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TENSILE MODULUS BY X-RAY DIFFRACTION; INSTRUMENT AND METHOD

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The design and use of an automated device to measure the axial tensile modulus of high modulus fibers by following the change in the meridional X-ray spacings as a function of applied tension is reported. The device, which mounts on a Picker 4-circle automated diffractometer, applies tension to the fiber sample by a cantilever arrangement. Tension, which is measured by a strain gauge bridge on the cantilever arm, is adjusted and read by the control computer, a VAX 11/730. The device can also be used to study sample orientation as a function of tension.

Techniques applicable to modulus measurements on a variety of man-made and natural fibers are discussed. The examples include rigid-rod polymer materials, poly(paraphenylene benzobisthiazole) (PBZT), and poly(paraphenylene benzobisoxazole) (PBO), carbon fibers with various degrees of order, KEVLAR™ 149, and degummed silk. These examples illustrate the range of techniques required to measure the X-ray tensile modulus on materials with modulus values from 20 GPa to 800 GPa, from highly ordered samples to materials with much less order, using reflections with spacings from 1.0 to 3.5Å (approximate 2θ of 25° to 95°).

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1. INTRODUCTION TO THE METHOD AND THE DEVICE

The Method

The axial tensile modulus measures the stiffness of a material. It is determined by taking the ratio of the applied stress, σ, to the measured strain, ϵ, thus, $Y_t = \sigma/\epsilon$, where σ is the ratio of the applied force (tension) to the cross sectional area of the sample and ϵ is the resulting extension of the sample divided by its original length. The full relation is,

$$Y_t = \frac{F/A}{\Delta l / l}$$

where Δl is the change in length of an object with a uniform cross section, A, when a tension, F, is applied. High performance polymer fibers owe their large tensile strength and high tensile modulus to a highly ordered molecular structure where fiber extension involves mostly covalent bond strain. The effect of tension applied to such a fiber can be observed in the diffraction pattern of the stressed fiber.

The mer repeat distance d is related by Bragg's law to the X-ray scattering direction which gives constructive interference,

$$n\lambda = 2\, d \sin\theta$$

where θ is half the X-ray scattering angle, λ is the wavelength of the X-rays and n is the order of the scattering maximum or reflection. Applied tension increases the mer repeat distance so that the diffraction angle for each reflection is reduced slightly. The X-ray tensile modulus, Y_x is thus given by

$$Y_x = \frac{F/A}{\Delta d / d}$$

where Δd is the change in d which results from applying a tension F to the fiber. The X-ray tensile modulus of the fiber is calculated from the change in d spacing observed with a moderate to high angle meridional reflection.

The change in d with tension was first observed and reported by Baker and Fuller (1943) who recorded the diffraction patterns of the stressed materials on film but did not calculate the tensile modulus from the diffraction data. Dulmage and Contois (1958) were the first workers to report a tensile modulus calculated from the 2θ values of meridional reflections. Their method involved a stretching device which allowed the strain of the sample to be measured at the same time the d spacing was measured. The X-ray tensile modulus was then calculated by multiplying the ratio of sample strain to lattice strain times the tensile modulus, to give the X-ray modulus. Tension was not explicitly measured; in effect, the tensile modulus and the strain of the sample were used to find the stress.

Several years later, additional measurements of the X-ray tensile modulus were reported by Sakurada, Nukushina and Ito (1962). Their apparatus consisted of a stretching clamp which held the sample and allowed the measurement of strain with the sample mounted on the diffractometer. Tension was supplied by weights suspended from a pulley arrangement. Values for 2θ were determined by scanning slowly through a reflection as the peak profile was recorded on a chart. Errors in determining d for typical materials were claimed to be 0.02%; for strains of 1% this gives a measurement error of 2% in the lattice strain.

In order to calculate the X-ray tensile modulus one must know the stress on the crystallite planes, not the stress on the sample as a whole. The usual assumption is that the stress is homogeneous and therefore the microscopic stress is equal to the macroscopic stress. This assumption has been examined by Sakurada, Ito and Nakamae (1964 & 1966) who studied the X-ray tensile modulus of polymer materials which have similar crystallite structure but different tensile moduli. Their results show similar X-ray tensile moduli for these samples, thus supporting the homogeneous stress assumption. In a second series of experiments, they found similar X-ray moduli for samples which had different degrees of hydration.

Measurement of the axial tensile modulus by X-ray diffraction requires an accurate measure of the mer repeat distance in the crystalline regions of the sample as a function of applied tension. For high modulus fibers the experimental problems are challenging. The relatively weak meridional scattering from many polymer fibers (see Fig. 2 to 6), coupled with the very small changes in the scattering angles, even at large tensions, requires long counting times and a very stable means of applying and measuring relatively large tensions. The apparatus and the experiment must be designed to optimize the modulus measurement within these limits. In the experiment, tension is applied to the fibers and the 2θ shift in one or more of the meridional reflections is observed.

The ratio of $\Delta\theta$ to the fractional change in d is proportional to $\tan\theta$ so it is clear that high angle reflections will give the best measure of $\Delta d/d$. However, a weak reflection, *i.e.,* one with a small count rate, will not allow 2θ to be determined to high precision so one must balance the need for a large $\Delta 2\theta/(\Delta d/d)$ with the count rate available. Accurate values of 2θ can be obtained by fitting the 2θ scans with a Gaussian function by least-squares to find the center point of every reflection scan. A series of 2θ scans made over a range of tensions provides $\Delta d/d$ as a function of tension, F, which allows Y_x to be calculated from a linear least-squares fit.

In order to measure the X-ray modulus of rigid rod polymers a device has been designed and constructed which mounts on the X-ray diffractometer so that tension can be applied to a fiber sample while it is held in the diffracting position. Such a device must be able to apply and maintain a tension of 0 to 200 N for several hours, measure the applied tension to better than 1% and allow adjustment of the tension easily with no motion of the fiber sample. Adjustments for centering the sample in the X-ray beam when it is initially mounted must also be provided. A preliminary report on the features and use of this device has been published (Lenhert and Adams, 1989).

The Fiber Deformation Device

The fiber deformation device (FDD) is based on a cantilever design shown in Fig. 1. It attaches to the rigid χ circle of the Picker diffractometer by the mounting pin, **a**, which is fixed and the base mount, **q**, which can be rotated. The bearing between the fixed mounting pin, **a**, and the suspension, **b**, allows the FDD to be manually rotated. Tension is applied by the cantilever mount, **f**, which holds the tension arm, **h**, and is activated by the tension screw, **d**, (a motor-driven screw activated by computer control). Adjustment of the tension screw rotates the cantilever mount (to which the tension arm is attached) about the pivot, **g**. Tension is applied to the sample when the upper sample mount holder, **j**, is raised by the tension arm and the resistance of the sample causes the arm to bend. The bending of the tension arm is proportional to the tension applied to the sample and is regis-

tered by the electrical output of the strain gauge bridge. The lower end of the sample is held fixed by the lower sample mount holder, **n**. Variations in the initial length of samples can be compensated by the length adjustment screws, **m**, and the lower part of the sample can be centered in the X-ray beam by the translation screws, **o**.

a Mounting pin, attaches to goniometer circle

b Rotatable suspension. The bearing is shown as ▨

c Nylon lock screws

d Tension screw (motor driven)

e Newport 860 series motorizer

f Cantilever mount, moved by tension screw

g Cantilever pivot

h Titanium tension arm (strain gauges on upper and lower surfaces)

i Sample mount hinge (groove and knife edge pivot)

j Upper sample mount holder

k Sample mount end pieces

l Fiber sample

m Sample length adjustment screws

n Lower sample mount holder

o Adjustment screws to center sample in the X-ray beam

p Goniometer head base

q Goniometer head base mount

r Strain gauge bridge leads

s Gap for spacing shims

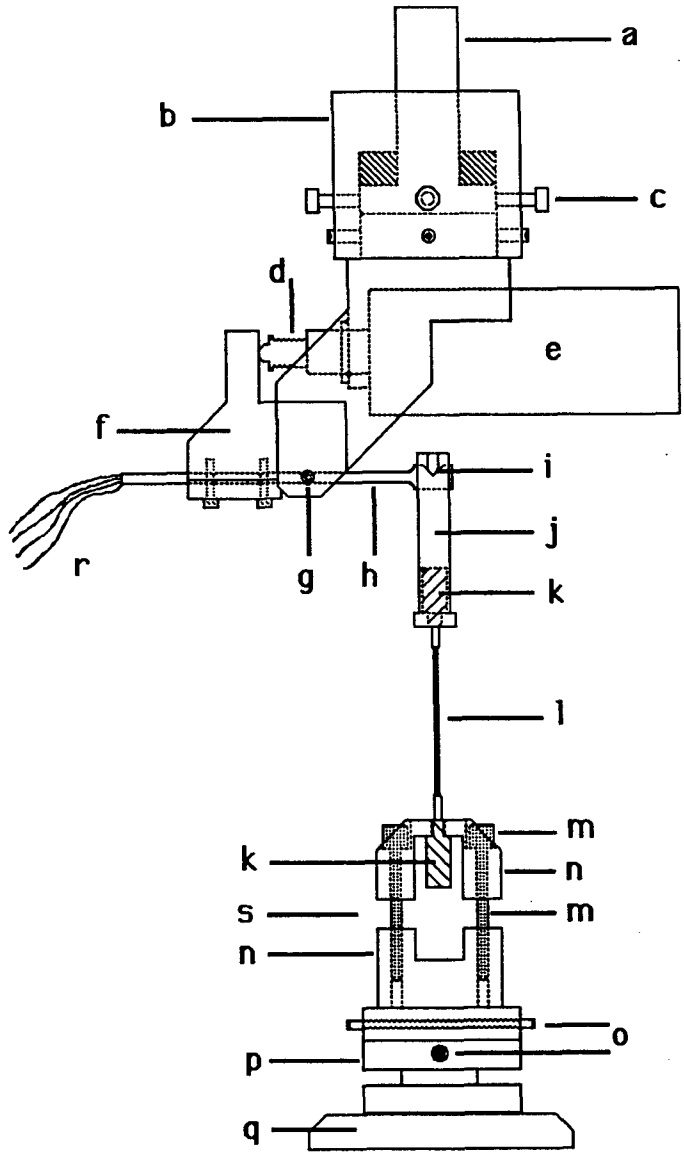

Figure 1. Fiber deformation device (FDD)

The upper part of the FDD is mounted on the Picker goniostat by attaching the pin, **a**, to the χ circle. Alignment is carried out with the aid of a brass weight suspended on a thin gauge rod centered in a sample mount end piece, **k**, which is placed in the upper sample mount holder, **j**. Adjustments made with the aid of the alignment telescope mounted on the goniostat allow the FDD to be centered on the ϕ axis of the diffractometer.

The relationship between the force applied to the tension arm, **h**, and the electrical output of the strain gauge bridge is determined by a simple calibration procedure. Lead weights are attached to the upper sample mount holder, **j**, to supply a known force which verifies the linear response of the strain gauge bridge and determines the force/voltage ratio.

The sample material for which the X-ray tensile modulus is to be measured must be mounted between two brass sample mount end pieces, **k**, and attached to them with a suitable adhesive, usually epoxy. Attention should be given to the tensile strength and X-ray scattering ability of the sample material in order to have sufficient X-ray intensity *and* a suitable tension range.

The fiber sample after attachment to the brass mounts, is placed on the FDD between the upper and lower sample mount holders. The tension arm, **h**, is placed in the measurement position (horizontal) by adjusting the motor drive tension screw, **d**, and the slack in the sample is taken up by adjusting the sample length adjustment screws in the lower sample holder, **n**. Metal shims are placed in the gap, **s**, between the upper and lower parts of the sample mount holder and the screws tightened to make the holder rigid. The sample is then centered by adjusting the screws, **o**, in the goniometer head base, and finally, the nylon lock screws, **c**, are tightened to prevent rotation of the FDD during measurement.

Tension values and scan parameters are selected and entered into the computer program which then carries out the requested scans at each tension, fits them to determine 2θ, calculates the corresponding value of d, and prepares a plot of the d *vs* tension values. The X-ray tensile modulus is calculated from the slope of the line.

The Diffractometer and X-ray Source

An early model of the FDD was used on the Picker FACS-I diffractometer system (Lenhert and Adams, 1985). The Picker FACS-I was automated with a PDP-8/I computer and had a conventional sealed X-ray tube. Early measurements (some of which are reported here) were made with this system.

The present diffractometer-FDD system uses the Picker diffractometer and is interfaced to a VAX 11/730 computer through an interface supplied by *Crystal Logic, Inc.** The diffractometer programs are described elsewhere (Lenhert, 1990).

