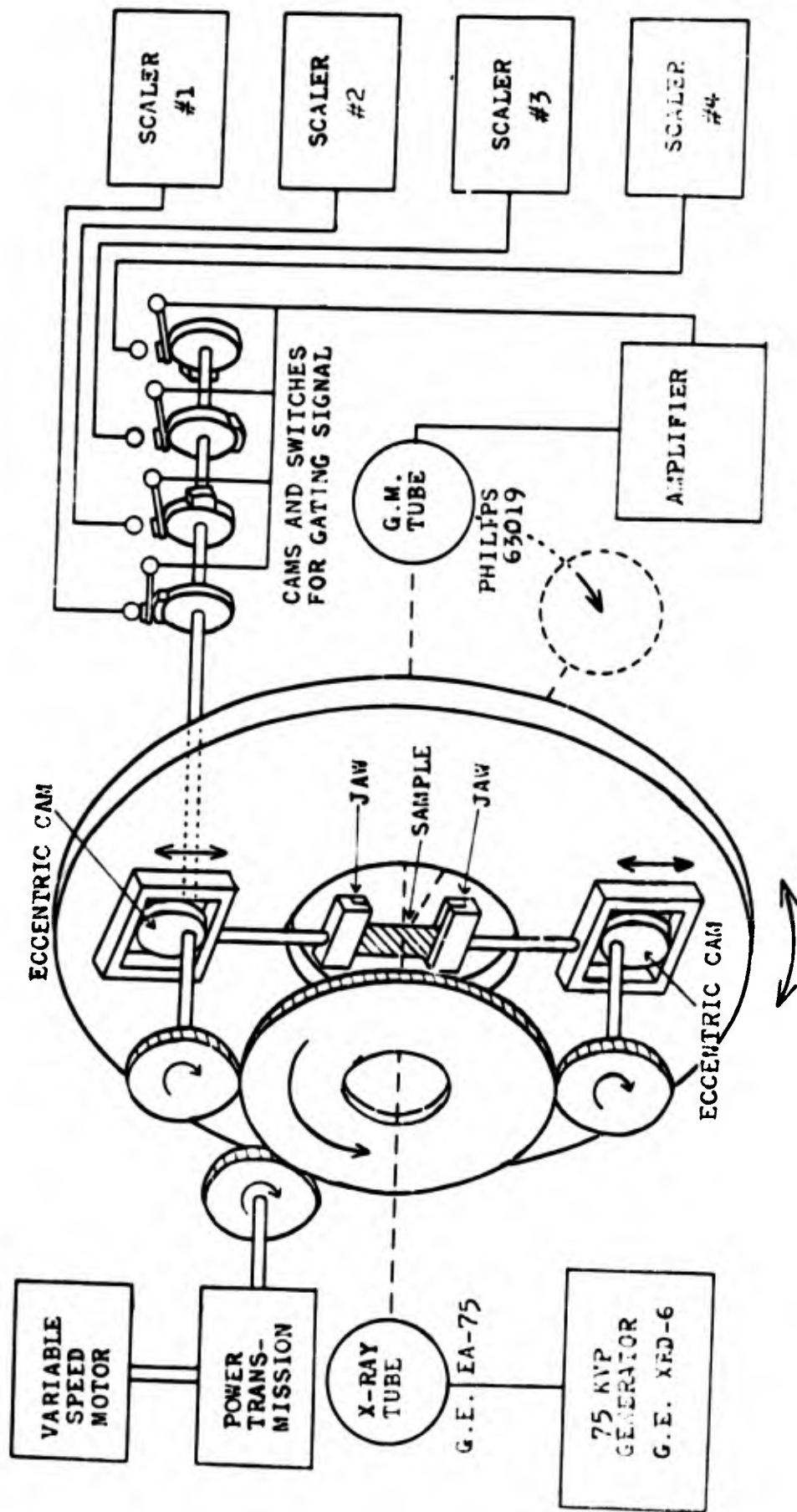


FIGURE 7

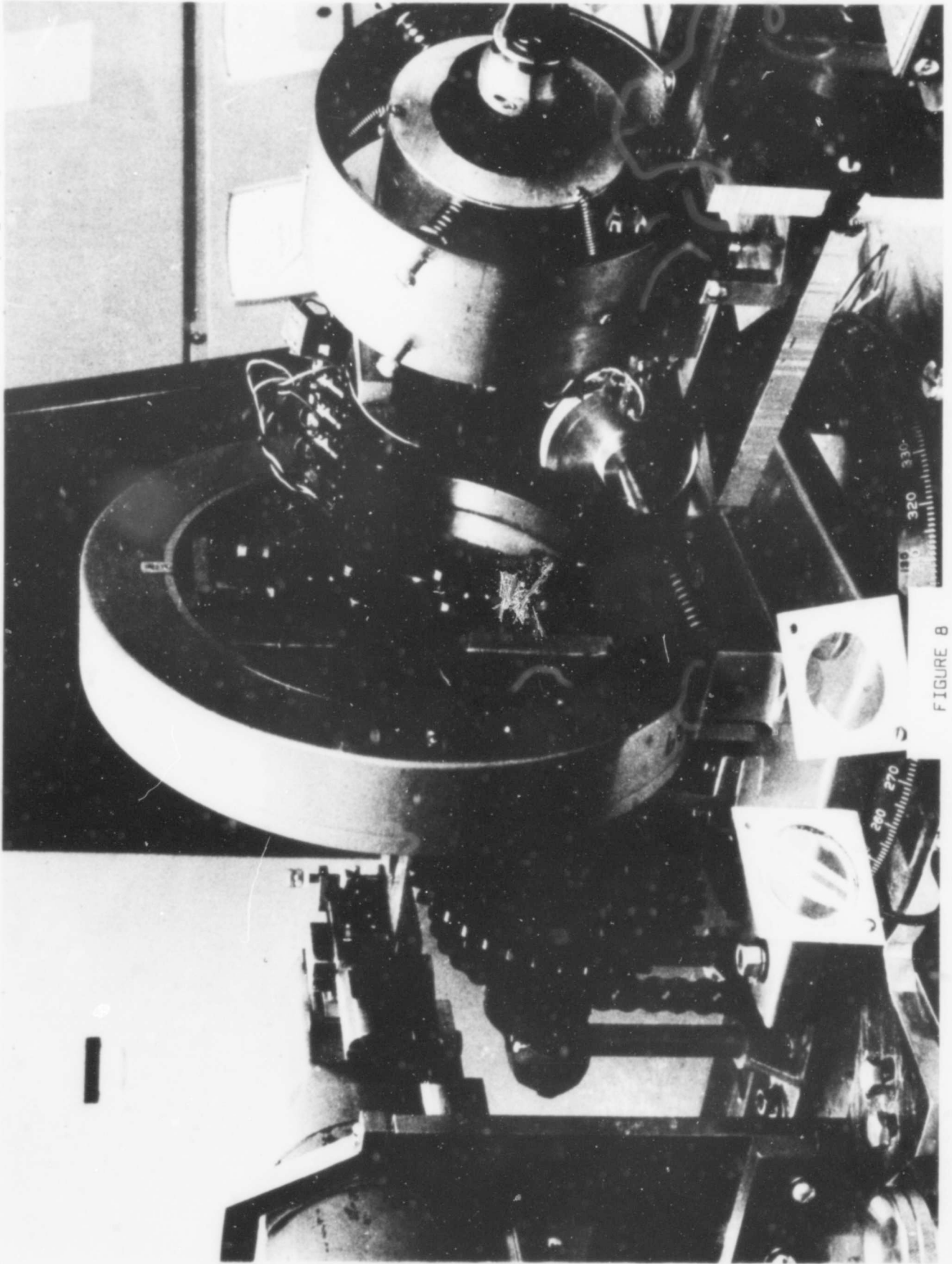


FIGURE 8

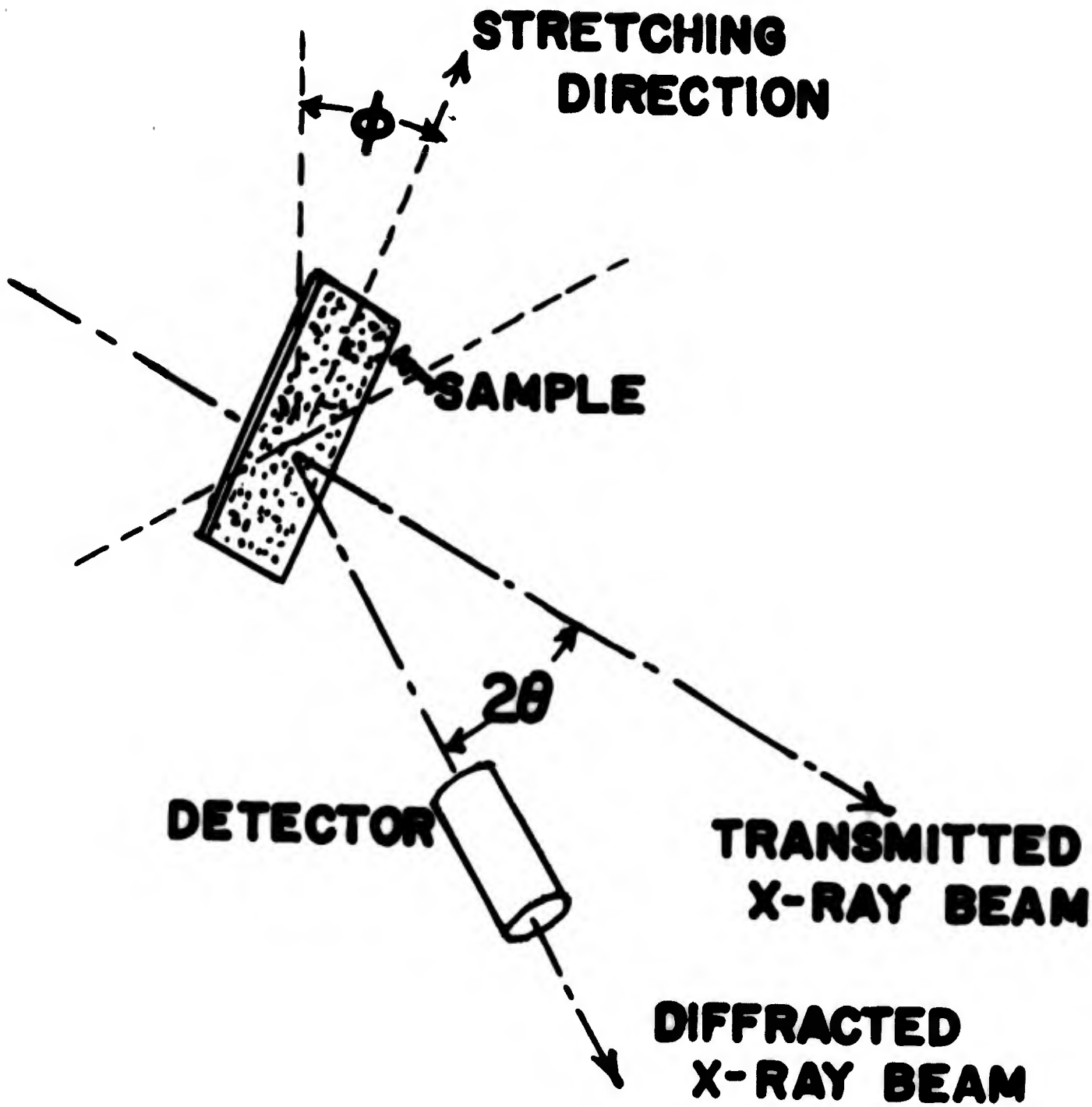


FIGURE 10

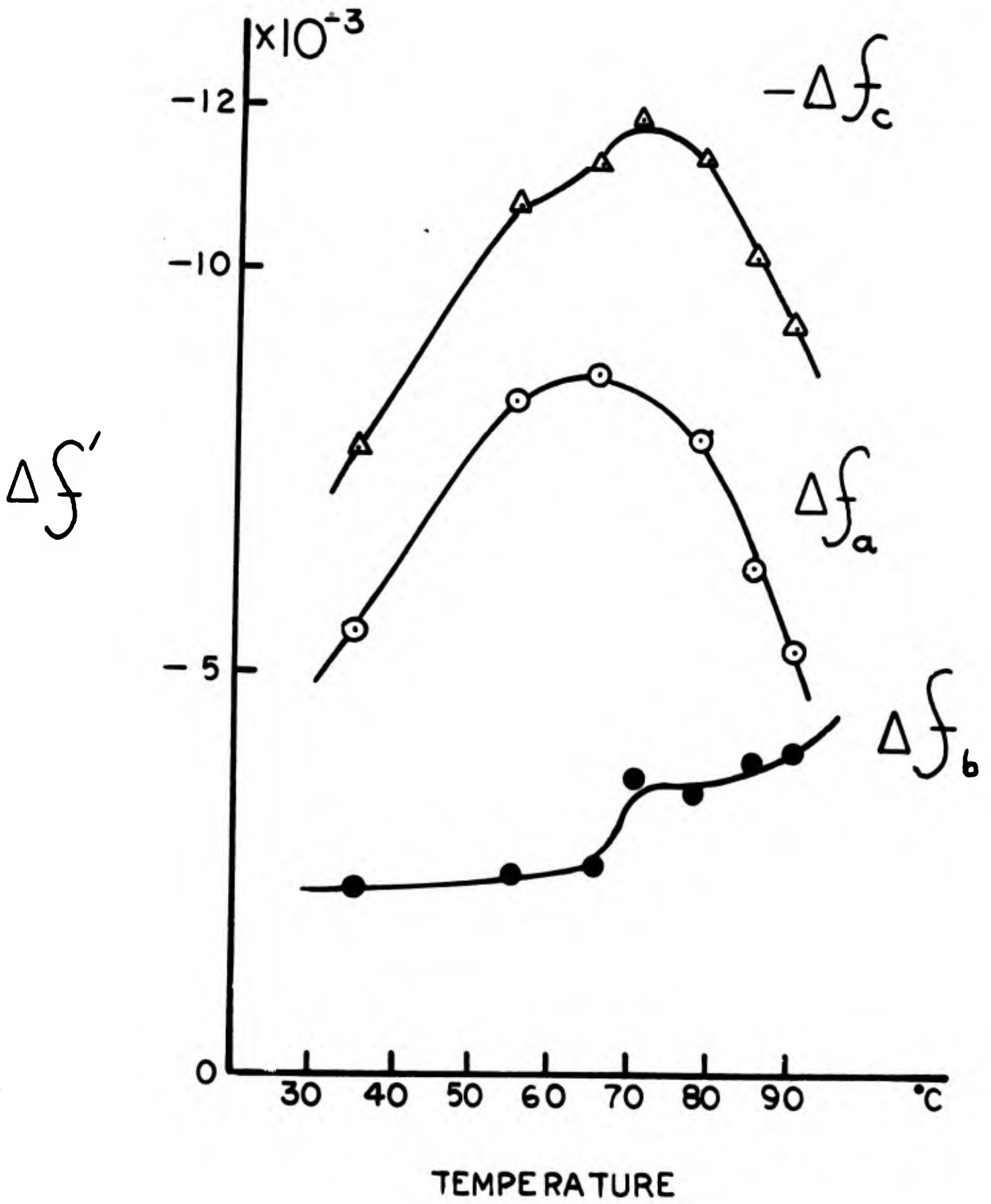
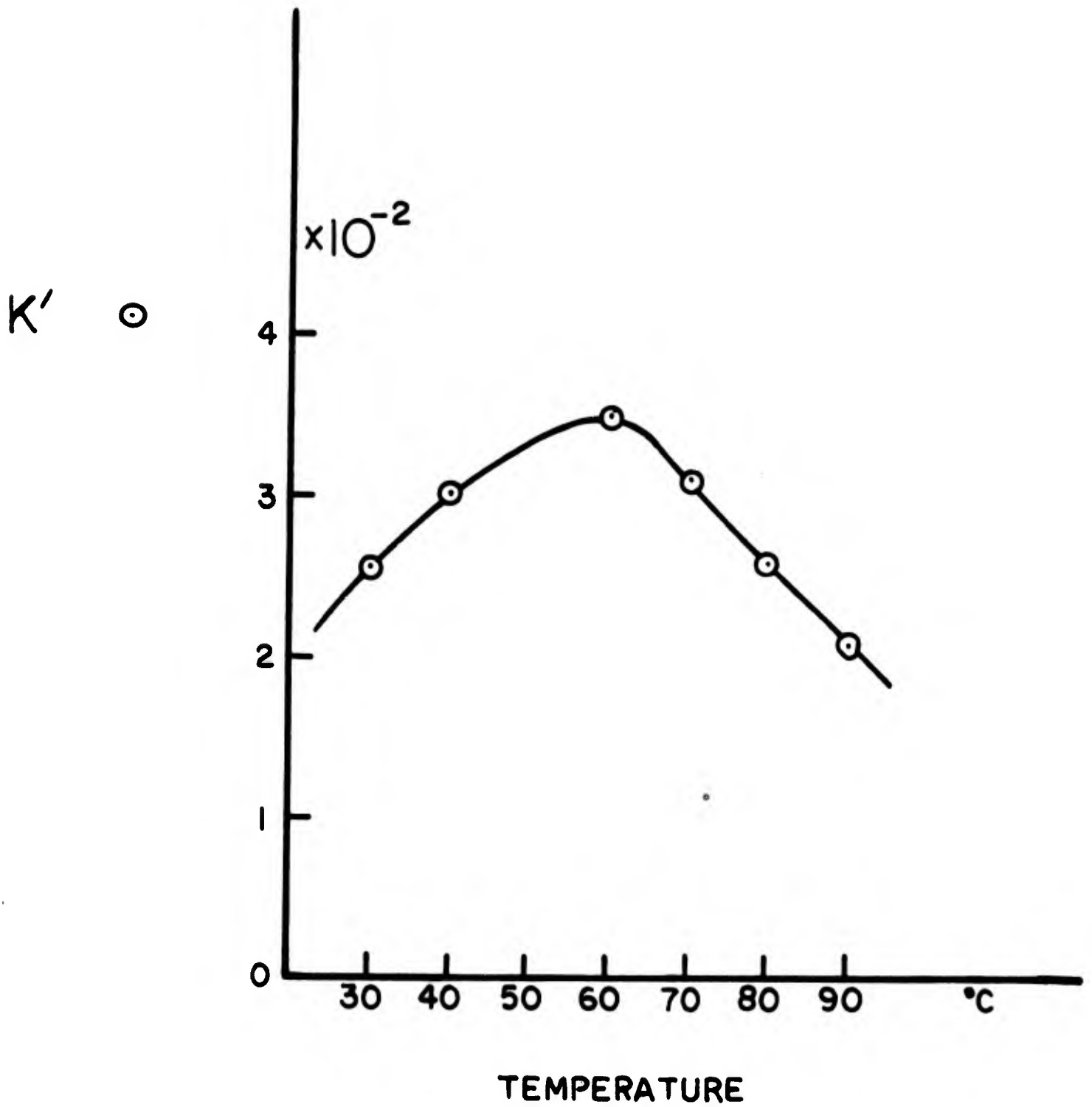


FIGURE 11

FIGURE 12



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	2b. GROUP

3. REPORT TITLE
Time-Dependence of Crystal Orientation in Crystalline Polymers

4. DESCRIPTIVE NOTES (Type of report and, inclusive dates)
Technical Report

5. AUTHOR(S) (First name, middle initial, last name)
Stein, R. S.

6. REPORT DATE November 1967	7a. TOTAL NO. OF PAGES 29	7b. NO. OF REFS 30
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8a. CONTRACT OR GRANT NO. NONR 3357 (01) b. PROJECT NO NR 056-378 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) 96
	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

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13. ABSTRACT

The results of two methods for studying molecular processes accompanying the deformation of polyethylene are described. The examination of spherulite deformation by observing light scattering patterns along with measurement of the birefringence, stress and strain during the rapid extension of polyethylene shows that this initial structural deformation is essentially instantaneous. Dynamic x-ray diffraction shows that this is followed by a slower relaxation involving change in the orientation of the crystals by two processes, the lower temperature one involving slipping of lamellae past each other and the higher temperature one involving viscoelastic flow of the crystals.