The present X-ray source is a Rigaku Rotaflex RU-200 rotating anode unit which is normally run at 45 Kv, 70 ma constant potential. The Cu anode has a 0.3x3 mm focal spot. The Picker diffractometer is normally used with a 1.0 mm incident beam collimator and a 1.5 mm diffracted beam collimator. The collimation of the incident X-ray beam is determined by the projected focal spot size (0.3x0.3 mm) and the irradiated sample dimensions. The diffracted beam collimator serves only to reduce air scatter. The effective diffracted beam aperture is set separately by a slit system which closes symmetrically in both vertical and horizontal directions (the SVA). The focal spot to sample distance is 30 cm, the sample to SVA distance is 23 cm. The system does not have a monochromator but an incident beam Ni filter (normally 0.001 in) can be used. The X-ray detector system consists of a NaI crystal, preamplifier, pulse height analyzer and scalar.

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* Crystal Logic Inc., 10573 West Pico Blvd., Suite 106, Los Angeles, CA 90064.

Example Materials

Five examples have been selected from the materials measured which illustrate the problems encountered in X-ray tensile modulus measurements. These problems, and their solutions will be discussed in detail later in this report. These materials also illustrate the range of tensile modulus that the method and equipment will accommodate. Meridional 2θ scans of the example materials; PBZT, Kevlar 149, G30 carbon, T50 carbon and silk are shown in Figs. 2 - 6. Data on the samples used for these scans are given in Table 1. All scans were made with Cu Kα radiation using a 0.001 in Ni filter, a 1.0 mm incident beam

Table 1. *Experimental conditions and physical data for samples shown in Figs. 2 - 6. Fiber diameter is in microns, sample area is in m^2 times 10^8, diffracted beam aperture (SVA) gives width x height.*

Material	Source	density gm/cm^3	denier/ fiber	fiber diam.	numb. fibers	sample area	SVA mm	Kv	ma	time (s) /step
PBZT	Celanese	1.57	1.896	13.1	715	9.54	3x6	40	80	100
Kevlar 149	Dupont	1.47	1.44	11.8	233	2.54	2x6	45	70	100
G30 carbon	Celion	1.78	0.603	6.9	3000	11.3	3x6	45	70	300
T50 carbon	Amoco	1.81	0.547	6.5	3000	10.1	3x6	45	70	100
Degum Silk	*Bombyx mori*	1.353	1.356	11.9	880	9.79	3x6	45	70	200

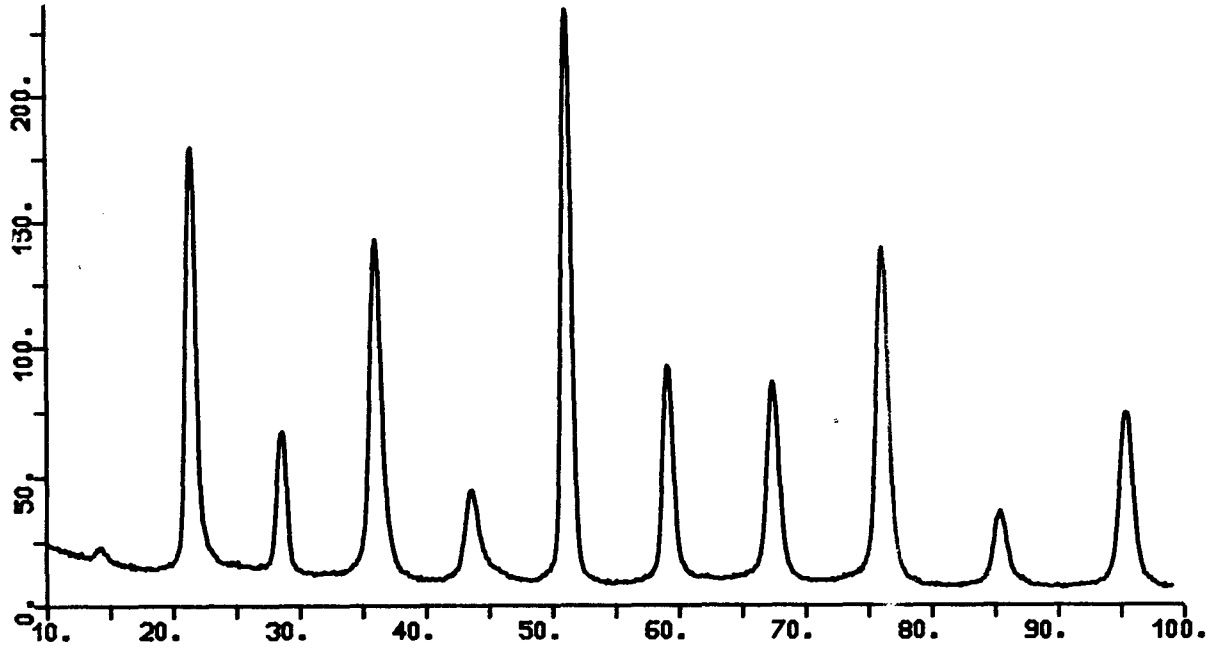

Figure 2. Meridional scan of heat treated (650° C) PBZT; x-axis, 2θ in degrees; y-axis, intensity in counts per second. Experimental and sample parameters are given in Table 1.

collimator and a 1.5 mm diffracted beam collimator. Step size for the 2θ step scans is usually 0.1° at the peak positions with each step counted for the time shown in Table 1.

The high modulus materials, T50 carbon and PBZT have reflections which are well suited for X-ray tensile modulus measurements. They have relatively strong, fairly sharp reflections at 2θ of 75° or greater. Their high modulus, however, means that 2θ changes are small, even for fairly high tensions. Kevlar 149 has strong, sharp reflections, but they

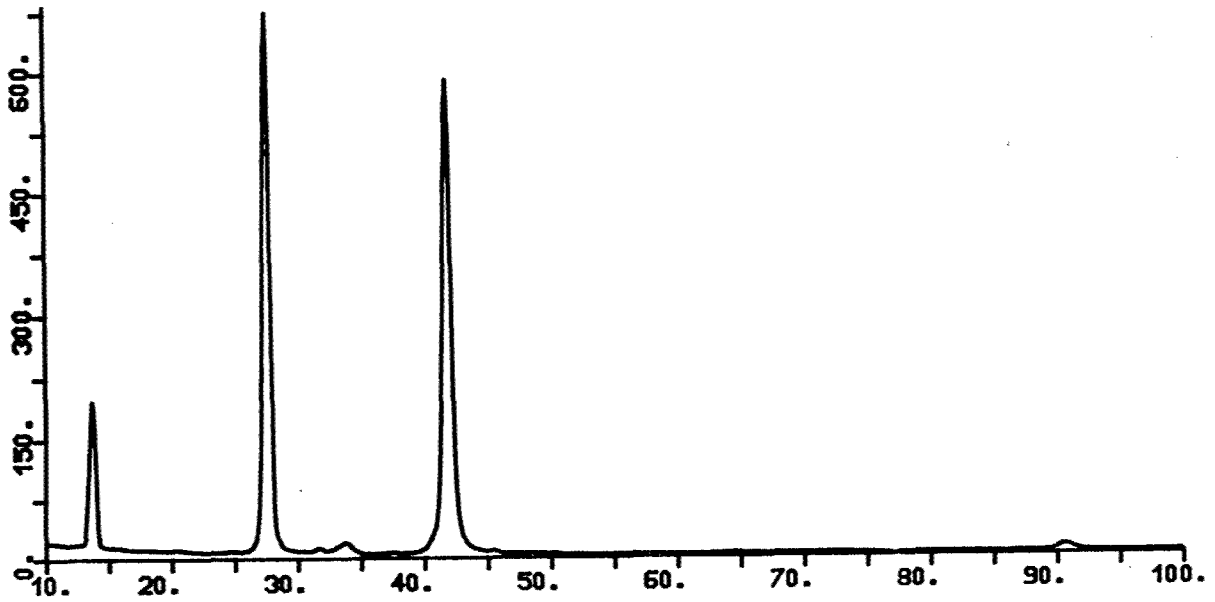

Figure 3. Meridional scan of Kevlar 149; x-axis, 2θ in degrees; y-axis, intensity in counts per second. Experimental and sample parameters are given in Table 1.

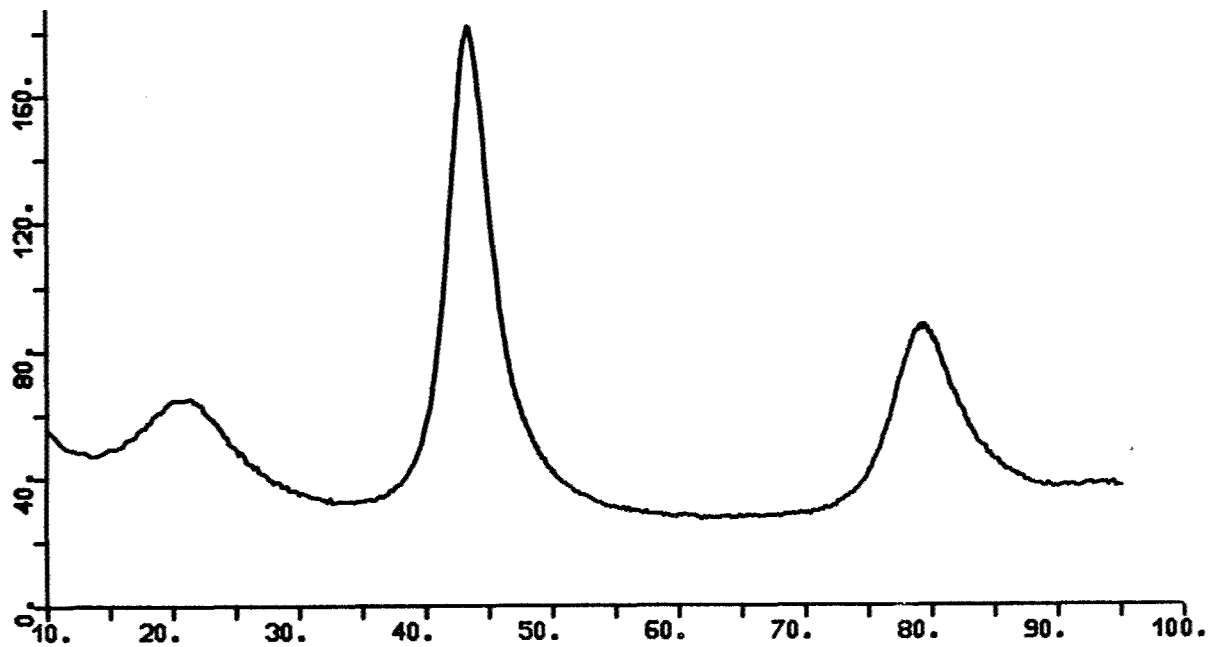

Figure 4. Meridional scan of G30 carbon; x-axis, 2θ in degrees; y-axis, intensity in counts per second. Experimental and sample parameters are given in Table 1.

occur at much lower 2θ values. The lower X-ray tensile modulus of Kevlar 149, however, makes accurate modulus measurements possible. Degummed silk from *Bombyx mori* has one moderately strong, moderately sharp reflection at low 2θ and a much broader, weaker reflection at high 2θ. The changes in 2θ with tension are, however, easily measured since silk has a fairly low X-ray tensile modulus, but being a weak material, compared to PBZT, carbon and Kevlar, measurements must be made at relatively low tension. Silk has an ad-

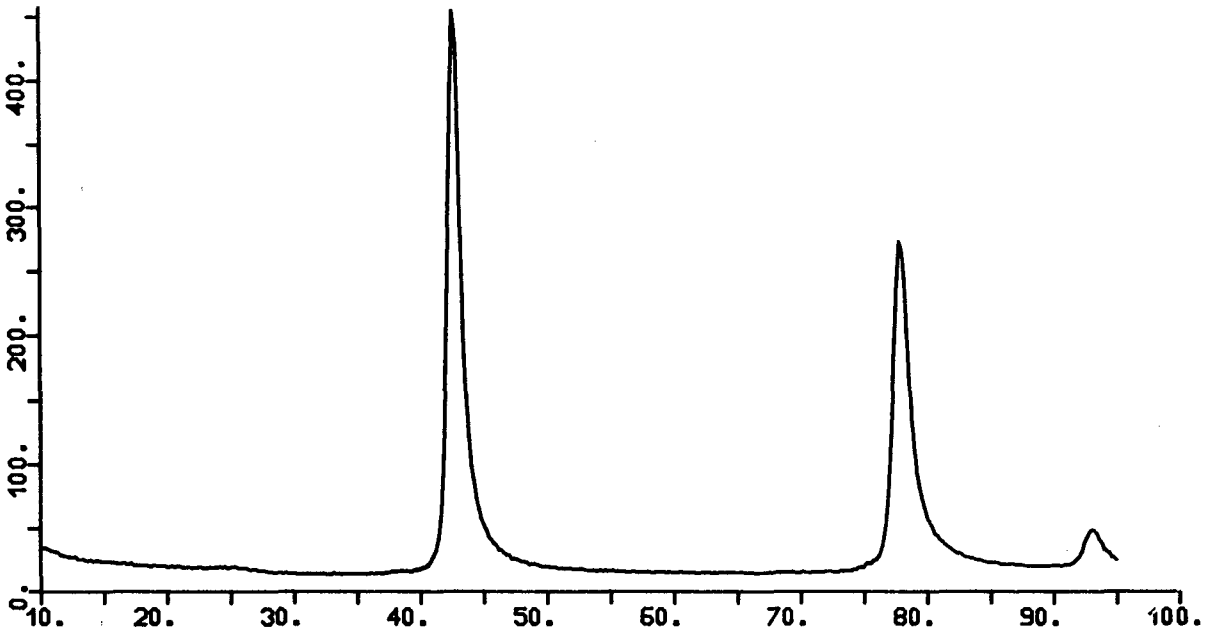

Figure 5. Meridional scan of T50 carbon; x-axis, 2θ in degrees; y-axis, intensity in counts per second. Experimental and sample parameters are given in Table 1.

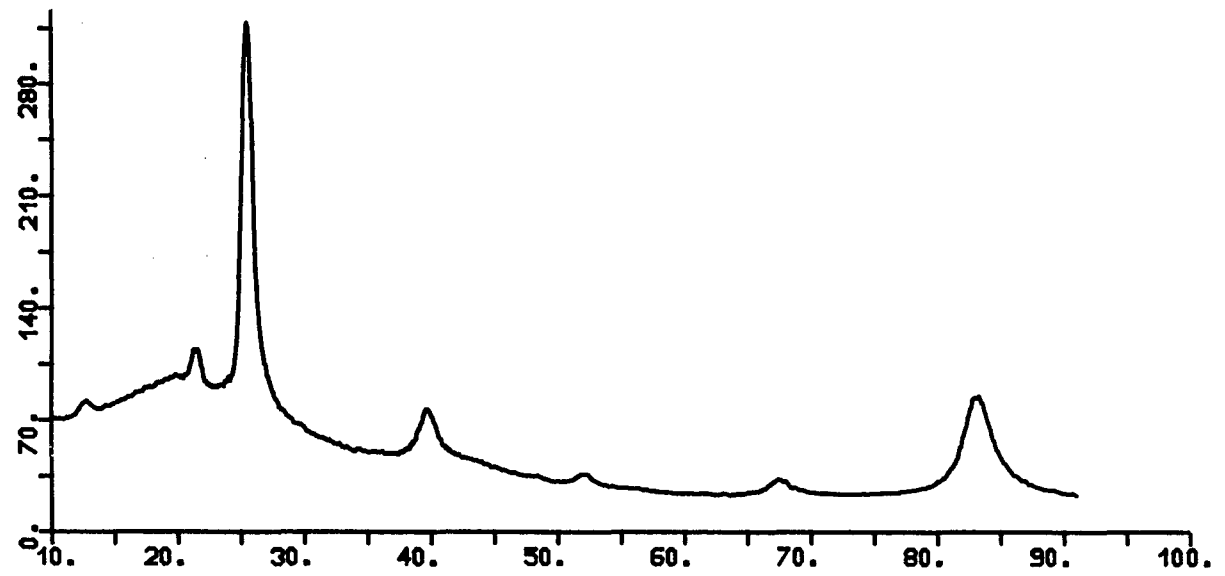

Figure 6. Meridional scan of Degummed silk from *Bombyx mori*; x-axis, 2θ in degrees; y-axis, intensity in counts per second. Experimental and sample parameters are given in Table 1.

ditional problem: it relaxes, so the tension drops with time and the experiments must be designed with this in mind. The final example, G30 carbon, has only one useable reflection at 2θ of about 43°. Unfortunately it is quite broad and not very strong. (A second reflection at about 80° is too weak and too broad to be useful.) To make matters worse, G30 has a fairly high X-ray tensile modulus, thus the broad, weak reflection changes little in 2θ.

These meridional scans show the range of materials on which modulus measurements have been attempted. A more detailed discussion of these measurements will be given in a later section of this report, **Examples of X-ray Modulus Measurements**. Some of these examples have been reported elsewhere (Lenhert and Adams, 1990).

2. THE FIBER DEFORMATION DEVICE

Construction, Wiring and Drive Characteristics

Modulus measurements will be in error if the sample moves as tension is applied. For this reason, it is imperative that the FDD be constructed so that all bearing surfaces are snug and all parts fit together tightly to eliminate unwanted flexing of the device. To achieve this, special care must be taken at several points when the device is fabricated and assembled. The mounting pin (**a** in Fig. 1) and the rotatable suspension (**b**) must have a "contact fit". Smooth rotation can be attained if the contact surfaces are lapped with fine Carborundum powder. A standard New Departure ball bearing (1#R8 954312) is positioned between the mounting pin and the suspension. The inner and outer surfaces of the bearing must fit snugly against the adjacent brass surfaces. The cantilever mount (**f**) must be free to rotate about the pivot (**g**) but it must be free of any other motion. In order to achieve this, it must be in contact with the body of the FDD, *i.e.*, there must be a snug fit which should be lapped to give smooth rotational motion. The pivot, two pieces of drill rod, must also fit tightly. Snug fits (lapped if necessary) are also required between the tension arm (**h**) and the upper sample mount holder (**j**) and between the sample mount holder and the sample mount end piece (**k**). Similarly, flex-free construction and assembly are required for the lower sample mount holder (**n**). The screw adjustments (**m**) require special attention, including undersized holes which must be lapped to fit the screws. In use, rigidity is increased by inserting shims and tightening the screws (**m**) against the shims after the sample is mounted in the FDD.

The tension arm is made from 6-4 titanium. It extends 2.8 cm in front of the clamp, is 1.3 cm wide and 2.3 mm thick. This is thicker (and stiffer) than a previously used tension arm. A thicker arm bends less and this will reduce the translation of the sample which results when the arm bends (at constant length). Reduced bending is also expected to lengthen the useful life of the arm since it is known that the strain gauges are loosened from the arm by repeated bending and partially loosened gauges give unreliable readings.

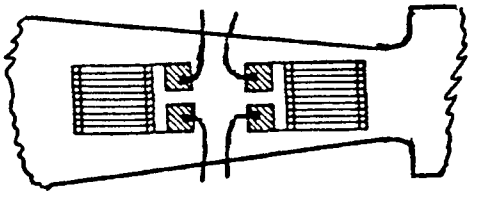

Figure 7. Active region of the tension arm showing strain gauges and leads in place.

Tension is measured by an arrangement of four strain gauges known as a full bridge. This consists of two CEA-06-125UN-120 Measurements Group strain gauges on both the upper and lower surfaces of the tension arm. The electrical resistance of the strain gauge elements changes with applied tension when the elements are stretched (if attached to the upper surface of the tension arm) or compressed (if attached to the lower surface of the arm). The resistance changes unbalance the bridge and the change in voltage is proportional to the tension. Temperature changes also change the resistance of the strain gauges, but these changes tend to cancel because of the arrangement of the gauges. The arm is tapered in the active region to make the strain gauge output more linear in relation to the applied tension. The knife edge pivot between the tension arm and the upper sample holder

insures free flexing of that joint and eliminates any possibility of torque at the pivot point. Pivot torque would affect the strain gauge output and friction might introduce nonreproducible hysteresis effects in the tension readings. The layout of the strain gauges on the tension arm is shown in Fig. 7. The circuit used for the strain gauge bridge is shown in Fig. 8 which also indicates the connections with the power supply and the digital voltmeters used to display the bridge input and output.

The strain gauges were cemented to the arm using the procedure described in Measurements Group Instruction Bulletin B-127-9 which describes the cleaning and surface preparation procedure for M-Bond 200 adhesive (cyanoacrylate cement). Leads of 32 gauge magnet wire were soldered to the gauges as follows. First a small drop of liquid rosin was placed on each strain gauge terminal, then a very small amount of solder was melted on a tiny soldering iron (1/16 in tip). When the iron was touched briefly to the terminals they tinned nicely. The insulation was rubbed from the ends of 8 lengths of wire with a small file. The wires were tinned, taped into position and soldered to the terminals by touching the iron to them. Each join was inspected with a microscope and tested electrically. The magnet wire was threaded into a tube of insulation, cut to length, laid next to the terminals at the end of the tension arm, and soldered to the terminal along with the cable leads. After the wiring was tested, the gauge area was coated with polyurethane (Measurements Group M-Coat A). This coating prevents moisture from attacking the cement and the gauges.

An Omni Amp III Signal Amplifier made by OMEGA Engineering, Inc. provides the driving voltage for the strain gauge bridge and amplifies the bridge output before it is fed into the computer interface. A potential divider allows continuously variable voltages from 0.8 to 1.2 V. In practice the adjustment is used only to set the bridge input to 0.900 V. With it one can compensate for warm-up transients and any slow drift of the power supply. The input voltage to the strain gauge bridge is continuously displayed on the Keithley 175 Multimeter which should be set to the 2 V scale. The Keithley 177 Microvolt DMM is set to the 20 mv scale to display the bridge output.

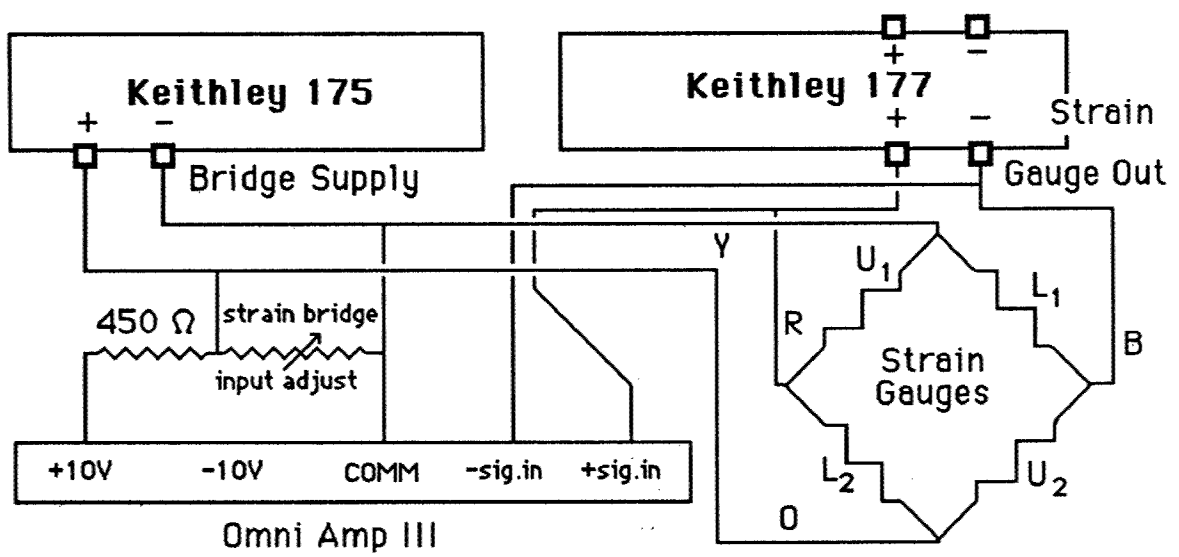

Figure 8. Strain gauge circuit diagram; strain gauges U_1 & U_2 are on the upper surface of the tension arm, L_1 & L_2 on the lower surface.

The Newport "860 - Series Motorizer," which moves the tension arm can be controlled manually by the NRC Control Box or automatically through the VAX 11/730 computer. The computer interface is an OMEGA WB-31 which includes an A/D converter to digitize the strain gauge bridge output after amplification by the Omni Amp III. All drive signals are sent to the Newport Motor through the NRC Control Box. Status signals, which show forward or reverse drive limits, originate *via* the NRC control box and are relayed to the WB-31 interface through the *Crystal Logic* box. The components are packaged together in a chassis box. Fig. 9 shows their arrangement as well as the principal connections.

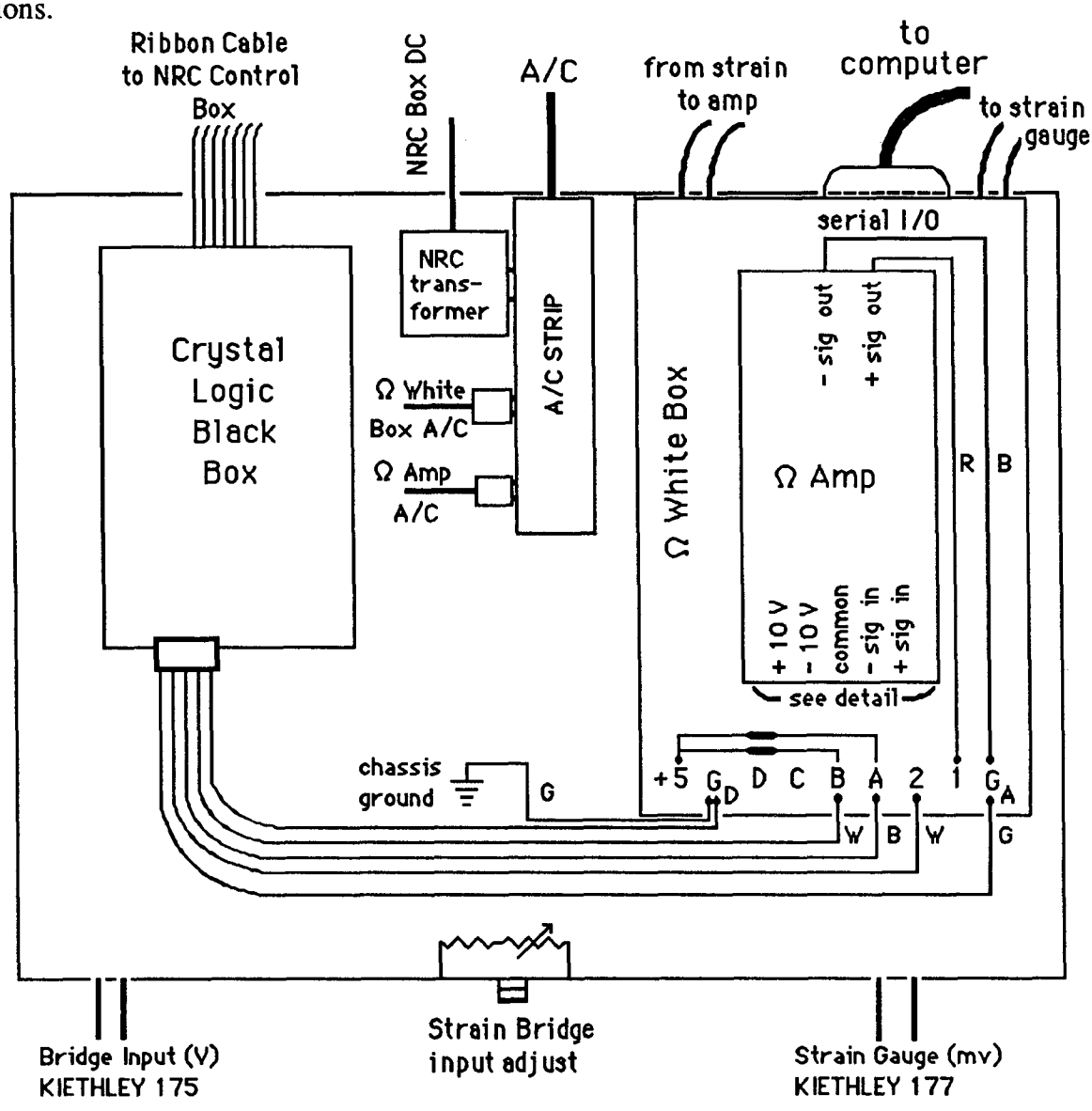

Figure 9. Chassis box showing FDD control devices and connections. The box outline, the Omega Amplifer, the Omega "White Box" and the Crystal Logic "Black Box" along with the principal connections are shown. For the detail of the amplifier connections and the digital meters, see Fig. 8.

Tension adjustment on the FDD is controlled by the VAX 11/730 (which also operates the Picker Diffractometer). The control programs which are written in FORTRAN can read

the output from the strain gauges and drive the Newport motor to adjust the tension. The FDD interface is connected to the VAX 11/730 computer through the TXA2: port, which is set at 1200 baud. The interface is activated and interrogated by reading and writing the required characters to FORTRAN unit 2. Typically, a specific tension is requested, the motor is driven incrementally forward (or backward) to increase (or decrease) the tension and the tension is read after each step. Driving continues until the requested tension is attained. The motor can also be controlled manually by means of the NRC box which also indicates visually if the motor encounters a forward or reverse limit condition.

The motor is not a stepping motor, so the smallest increment of motion is that produced by turning the motor *on* with one FORTRAN instruction and *off* with the next one. The travel of the motor shaft which results from the the on-off sequence depends on the load and on the direction of the motor. At the following tensions (strain gauge output in mv) one observes the corresponding number of steps for full travel forward:

Load (mv)	0	1.04	1.85	2.51	3.40
No. Steps	394	424	460	503	551

When the motor is driven in reverse, the step size is found to be slightly larger for all loads so that fewer steps are required to cover the same distance. That is, when the motor drives against the tension, it moves less per "step" than when it is aided by moving with the force of the tension.

Mounting, Alignment and Calibration

The FDD mounts on the χ circle of the Picker goniostat. It is secured in the hole opposite the goniometer head mount by a set screw which is exposed by removing the degree scale of the χ circle. The mounting peg on the top of the FDD (**a** in Fig. 1) is inserted into the hole and the set screw tightened against the flat surface of the peg. The degree scale is then replaced on the χ circle in the correct position and attached. The FDD must be aligned before calibration and use. Alignment consists of adjusting the position of the tension arm so the alignment device, constructed for this purpose, hangs exactly *on* the ϕ axis.

The alignment device consists of a symmetrical brass weight (5 cm high and 3.8 cm in diameter) attached to a sample mount end piece by a gauge rod 5 cm long and 0.508 mm in diameter. The device is mounted on the FDD by placing the sample mount end piece in the upper sample mount holder (**j**). The brass weight acts as a plumb bob so the gauge rod will be exactly vertical. The point of suspension, *i.e.*, the center of the knife edge of the upper sample mount holder, will be exactly on a vertical line above the rod. By observing the position of the rod in the diffractometer telescope the required adjustments can be made.

The first step in the alignment procedure is to place the FDD at the top of the χ circle by setting χ to 180°. To make the alignment adjustments, set the tension arm so it is exactly horizontal. Use the FDD alignment command in the XRYMOD program (see below) to position the arm for alignment. The incident and diffracted beam collimators are removed and the alignment device is placed in the upper sample mount holder and allowed to hang freely. The alignment procedure to be followed requires that the diffractometer be exactly level, *i.e.*, that the alignment device hang *parallel* to the ϕ axis. This can be checked by observing the alignment device when the FDD is in each of two positions 180° apart (rotation about the ϕ axis). If the diffractometer is level, the telescope, which must point exactly at the ϕ axis, will show the suspending rod translate between two positions that are

symmetrical about the ϕ axis. If the extreme positions are not symmetrical about ϕ, the diffractometer must be adjusted to make it level. Leveling is accomplished by adjusting the feet attached to the diffractometer base. If adjustment is required, try to level the diffractometer without changing its alignment with respect to the X-ray source.

With the diffractometer level, alignment of the FDD can proceed. Loosen the four cap screws holding the tension arm until they are just less than snug and adjust the tension arm to place the alignment rod on the ϕ axis. Verify this by rotating the FDD through at least 270° about ϕ and observing that the rod remains centered. When the alignment is satisfactory, tighten the four cap screws and recheck the alignment. Repeat the adjustments as required.

It is good practice to make one additional check to be sure the knife edge on the upper sample mount holder is perpendicular to the holder. This can be done by removing the holder from the tension arm and rotating it 180°. If the alignment device is still centered, the knife edge is perpendicular to the sample mount holder. If it is not, it can be adjusted by placing a piece of plastic shim stock under one end of the knife edge. Repeat the FDD alignment test with the sample mount holder in both positions and make further adjustments as indicated. When you have it right, reversing the sample mount holder will not affect the centering of the alignment device. If you have inserted shim stock to adjust the knife edge you will probably have to repeat the adjustment of the tension arm to center the alignment device again. When you have done that you are ready for calibration.

The object of calibration is to determine the ratio between the applied tension and the output voltage of the strain gauge bridge on the FDD tension arm. Two factors influence this ratio and they must be controlled in order for the calibration to be useful. One factor is the input or driving voltage applied to the strain gauge bridge, the other is the position of the tension arm.

The strain gauge bridge output of the FDD is a linear function of the applied strain but it is also affected by the position of the tension arm. If readings are taken with a calibration weight, they show a maximum value in the center of the micrometer motor range (tension arm approximately horizontal) with lower values at the extreme forward and reverse limits of the motor drive. The difference between the maximum and minimum readings for loads in the useful range is typically 1.5%. Because of this variation with position, the calibration of the tension arm is carried out near the mid-point of the motor range. Modulus measurements should also be made in the mid-range.

A driving voltage of 0.900 V has been selected to give a satisfactory tension/output voltage ratio in the tension range normally used without danger of significant ohmic heating of the gauges. The driving voltage can and should be adjusted before calibration. The input voltage used for the strain gauge bridge is expected to be proportional to the bridge output at a given tension, but this has not been verified.

To make the measurement reproducible, tension must be applied perpendicular to the tension arm. To maintain this condition, χ must be set at 180° and the tension arm must be horizontal. The calibrate command of the XRYMOD program positions the tension arm as required and it should be used to set up and carry out the calibration.

Before proceeding with the calibration, be sure all cables are connected and the driving voltage display (see Fig. 8) is adjusted to 0.900 V. If the FDD circuits are not already on, turn them on and allow several hours of warm-up time to stabilize the voltage. The meter showing the strain gauge bridge output may be set to read zero if you wish, but the reading used in tension measurements comes directly from the amplified strain gauge

bridge output. Then, with the incident and diffracted beam collimators removed, place each of the four weights on the FDD in turn, hooking them onto the upper sample mount holder. If you are using the XRYMOD program to carry out the calibration, the output for each weight will be read automatically.

The four calibration weights were made from lead bricks. The masses shown in the following table were determined on a large double beam balance at Vanderbilt University and they should be accurate to better than one gram.

Table 2. *Example computer output for a typical FDD calibration run. X-OBS is the mass (gm) of the calibration weight. Y-OBS is the strain gauge output as amplified (mv).*

```
Calibrated: DATE IS 13-OCT-89 AT 13:40:12
      Y-INTERCEPT =-0.0009 +/- 0.0014 mv
 SLOPE = 0.37658E-03 +/- 0.25126E-06 mv/gm
 X-OBS      Y-OBS     Y-CALC     Y-DELT
   0.0      0.001     -0.001      0.001
2782.5      1.045      1.047     -0.002
4934.0      1.858      1.857      0.001
6683.0      2.514      2.516     -0.001
9061.0      3.412      3.411      0.001

Calibration factor 2655.5 +/- 1.8 gm/mv
```

Table 2 shows the results for a calibration run made as described above with XRYMOD, which calculates the calibration coefficient by linear least-squares. Note the agreement between the observed and calculated values for the tension. Calibration by this method, using XRYMOD, takes only a few minutes so it can be easily checked. A slow change in calibration has been observed, therefore recalibration every few months is recommended. Similarly, the device should be checked for stability by letting one of the calibration weights hang for a day or two. Adjust the input voltage and record the bridge output at intervals. You should not find a variation of more than a few microvolts.

Sample Translation and the Lower Sample Holder

Inconsistent modulus values measured initially with the FDD suggested that differences between modulus values measured with the FDD in different positions might be due to anomalous translations of one part or another of the device. The first attempt to study the stability of the FDD involved the construction of a microscope holder and a mirror which allowed the modulus sample to be observed when it was in the measurement position (horizontal, with χ at $\pm 90°$). Measurements of the sample position as tension was applied and released showed sample motion along the X-ray beam. Because the shape of the fiber bundle changed as it was stressed, accurate measurements of the translation could not be made.

Various modifications were made to the FDD in an effort to make it more rigid but problems which were possibly attributable to anomalous sample translation persisted. A new approach to quantifying the translation was taken. A measuring aid to replace the sample was constructed from a small round gauge rod. Two brass end pieces were se-

lected and cemented to the gauge rod which fit snugly into the holes in the end pieces intended for a fiber sample. Before applying epoxy, a small diamond saw was used to score the gauge rod in various places to give a rough and uneven surface for the epoxy. The epoxy was applied and worked into the contact area between the brass end piece and the gauge rod. After the usual baking step, the gauge sample was ready to use.

The FDD was mounted in the Picker Diffractometer and aligned in the usual way. The gauge rod sample was then mounted according to the usual sample mount procedure. The adjustment screws in the lower sample holder were tightened against metal shims selected to correspond to the length of the gauge rod sample. This pulls the top and bottom of the sample holder together, thus making it rigid. Adjustment for various sample lengths is accomplished by using thick or thin shims.

With the gauge rod sample in position and the diffractometer set to $\chi = 0°$, the tension was increased in increments and the diffractometer telescope was used to measure the change in gauge sample position. The manual FDD control program, MOTOR, was used to change the tension and read the strain gauges. The first measurement was made at about 0.15 mv tension and the gauge sample position was measured again after tension increases of 10 steps forward for the FDD motor. The highest tension was always about 3.1 mv. A final position measurement was made after the tension was reduced to the starting value.

A series of position measurements, made after each increase in tension, was repeated for the four usual positions of the FDD (motor toward detector, up, toward tube, and down). As would be expected, the second two positions showed the same translation as the first two, but in the opposite direction. In most subsequent measurements only the motor to detector and the up positions were used. The measurements were fairly reproducible and consistently showed translation of the sample in one direction. The direction of translation was found not to depend on the orientation of the gauge sample but it was reversed in direction if the lower sample holder was rotated 180° with respect to the gauge sample and the upper portion of the FDD. This observation suggested that the sample translation being observed resulted from the bending toward the center of the lower sample holder or some part of it. One can easily see how this could occur if the lower sample holder were tipped slightly to place it a little off the ϕ axis. Tension parallel to that axis would then cause the holder, and therefore the lower part of the sample, to translate. Plastic shim stock was inserted at various points in the lower sample holder and the effect on the measured translation of the gauge sample was determined. The lower sample holder was also partially disassembled and various parts rotated 180° before it was reassembled to ascertain the source of the observed translation.

After many trials it was determined that the translation could be eliminated by two changes. Rotation of the lower sledge with respect to the other parts of the lower sample holder eliminated translation along the direction perpendicular to the tension arm. The addition of two shims (one sheet each of tan and red plastic shim material, a total thickness of 0.15 mm) placed on one side above the top sledge almost completely eliminated translation along the direction parallel to the tension arm. The remaining translation, which is 0.02 mm at 3.1 mv tension, was observed to reverse direction when the gauge sample was rotated 180°. Apparently it is due to a slight asymmetry in the gauge sample itself.

Attachment of the lower sample mount holder to the diffractometer must be done carefully and as follows to be sure the translation problem does not recur. When the brass base is mounted on the diffractometer, it must be oriented with the mark toward 240° ϕ. The

lower sample mount is then placed on the base with its mark lined up with the mark on the base plate and the screw ring tightened snugly.

It is good practice to use the gauge rod sample to check for translation each time the lower sample mount holder and/or the base plate are replaced on the diffractometer. To do this, mount the gauge rod sample as described above. Set the tension to about 0.2 mv and use the diffractometer telescope to measure the position of the left side of the rod. Apply tension in several steps up to about 3.0 mv and check the position of the rod after each step. Lower the tension to about 0.2 mv and check the position again. Maximum movement of up to 0.02 mm is acceptable. Repeat the measurement after rotating the FDD and the lower sample holder by 90°. Application of tension should give a similar result.

3. PREPARATION OF X-RAY MODULUS SAMPLES

Polymer materials are usually received as yarn strands of several hundred to several thousand fibers. In order to make X-ray modulus measurements an appropriate number of fibers must be mounted and placed in the diffractometer where tension is applied. Polymer fibers in suitable mounts have been prepared by several methods which are described below. All require the use of metal sample mount end pieces.

Preparation of Sample Mount End Pieces

The FDD has been designed to mount fiber samples which have a specially designed metal end piece attached to each end of the fiber sample. The end pieces were originally fabricated from standard reusable hypodermic needles, size 19 or 20, which have hollow stainless steel points and a plated brass base. The base of the needle was modified to make a holder which fit into the upper and lower sample mount holders of the FDD while the shortened needle end held the bundle of fibers cemented in place by epoxy.

The hypodermic needles were cut on a small diamond saw to remove most of the needle portion. The cutting procedure leaves a rough inside edge which might weaken the fibers during the construction steps. The inside edge of the needle can be smoothed by taking relatively coarse Carborundum powder, mixing it with oil and applying it to the rough edge. The grinding compound is applied to the cut end of the needle using a small wire ground to a fine point, and mounted in an electric hand drill. When the wire tip, dipped in grinding compound, is pressed against the cut end of the needle for a few minutes, the grinding appears to give a slight flare and a smooth inner surface to the opening. The fibers can come in contact with this surface without damage.

The next step in preparation of the sample end pieces was to cut the needle end of the base down to the diameter of 0.161 in to create a square shoulder. This is conveniently done by using a lathe with a collet chuck. The square shoulder replaces the irregular taper on the needle base and allows the needle to mount solidly and reproducibly in the sample mount holders of the FDD.

Precise machining of the hypodermic needles proved difficult and the sample mount end pieces are now fabricated from brass stock in the Materials Laboratory shop. Fig. 10 shows a fiber sample mounted in holders of the present design. The diameter of the center hole can be changed to accommodate fiber samples of various sizes, a desirable feature as we note below. A shop drawing showing all dimensions is given in the Appendix.

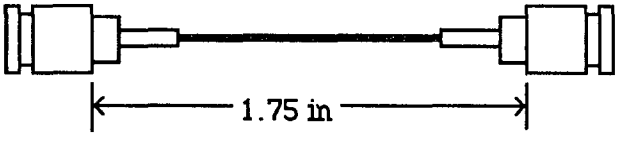

Figure 10. Diagram showing a fiber sample mounted in sample end pieces of the present design. Note the 1.75 in distance between holder shoulders. This must be maintained for all samples.

Sample Size Considerations

How many polymer fibers should be used in a sample? There are several considerations. One is the optimum tension range of the FDD. Ideally one would like to use the full tension range from 0 to 4.5 mv (0 to 115 N), however, in the horizontal measuring position the sample tends to sag a little if the tension is too small. The practical lower limit is about 0.3 to 0.5 mv unless special considerations dictate smaller tensions. At the upper limit of the tension range, the epoxy that holds the fiber sample to the brass end pieces may fail. Also, we have not verified the linearity of the tension measurement beyond 3.5 mv.

Next the properties of the fiber sample must be considered. The sample should not be more than 0.7 to 0.8 mm in diameter since the 1.0 mm incident beam collimator is normally used. The tensile strength of the material must be considered. Generally the sample should be large to give stronger diffraction and to withstand all tensions in the optimal range of the FDD, 0.5 to 4.0 mv. But, the modulus of the material must also be considered. If the sample is too stiff, the elongation (for our purposes the increase in d-spacing) will not be large enough to permit accurate measurements of Δd. Adequate stretching for good accuracy in Δd measurements may put an upper limit on the sample size.

In a low modulus material (usually low strength also) one would make the sample as large as the X-ray beam size permits since this will permit a greater part of the FDD tension range to be used. The increase in d with tension will usually be easy to observe because of the low modulus.

If preliminary X-ray measurements are available, the estimated change in d can easily be calculated for a given sample size stressed to either the maximum FDD range or the tensile strength of the fiber sample. If one must rely on nominal or manufacturers stated tensile modulus values one should assume that the X-ray modulus will be about twice as large as the mechanical modulus. A note of caution about the nominal tensile strength: experience shows that it is best to be conservative. Don't go beyond about 50% of the nominal tensile strength.

In a high modulus material a large sample would require a very large tension to give a significant increase in d, therefore, one must normally restrict the size of the sample so that the maximum tensile strength of the sample approximates the tension available from the FDD. With a smaller fiber sample the X-ray diffraction intensity may become a consideration. One needs fairly strong reflections to provide the required accuracy in the d-spacing measurements.

In summary, for a strong high modulus material one must balance the diffraction intensity available against the Δd expected for a sample that can be stressed to the FDD limit of about 4.0 mv. For a lower modulus material, the concern is to use as much of the FDD tension range as possible without making the sample too large to fit in the X-ray beam.

Making an Equi-tension Fiber Sample

When a fiber sample is stressed and the strain measured, it is important to know that every fiber in the bundle has experienced the same stress. If it has not ,then there will be a distribution of stresses and, consequently, a distribution of strains. If it is important that

the diffraction measurements be made on equi-stressed fibers,* the following technique or a similar one must be used. This will give a fiber sample with every fiber of equal length.

The material used for the first equi-tension sample was Dupont PBZT AFTECH II heat treated yarn, 2.42 denier per filament (as measured in the Materials Laboratory). The first several attempts to make an equi-tension sample with this material resulted in tangles. After several tries, the following technique was successful. The task can be divided into several steps. First one must take a *loop* of yarn and without twisting it, thread it through both sample end pieces. It then must be hung from a support so that weights can be attached to each loop of fiber. Finally, with the weights in place, the end pieces must be glued to the fiber bundle with epoxy. This technique has the advantage not only of ensuring that each fiber is under equal tension when the experiment is performed, but one is also certain how many fibers there are in the bundle.

To prepare the yarn sample, cut about 5 ft of yarn from the roll. The free ends are kept separated initially and the mid point of the yarn is attached to a smooth roller (a clean metal Coca Cola can works fine). The yarn is then wound carefully onto the can, taking care not to twist or overlay one layer on another. When about 10 in remains free, the two ends are placed together and trimmed neatly. The free ends must now be threaded into a glass capillary of the type used to prepare powder samples for X-ray diffraction. Select a capillary which is as large as possible, but be sure it will go through the two metal end pieces selected for the fiber sample. Thread the two free ends together into the capillary. Push them all the way to the end, then insert the capillary into the metal end pieces. The end pieces must be oriented so that the tips are together. Be sure to maintain the 1.75 in distance as shown in Fig. 10. This length is fixed by the design of the FDD. It is convenient to glue a short length of Q-tip handle to the two end pieces so that this distance will be maintained when the glass capillary tube is removed. After pushing the capillary through the end pieces, break off the small end and pull the yarn gently through.

Prepare to hang the fiber bundle by selecting a large cork borer and wrapping the free end of your fiber around the middle of the borer. Attach the fibers to the borer with 5 minute epoxy. After the epoxy has set, roll up the yarn, again being careful not to twist or overlay the strands. You must take up the yarn on the cork borer as you unroll it from the Coke can. When you have about one foot free, place the cork borer in a holder and hang a weight on the free loop so that it is just far enough above the table to allow all weights you add to hang free. You are now ready to begin the task of hanging a weight on each single fiber loop.

The weights are short lengths of 30-70 solid core solder wire, 0.216 cm in diameter, cut to 18 cm lengths and bent to make a hook which can be conveniently placed on each fiber loop. Each piece weighs about 6.6 gm and therefore gives a tension of 3.3 gm weight per fiber. This should be enough to ensure that the fibers are taut.

Begin to separate the fibers by using a sewing needle and, where convenient, your fingers. As each loop is isolated, hang a weight on it. If some fibers become tangled, cut them and remove them as completely as possible from the work. Continue working on the free loops until it becomes impossible to separate more fibers. When you are no longer able to separate free loops, remove all fibers that do not have weights hanging on them. Work them free up to the metal end pieces and cut them off. This is at least as tedious as hanging the weights, but it is just as important. When you have all fibers, except those

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* See the section on **Multi-Fiber Samples with Non-Uniform Tension.**

supporting weights, removed, you are ready to break off the glass capillary. (Alternatively, the capillary can be removed after the fiber has been hung, but before the weights have been attached.) Use a small loop of wire wrapped around the fibers to compress them into a small bundle so that the capillary can be slid down free of the metal holders. Carefully crush the capillary with a needle nose pliers and clean (blow) the glass pieces out of the fiber bundle. Move the two metal end pieces, which are now a unit, down the sample to a point where they are clear of all loose fiber ends.

Prepare the epoxy (Miller-Stephenson Chemical, Epon 828 resin and M-S C Versamid 140 hardener) and place it in a syringe fitted with a cut off needle inserted into a short piece of fine flexible tubing. Work epoxy around the fibers just below the lower end piece. Be sure epoxy contacts all fibers. This is relatively easy to do since the fibers will be spread by the weights. Next, move the metal end pieces down so that the epoxied area is in the tip of the end piece. Now add epoxy to the top of the upper end piece. Work it down into the tip. Do not disturb while the epoxy sets. After 24 hr or more, the weights should be removed and counted and the fiber ends cut off. Handle the sample with care, label it clearly and place it in a safe place until you are ready to use it.

Standard Sample Preparation Technique

The method described here results in a sample with all fibers of nearly the same effective length but preparation is much easier and quicker than the equi-tension method discussed above. Materials needed in addition to the polymer fibers and the metal sample end pieces are the epoxy and hardener and the glass capillaries.

First select a capillary that will fit into the sample end pieces, which must slip all the way down the enlarged end of the capillary. Determine how many fibers you want in the sample and if possible select a yarn with the right number. It is better to combine yarns to get the number of fibers you need than to use a partial yarn. If there is no other choice, carefully separate part of a yarn to make the sample. The capillary must be a snug fit on the sample fibers since this is what keeps them parallel. Next cut a length of polymer yarn to give about 10 in of yarn to work with and thread it into the capillary all the way to the sealed end. (Do not touch the fibers more than necessary and try especially to avoid touching them at points where they will be epoxied into the metal end pieces.) Push the capillary with the yarn inside into the first end piece through the large end and into the second end piece through the small end. Position the end pieces on the capillary so the first is as far toward the large end of the capillary as it will go and the second is near the small end of the capillary. Mix a few drops of 5 minute epoxy, place a small amount at the points where the capillary enters the end pieces. Adjust the end pieces so the pressure surfaces are 1.75 in apart and allow the epoxy to set. Prepare a small piece of wood (a section of cotton tipped applicator will do fine) and glue it to the side surface of the sample end pieces with a very small amount of 5 minute epoxy. This will keep the sample rigid and protect the capillary until you are ready to remove it.

You are now ready to prepare to glue the polymer fibers in place in the metal end pieces. Break the seal on the small end of the capillary and slide the metal end pieces and the attached capillary along the fibers until the fibers extend several inches from each end. Mix a few drops of the 828 resin and the 140 hardener, break away as much of the small end of the capillary from the inside of the sample end piece as possible, and with the sample in a vertical position, fill the end piece with epoxy. Work the epoxy down with a small object and hang it, epoxy end up, in a vertical position overnight. Next day repeat

with the other end. It is helpful to glue the uncemented end of the yarn to a small wood stick with five minute epoxy. The sample can then be suspended from the free end of the fiber bundle to be sure that the fibers are under a little tension and therefore parallel while the epoxy is allowed to harden in the second end.

Three things remain to be done before the fiber sample is ready to use. The epoxy must be heat cured, in a vacuum oven if one is available, at 100° C for 2.5 hr. If the sample material is heat sensitive, the temperature and/or heating time must be reduced appropriately. Label the sample by gluing a small identifying number to one of the metal ends. And, finally, determine the number of fibers.

If the sample fibers are more than 10μ in diameter, you will probably get the best estimate of the number in the sample by counting them. They could be counted by destroying the sample after it has been used but a better plan is to cut the yarn bundle at the point where it enters the large end of the sample end piece. Keep the bundle together and cut off about 2 mm at the end. Be sure your 2 mm sample includes all fibers. Place them under a long focal length microscope to count. Separate off a dozen or so fibers, count them, record the count and dispose of those counted. Repeat until the entire tuft is gone. It is good practice to repeat the count with a tuft taken from the other end of the sample.

If you have used a full yarn with a known number of fibers, the nominal count may be accurate enough for calculating the modulus. If the fibers are too small to count and you do not know the number in the sample, the only alternative is to weigh a length of yarn with the same count as the sample and calculate the number from the nominal fiber diameter, the density and the weight of a known length of yarn.

4. THE X-RAY MODULUS PROGRAM

The X-ray Modulus Program, XRYMOD, is the software interface between the automated diffractometer, the FDD and the user. It is always used in the interactive mode. XRYMOD requests all the information needed for an X-ray modulus determination and issues instructions to the user *via* the CRT screen for alignment and calibration of the FDD and for mounting the sample. In a modulus run the program adjusts the tension as requested by the user, carries out the measurements and calculates the X-ray modulus based on the tensions and the reflections specified. A plot file is generated which can be plotted on a Calcomp compatible plotter. The workings and features of XRYMOD are discussed below.

Sample Data File, MOD.IN and the Log File, XRYMOD.TMP

Information about the material being studied and the particular sample currently mounted is entered from the CRT terminal and stored in the VAX file, MOD.IN. Table 3 shows an example of a MOD.IN file for PBZT. The user responds to requests from XRYMOD for the required information: title of the experiment, identifying information about the substance and sample history, number of fibers in the sample, fiber density, denier per fiber, and expected modulus (used to predict the approximate position of diffraction peaks as a function of strain). Up to five reflections can be scanned at each tension

Table 3. *MOD.IN file for a PBZT modulus sample. Line 1 is the experiment title; line 2, sample and processing data; line 3, number of fibers in the sample, fiber density (gm/cm^3), denier per fiber and expected modulus; line 4, FDD calibration factor (gm/mv), and maximum allowable tension (mv); line 5, number of peaks to scan, zero tension 2θ for the 5 peaks; line 6, low angle background increment (in deg.) for the 5 peaks; line 7, same for high angle background; line 8, number of steps to scan on each side of the peaks; line 9 and line 10, step increments (in deg.) for side steps and center steps; line 11, counting time in seconds; line 12 and 13, number of tension values to use and the 11 values specified. (See* **Choice of Measurement Parameters,** *for an explanation of lines 5 to 10.)*

```
PBZT SAMP #8 FDD NEW TEST
BT 32508-18-14 14 IV 650 C HT
 650.0000     1.5700     1.8960   440.0000
2665.0000     3.7000
   5    21.41    36.00    51.17    76.13    95.50
   1.20     1.40     1.40     1.40     1.60
   1.20     1.40     1.40     1.50     1.70
   3     3     3     3     3
   0.20     0.20     0.17     0.22     0.24
   0.25     0.25     0.23     0.25     0.28
  60    90    40    90   120
  11    0.500    3.500    2.833    2.167    1.500    0.833
        1.167    1.833    2.500    3.167    0.500
```

and the modulus calculated separately for each reflection. Step scan parameters, 2θ at zero tension, counting time and 2θ for background measurements are entered separately for each reflection to be used. The MOD.IN file is read by XRYMOD anytime information about the sample is needed.

Either the EP or the IO commands (see XRYMOD Menu, below) allow changes in the sample and experiment parameters in MOD.IN. The calibration procedure, initiated by CS, stores the FDD calibration in MOD.IN.

The experiment log file, XRYMOD.TMP, is initiated by the IO function. This command causes data about the sample from MOD.IN to be entered into XRYMOD.TMP. This log file serves as a record of the experiment. It is updated at each measurement to record all tension and scan data as well as the modulus calculation. The time of day is entered at the beginning and the end of each experiment. All measurements performed will be recorded in the same file until a new file is initiated.

Table 4 shows an example of the beginning of a typical log file down to the point where the first background measurement is reported. Reflection scan and fitting records are displayed in Table 5 of the DATA ANALYSIS section and the modulus calculation summary is shown in Table 6 of the same section.

Table 4. *Experiment information as recorded in the log file, XRYMOD.TMP.*

```
 S2 DEGUM SILK 100 YARNS 20/22 DEN
 MARY B SAMPLE S2 1.364 DPF
  FIBERS in sample =2200                DENSITY =  1.353 (gm/cm**3)
  DENIER per fiber = 1.364   Expected Modulus =   26.00 GPa
  FDD calib. is 2655.5 gm/mv
  2 Reflections can be scanned, the params ARE:
REF No.  2 THETA  No. STPS  SIDE INCR  CENT INCR  SEC   BKGL   BKGH
   1      83.25        3        0.55       0.60    180   4.70   4.80
   2      25.47        3        0.22       0.25     60   1.65   2.80
INCIDENT BEAM COLLIMATOR IS 1.5mm, DIFFRACTED BEAM COLLIMATOR IS 1.5mm
DIFFRACTED BEAM APERTURE SET AT  3.0 mm WIDE,  6.0 mm HIGH
Kv = 45, ma =  70, Filter is: NI .001 IN
File initialized: DATE IS 23-APR-90 AT 21:06:07
BRIDGE INPUT AT START = 0.8930 V
FDD orientation with micrometer (motor end) pointed TOWARD DTECT
CURRENT SETTING FOR Kv = 45 Ma = 70
Run started: DATE IS 23-APR-90 AT 21:11:25
ESTIMATED RUN TIME IS  1308. MINUTES: FINISH AT 18:58,  1 Days hence
 10 TENSION VALUES WITH STEPS COUNTED FOR THE FOLLOWING (sec): 180  60
DELAY  900sec. AFTER TENSION IS SET, BEFORE SCAN.
DIFFRACTOMETER CONFIGURATION IS:   NEG 2TH     CHI -90
     ***BACKGROUND***
TENSION   0.245  0.253
2 THETA   78.55  88.05
  CPS      99.2  100.8
```

XRYMOD Menu

- EP -- *Enter sample or scan Parameters.* This command uses subroutine MODIN to create or to update an existing MOD.IN file. If a new file is to be created, all the items of information required will be requested in a logical order: 1) title, which should include information that will identify the experiment; 2) sample ID data, such as the sample ID

number, heat treatment or other preparation data, *etc.*; 3) the number of fibers in the sample, fiber density, denier per fiber and approximate modulus are requested. The FDD calibration (gm/mv) can be entered, but if the calibration is determined by the CS command (see below), it will be stored in MOD.IN automatically. The expected 2θ at zero tension and the expected modulus are used to predict 2θ for the peaks so the scans will be optimally located for each tension. Scan parameters, *i.e.*, the number of steps to be measured on the sides of the peak, their separation in degrees 2θ, the separation of the center point from the steps on the sides and the counting time for each step are entered. If several reflections are to be used for the modulus measurement, separate parameters and counting times are entered for each. Tension values to be used may be entered individually or you may specify the number of tension values and the minimum and maximum tensions. The program will set up the sequence of tensions and display it on the screen.

- IO -- *Initialize Output.* This command opens a new XRYMOD.TMP file, reads and displays the MOD.IN file containing sample and experiment data and uses subroutine MODIN to enter changes to MOD.IN if any are requested. X-ray Kv and ma, filter and SVA (diffracted beam aperture) are also requested and written in XRYMOD.TMP along with the standard collimator sizes and the current date read from the VAX clock.
- AL -- *Make FDD Alignment Adjustments.* This command drives the FDD tension arm to the alignment position and provides a prompt to start the alignment procedure. For details, consult the section on FDD Alignment, above.
- CS -- *Calibrate Strain gauge.* The strain gauge calibration is done by subroutine CALIBR. The first step in the calibration procedure is to drive the micrometer motor to the center of its range. This places the tension arm in a nearly horizontal position. The user is instructed to adjust the bridge driving voltage, zero the tension reading, and signal with GO when ready to record the zero tension reading. Requests to hang the various calibration weights are then issued and the user signals with GO when each one is in place. Finally, the zero tension reading is again checked and a least-squares straight line is fit to the tension readings and the masses of the calibration weights (they are in the program). The least-squares fit is done by subroutine LINFIT, and the calibration data, a summary of the fit, the slope and the date are recorded in XRYMOD.TMP. For details, consult the section on FDD Calibration, above.
- DF -- *"Manual" Mode for the Diffractometer.* This command allows the user to manipulate the diffractometer using a subroutine PMAN which is a version of the program PIKMAN. The available commands are displayed in a "menu" which appears when DF is selected. For details on these commands, see *A User's Manual for Fiber Diffraction: the Automated Picker and Huber Diffractometers* (Lenhert and Adams, 1990)
- MD -- *"Manual" Mode for the FDD.* The "Manual" Mode command allows the user to issue commands to drive the micrometer motor, check the motor status and read the strain gauge bridge output. The available commands are displayed in a "menu" which appears when MD is selected. The "Manual" Mode is useful for checking the *Crystal Logic* FDD interface function and the motor and strain gauge operation. It is recommended that the motor function, status read, and strain gauge output be checked anytime the FDD is used. The subroutine used, FDDMAN, is a version of MOTOR.
- MS -- *Mount Sample.* This command first fetches the data from MOD.IN needed to initiate an X-ray modulus measurement. Next the tension arm is lowered to allow convenient mounting of the sample. Then, with the sample in place the tension arm is posi-

tioned for tension measurements. Tension is checked after every ten micrometer motor steps to be sure it does not exceed 0.3 mv. If 0.3 mv is reached before 190 steps have been driven, *i.e.*, before the horizontal position is reached, the number of steps remaining is displayed. The user receives reminders as to what adjustments must be made to mount the sample. When the user indicates by GO that all is ready a new command is requested. For details, see **Mounting the X-ray Modulus Sample**, below.

- MR -- *Modulus Run.* This command initiates a modulus measurement. Data from MOD.IN is read, XRYMOD.TMP is opened in the append mode and the strain gauge input voltage is adjusted by the user (if needed) and recorded. The measurement options are presented: choice of peaks to use, *i.e.*, pick any or all of the reflections in the MOD.IN file; choice of $\pm 2\theta$ ranges and $\pm\chi_{90}$ ranges in various combinations for multiple modulus runs; choice of tension ranges if you want a set(s) of tensions other than the one in MOD.IN; choice of treatments for sample relaxation (either wait for relaxation to be complete and readjust tension or wait but don't reset tension) and choice of relaxation time if delay is requested. The projected run time for the experiment is reported, if it is not satisfactory, the counting time can be changed without reentering all the above information. Finally, other experiment parameters such as Kv and ma settings and FDD position are requested after which the run proceeds automatically.

  The tension is adjusted to the requested values by SETTNS and the scan is set up by SETMSC. Zero tension *d*-spacing, estimated modulus, fiber density, denier and number of fibers in the sample are used to calculate the expected 2θ for the points to be measured. Next the step scan parameters are used to set up the 2θ points to be counted for the peak profile. The peak is then scanned by the 2θ step scan subroutine TTSSCN and the step scan data are passed to subroutine PKFIT where a Gaussian curve is fit to the intensity as a function of *d* spacing. The tension is adjusted to the next tension value in the list, new scan points are calculated by SETMSC, the scan is made by TTSSCN and the fit parameters are obtained by PKFIT. When all points on the tension curve have been measured, subroutines CALMOD and LINFIT are called to calculate the slope of the tension *vs d*-spacing line and from it the X-ray modulus. Finally, the modulus, its uncertainty and all observed points on the curve are printed along with their residuals. A plot of tension *vs d* spacing is stored in PLOT.PLT. When the file is plotted, the plot shows the experimental points, the line and the modulus calculated by least-squares. The run title, date and the sample data are also shown on the plot.

MUTIL and MHARD, XRYMOD Subroutine Files

MUTIL contains the following subroutines of interest. RMODIN reads all the data from MOD.IN and loads it into the labeled common block /PARAM/. WMODIN performs the reverse, taking the parameters in /PARAM/ and writing an updated copy of MOD.IN. LINFIT is the linear least-squares program that fits the tension, *d*-spacing data. TDATE, which fetches the time and date from the VAX clock is in another file, GUTIL.

The subroutines of **MHARD**, used to drive the *Crystal Logic* FDD interface, are summarized below.

FDDLIM requests and/or modifies the maximum tension permitted for the FDD. This is a "software" limit. Any subroutine which changes the sample tension will check the requested tension against this limit. An error will be indicated if the requested tension is greater that the limit set.

STVAL is called at the beginning of a run to set the acceptable limits on the FDD interface status word for the micrometer motor. Motor status can be normal, forward limit, or reverse limit. The status is determined by interrogating the *Crystal Logic* FDD interface. The status word returned is compared to the values set up in STVAL. A match is expected for normal status or one of the limit conditions.

TENSN (T) reads the strain gauge tension in μvolts. Ten readings are made and the average value is returned as T in millivolts.

RSTAT (IST) compares the status value supplied, IST, with the status value limits set up by STVAL and reports abnormal or limit indications.

RLIMIT drives the micrometer motor to the reverse limit and turns the motor off when the limit is reached. This procedure is used to put the FDD in a standard state from which it can be set to the center position for alignment, calibration or sample motion.

MSTEP (NSTP,NSD,ISTAT) drives the micrometer motor forward or reverse by NSTP steps. If NSTP is positive, the motor is driven forward (tension increases), if negative, the motor direction is in reverse and tension decreases. For forward motion, the actual distance of travel per step is less for larger loads. For reverse motion, the distance of travel per step is greater than it is for forward motion at the same load. For details see the section of this report on "FDD Drive Characteristics". If the execution of a step causes an abnormal status, for example, a forward limit signal, control returns to the calling program and the status word encountered is returned as ISTAT. This abnormal return causes NSD to be set to the absolute value of the number of steps completed. NSD is zero for a normal return when NSTP steps have been completed. If status reads give inconsistent results, a hardware error is assumed and a "Status Error" stop is executed.

SETTNS (TREQ,TOBT,NSTP) drives the micrometer motor to the tension requested, TREQ. Motor motion is forward if increased tension is requested and reverse if a tension decrease is needed. Since a "step" is the smallest motor increment possible, it is not possible to adjust tension to exact values. Actual tension on return is TOBT. Motor motion stops if the requested tension differs from the actual value by less than half the one step change or if the requested value is passed. Subroutine MSTEP is called to move the motor one step at a time. Subroutine TENSN is called to check the tension after each step. If the requested step is not completed at any point in the tension adjustment sequence, the resulting status is reported and written into the experiment log file by XRYMOD. A near zero tension, not requested, causes a "Broken Sample" stop.

Problems with false indications of forward and reverse limits have been encountered. SETTNS deals with these in the following way. If a forward limit status is encountered, the micrometer is backed up one step. This restores the normal status. The forward step is then retried. If the retry again gives a forward limit status, the backup, forward step sequence is repeated two more times before the program gives up and accepts the existing tension. The first retry usually gets past the problem spot. If false forward limits occur while a modulus run is in progress, they will be indicated on the CRT screen and in the XRYMOD.TMP file by a message and an abnormally large number of steps reported to attain the requested tension. False indications of reverse limit status are dealt with by a step forward to reset the normal status. The reverse step is then retried with two repeats if needed. As with forward motion, the existing tension is accepted if the procedure fails. Experience shows that this technique can be relied on to eliminate the problem of false limits.

5. MAKING A MODULUS MEASUREMENT

After the modulus sample has been prepared, it is mounted on the FDD and the measurement parameters are selected and entered. The following discussion describes the details of these steps. Don't forget to check the FDD alignment if it has not been aligned since it was last mounted on the diffractometer. Also recalibrate if the FDD has not been used for some time.

Mounting the X-ray Modulus Sample

After χ has been set to 0°, the mount command in XRYMOD should be used to mount the sample. This will lower the tension arm of the FDD to make inserting the sample in the upper and lower sample holders more convenient. It is usually best to remove the upper sample holder from the FDD and place the sample in it. With the tension arm down and the length adjustment screws of the lower sample holder loosened, the sample can be placed in the lower sample holder and the upper sample holder replaced on the tension arm.

Now initiate the next step in the mount program which will move the tension arm to the measurement position. The program checks the sample tension as the arm moves and if the tension reaches 0.3 mv, motion stops and the length adjustment screws must be loosened further before motion is resumed. When the tension arm positioning step is completed, select suitable metal shims[+] and insert them in the gap in the lower sample mount holder and tighten the adjustment screws against them. The tension should read 0.3 to 0.4 mv when the tension arm is set and the adjustment screws are tight.

If the setting procedure was interrupted to allow the adjustment screws to be loosened, you should repeat the mount command. This is because when sample tension is encountered, tension arm motion will be reduced and the normal measurement position will not be reached. This can be avoided by ensuring that the length adjustment screws are sufficiently loose before the sample mount command is issued.

When the tension arm is positioned and the adjustment screws are tight, center the sample in the X-ray beam. Use the diffractometer telescope to observe it as the FDD, both upper and lower parts, is rotated. Adjust the centering as indicated using the translation screws on the lower sample mount.

Choice of Measurement Parameters

A preliminary meridional 2θ scan is a prerequisite for choosing scan parameters for a modulus run. As noted above, reflections suitable for modulus measurement should be intense, sharp and at high 2θ. All these features contribute to improving detection of small 2θ changes.

[+] Several slotted shims which fit the FDD are available. They slip into the gap in the lower sample mount holder with the adjustment screws in the shim slot. If you cannot get the needed thickness with these shims, add one or more thickness gauges. We have two sets so you should be able to find a pair of any size you need.

Before proceeding with the choice of scan parameters, set up the appropriate experimental conditions. Use an SVA setting of 3x6 mm unless the reflection to be scanned is very sharp (FWHM less than 0.7° 2θ) in which case the SVA width can be reduced to 2 mm. It is not necessary to use a β filter unless there is interference from the Kβ peak of a higher order reflection or unless you are using a broad low angle reflection and must filter out the Kβ to get a good background measurement. Unless the sample is more than 0.7 mm in diameter, use the 1.0 mm incident beam collimator and the 1.5 mm diffracted beam collimator. For larger samples, the 1.5 mm incident beam collimator should be used.

Check the profiles of the peak(s) selected by making a 2θ step scan using the modulus sample. This will help to choose the counting time and the step size for the peak scans and to determine appropriate points for measuring the background. The scan range for each 2θ measurement should consist of seven points symmetrically located on the peak with sufficient counts at each point to determine the intensity to a standard deviation of 2% or better. If you must use broad peaks for the modulus measurement (FWHM of 2° 2θ or more) higher precision at each step in the scan will be needed to obtain a result of acceptable accuracy.

The step scan profile can be used to approximate the zero tension 2θ value. To get an accurate value it is best to set up a three point modulus run with your preliminary values of step size and expected modulus. The *d*-spacing intercept and the X-ray modulus calculated by XRYMOD for the three point run can be used in subsequent runs for the expected modulus and the zero tension 2θ. The initial choice of step widths can also be adjusted on the basis of this initial modulus run. The three points on each side of the peak should extend down at least halfway to the background level. The background should be measured at points where the intensity profile has leveled out. Low and high background points are set individually so they need not be spaced equally.

The scan and background points for each reflection are entered with the EP command from the XRYMOD Menu. Specify the low and high angle background points as positive values in degrees 2θ since they are subtracted and added, respectively, from and to the zero tension 2θ value for the peak. The seven step scan normally has three equally spaced steps on each side with one additional point measured at the expected center of the peak. The number of side steps is therefore three and the 2θ increment between the side steps is entered in degrees. The center step is the 2θ increment between the center of the peak and the nearest point on each side. It is entered separately. These positive values are stored for each peak in MOD.IN as shown in Table 3 and in XRYMOD.TMP as shown in Table 4.

The tension range should run from about 0.4 mv to 3.5 mv and, as noted above, the sample size should be selected to allow this range to be used without danger of the sample breaking. Danger of sample breakage is minimized by using 50% of the expected tensile strength. For low tensile strength materials, it may be necessary to reduce the maximum tension to avoid a sample that is too large. The tension values to use can be specified by entering the number of tension values and the maximum and minimum tensions.* This will result in measurements at tension values selected to show whether or not there is

---

* With this option, the minimum tension is measured first, then the maximum. Every second intermediate tension value is omitted on the decreasing tension measurements and those omitted are measured as the tension is increased. Finally, the low tension measurement is repeated. The first column of Table 6 shows the sequence of tensionvaluesset up by this option.

hysterisis in the *d*-spacing *vs* tension relation. If the material being measured does not show relaxation, this is the preferable option.

In cases where the sample exhibits relaxation, the measured *d*-spacing values may depend on the tension history. In these cases, care must be taken to allow for the relaxation, and the sequence of tension values generated by the XRYMOD program should not be used. For such materials, the tension values can be entered individually and one can choose to calculate a separate X-ray modulus value from a series of increasing tensions and/or a series of decreasing tensions.

Several options relate directly to the relaxation problem. In one option, the program allows a relaxation time to be entered. This causes a delay after the requested tension is set. The delay continues until the tension change observed during the specified relaxation time is less than 0.006 mv at which time the peak scan begins. If several reflections are being scanned, the delay is ignored for all but the first reflection since the tension is adjusted only before the first peak in the list is scanned. Another option allows a fixed delay after the tension is set and before the scan begins. A third option, which must be used with care, resets the tension to the requested value after the relaxation delay time.

6. DATA ANALYSIS

Least-Squares Gaussian Peak Profile Fit

An accurate determination of 2θ for each reflection scan is mandatory for X-ray modulus studies. This requires that the step scan of the reflection measured must be fit with an appropriate function which will determine the center of the Bragg peak as accurately as possible. For most materials, a Gaussian curve has been found to be an adequate approximation for purposes of locating the center of the peak, *i.e.*, finding 2θ.

The least-squares equations for the Gaussian function,

$$I = I_o \exp\left(\frac{-(x-x_o)^2}{a^2}\right)$$

are included in the X-ray modulus code, XRYMOD, so that the fit is calculated automatically when the experimental data are measured. In this expression, I is the observed intensity expressed as a function of x in units of $2\sin\theta/\lambda$. I and I_0 are in counts per second (cps) after correction for the background, x_o is the center of the peak and a is the width parameter. When the linearized least-squares equations are solved, the parameters I_o, x_o and a are obtained. The X-ray background (measured for the first scan only) is subtracted before the fit is carried out. The full width at half maximum in $Å^{-1}$ is 1.66a. In degrees 2θ it is $\Delta 2\theta = 4\sin^{-1}(0.64182a)$.

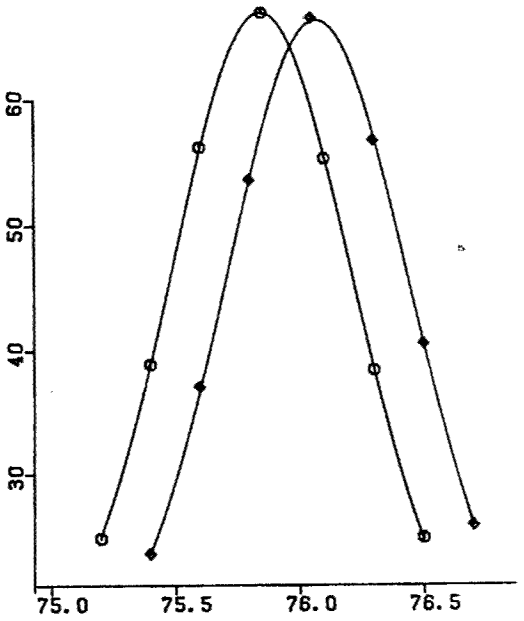

Figure 11. 2θ scans of PBZT at 20 N (right), 120 N (left); x-axis, 2θ, degrees; y-axis, cps.

The linearized least-squares calculation is done by subroutine PKFIT which takes a preliminary look at the scan data and selects an approximation to the peak height and width parameter. The 2θ value at maximum intensity provides the starting estimate of the *d*-spacing. The measured background is assumed to be linear. Fig. 11 shows the plot of a typical fit for the (0 0 10) reflection of PBZT made with program PKFTPL as discussed in the Appendix. Scans at two tensions are shown with the calculated Gaussian curves superimposed on experimental points. The final parameters and fit residuals are printed and recorded in the log file, XRYMOD.TMP.

Table 5 shows the PKFIT output for the (0 0 10) reflection of a different PBZT sample. This result is typical of materials with fairly sharp symmetrical peaks. In the table, successive lines show tension (mv), 2θ (degrees), observed intensity (cps), calculated intensity (cps) and the observed-calculated intensity difference for each of the seven steps of the scan. Both the observed and calculated intensities include the background. The final line gives 2θ for the peak center, *d*-spacing, I_o, a, goodness of fit and the observed background count at the peak center.

Table 5. *PKFIT output for a Gaussian fit of a seven step scan of the PBZT (0 0 10) reflection. The RU-200 X-ray source was used.*

```
          POINT  1 of 11 POINTS (PEAK # 1)
TENSION: requested = 0.600, set = 0.595 No. steps=    5
TENSION    0.593    0.592    0.593    0.590    0.591    0.593    0.591
2 THETA   75.41    75.61    75.81    76.06    76.31    76.51    76.71
  CPS     163.6    238.8    319.0    372.8    335.8    257.5    179.5
CLC CPS   161.1    240.9    320.3    370.9    335.0    260.2    178.0
DELTCPS     2.5     -2.0     -1.3      2.0      0.8     -2.7      1.5
     2TH      d        Io         a          SIG       BKG
  76.083 1.25098   326.8   0.005909   0.000249    44.5
```

Modulus Calculation

Modulus values are calculated from a linear least-squares fit of the tension readings (x axis in mv) and the d-spacings (y axis in Å). The reciprocal of the slope thus calculated, when scaled to give MKS units, is the ratio of force (in Newtons) to change in length (in meters). To find the modulus, this ratio must be multiplied by the ratio of length to cross sectional area. The length required is the average value of d for the reflection used. The area is the area of the sample which could be calculated from the number of fibers and the average fiber diameter. In practice, it is usually more convenient and probably more accurate to calculate the sample area from the fiber denier and density. If reliable denier and/or density data are not available, they can be measured. Flotation is the method of choice for measuring the density. Take care to be sure that the flotation liquid wets the fibers well, otherwise air bubbles are likely to introduce error.

The standard deviation of the y intercept and slope are calculated by the least-squares program which takes the tension values to be exact. This assumption is justified by the fact that the error in the tension measurement is normally small compared to the errors in d. The other quantities used to calculate the modulus from the slope, denier, density, *etc.*, are also assumed to be known exactly. Although this is not true and errors in the denier and density may not be negligible, they are usually difficult to estimate.

Input to the XRYMOD program includes the denier per fiber, the density of the material and the number of fibers in the sample. If the fiber area is to be used, it must be expressed in terms of fiber density and denier. In the following formula, Y_x is the X-ray tensile modulus, the slope of the lattice spacing *vs* tension curve is M (in Å/mv), d_o (Å) is the average lattice spacing, S (gm/mv) is the strain gauge calibration, ρ (gm/cm^3) is the fiber density, D_f is the denier per fiber and N_f is the number of fibers in the sample.

$$Y_x = \frac{0.0882\ d_o\ S\ \rho}{M\ D_f\ N_f}$$

The numerical factor converts the result to the normal MKS modulus unit, GPa (10^9 Pascals). One Pascal is one Newton per square meter and for comparison, one pound per square inch is 6894 Pascals. The program presents a summary of the modulus measurement as shown in Table 6.

Table 6. *Summary of a modulus measurement presented by XRYMOD. The data are for the (0 0 10) reflection of PBZT.*

```
Y-INTERCEPT =   1.250132 +/-0.33131E-04
      SLOPE = 0.85444E-03 +/-0.15447E-04
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2TH-DELT
0.589	1.25073	1.25064	0.00009	76.102	-0.007
3.472	1.25315	1.25310	0.00005	75.929	-0.004
2.842	1.25259	1.25256	0.00003	75.968	-0.002
2.219	1.25197	1.25203	-0.00006	76.013	0.004
1.557	1.25144	1.25146	-0.00002	76.051	0.002
0.922	1.25092	1.25092	0.00000	76.088	0.000
1.250	1.25120	1.25120	0.00000	76.068	0.000
1.898	1.25168	1.25175	-0.00007	76.034	0.005
2.533	1.25230	1.25230	0.00000	75.989	0.000
3.159	1.25283	1.25283	0.00000	75.951	0.000
0.606	1.25063	1.25065	-0.00002	76.109	0.001

```
MODULUS IS 405.1 +/-  7.3 GPA
```

In Table 6 the y intercept given is the d-spacing in Å at zero tension and the slope given is the slope of the line with x in mv and y in Å. The uncertainties are the standard deviations. The first two columns give the tensions used (in mv) and the d-spacing (in Å) for the corresponding scan from PKFIT. The last two columns give, for convenience, the 2θ values corresponding to the "observed" d (from the Gaussian fit) and the 2θ difference between observed and calculated values. The last line gives the calculated modulus and its standard deviation in GPa. It should be noted that repeat runs with the same sample, the same tension values and the same FDD and diffractometer positions give results where the calculated standard deviations can differ by up to a factor of two. This shows that the number of points used to determine the line, normally ten to twelve, is too small to give a fully reliable error estimate for the random error in Y_x.

A program, REPLOT, is useful if modulus calculations or plots need to be repeated. The program, discussed in the Appendix, can be used to divide a set of measurements or to combine two (or more) sets to investigate the effect on the calculated modulus of different tension ranges. The normal summary (as in Table 6) and plot are generated.

Calculation of the Modulus, Systematic Errors

As noted earlier, systematic errors can result from sample motion which is a function of tension. Various steps have been taken to minimize this source of error. The FDD has been constructed to be as rigid as possible, consistent with other requirements. Sample translation due to tension arm motion has been minimized by setting the arm position at the point where arm rotation will give minimum translational motion. A test for translation has been devised using a "sample" constructed with a gauge rod and the test used as a criterion to adjust the lower sample holder to minimize sample translation from this source.

Whatever residual errors remain in the modulus values from translation-related sources should, in principle, be eliminated by averaging the modulus values determined

with the FDD in different positions. For example, if a tension-related translation moves the sample in a direction to increase the modulus by δY_x, rotating the FDD by 180° would be expected to give a modulus in error by $-\delta Y_x$. The error would be eliminated by averaging the two results. This method has been extended to include four FDD positions, two pairs at right angles to each other and two diffractometer positions (2θ, $\chi = 90$ and -2θ, $\chi = -90$) for each of the FDD positions. Thus eight modulus values are available to compare and average. If the spread in the eight values is consistent with the average $\sigma(Y_x)$, it is likely that systematic error is not present, in any case, translation related systematic error should be eliminated by averaging the set of eight modulus results.

An example of such a series of measurements on the (110) reflection of T50 carbon is shown in Table 7. The zero tension 2θ value for this reflection is 77.93°. Experimental parameters were: 7 steps in the scans, each step counted for 80 s, side steps 0.23° apart, center step size 0.30°, incident beam collimator 1.0 mm, diffracted beam collimator 1.5 mm, diffracted beam aperture 2 mm wide and 6 mm high and a tension range from 0.4 to 3.1 mv. The peak count for this reflection was 920 CPS and the FWHM, 1.0° 2θ. A full series of measurements was made with $+2\theta$, $+\chi 90$ and -2θ, $-\chi 90$ for each of the four FDD positions.

Table 7. *X-ray modulus values for a series of measurements on the (110) reflection of T50 Carbon. Values in GPa.*

FDD Position	$+2\theta$ $+\chi 90$	-2θ $-\chi 90$	Ave. ++,--	U-D, D-T ave
DET	608.7 ± 11.5	624.2 ± 12.3	616.5	
TUBE	604.8 ± 12.5	592.2 ± 13.1	598.5	607.5
Ave D-T	606.8	608.2		
UP	528.7 ± 10.5	545.1 ± 11.9	536.9	
DOWN	745.1 ± 11.3	729.4 ± 16.5	737.3	637.1
Ave U-D	636.9	637.3		
				AVE 622.3 GPa

The σ's for the individual modulus values range from 10.5 to 16.5 GPa. The precision would be improved by using a greater tension range or fewer fibers. The fairly good agreement between the toward detector and toward tube positions suggests that for these FDD orientations there is little systematic error. This is the position where motion of the tension arm would cause sample translation. Apparently this has been minimized by optimal choice of tension arm position as noted in an earlier section.

There appears to be considerable systematic error between the up and down positions since the modulus values are seen to differ by about 200 GPa. Even so, the average value of 637 GPa differs by only 30 GPa from the average for the tube and detector measurements. Sample translation of 0.07 mm would be required to explain the 200 GPa difference between the modulus values in the up and down FDD orientation. This much sample motion as the tension changes from 0.4 mv to 3.1 mv seems unlikely but possible.

This example illustrates the value of averaging a set of eight measurements taken as described and gives some confidence in the result even when substantial systematic error is present.

7. STUDIES RELATING TO MEASUREMENT ERRORS

Peak Scan Study

The scan parameters for representative modulus samples have been examined in an effort to optimize the precision of the 2θ determination within a reasonable measurement time. The initial study was made on the Picker FACS-I system with a standard focus Cu X-ray tube (30 Kv, 20 ma, 3° take off angle), a highly oriented graphite monochromator and a diffracted beam aperture of 2x5 mm. The modulus samples used normally gave peak count rates of 5 to 20 cps with this system. In order to determine the peak position with the precision required for accurate modulus measurements, fairly long counting times are required. The variables available are the number of steps, counting time per step and the placement of the steps along the peak profile. Repeated runs for various combinations allowed an estimate of the standard deviation of *d* for each of the combinations tested.

An AFTECH II sample which gave approximately 14 cps at the peak was used to investigate the optimum scan conditions. The step size was adjusted so that each scan covered a 2θ range of 1.2° to 1.4°. Scans were approximately centered on the peak and the count rate was 4 to 6 cps at the scan limits. Scans for each set of scan parameters were repeated 25 to 35 times. The results are in Table 8.

Table 8. *Results of scan experiments on an AFTECH II sample. Total count at peak: 5,600 for 400 s, 2,800 for 200 s. σ(d) is the standard deviation of an observation.*

No. steps	step size Δ2θ°	count time per step (s)	ave. *d* Å	σ(*d*)* Å	time/scan (s)
4	0.4	400	1.25164	0.00005	1600
5	0.3	400	1.25164	0.00005	2000
6	0.3	400	1.25163	0.00004	2400
7	0.25	400	1.25167	0.00005	2800
6	0.3	200	1.25166	0.00006	1200
8	0.2	200	1.25167	0.00007	1600
10	0.15	200	1.25161	0.00007	2000

*0.00005 Å = 0.0035° 2θ for this reflection

In an effort to shorten counting time without sacrificing precision, the scan was modified to concentrate the counting time on the sides of the peak where $|\partial I/\partial 2\theta|$ is maximum. Three sets of scans were made with this technique. In each scan one measurement was made at the center of the peak with two, three or four steps on each side. The scans were centered on 2θ = 76.05°, the first point measured was at 75.4° or 75.5°. The results are in Table 9.

It would appear that large numbers of steps and long counting times do not significantly improve the precision of the *d*-spacing determination. Subsequent measurements suggest, however, that if less than about 2,500 counts are recorded at the peak center, a significant increase in σ(*d*) will be observed.

Table 9. *Step scan test. Steps on sides of the peak placed in region of maximum slope with one step near the center. Number of steps varied, scan range 1.3° to 1.5°.*

No. steps	count time per step (s)	ave. *d* Å	σ(*d*) Å	time/scan (s)
5	400	1.25146	0.00006	2000
7	400	1.25147	0.00006	2800
9	200	1.25148	0.00005	1800

The seven step scan has been adopted as standard procedure. The center point of the scan is near the peak maximum and the three points on the side extend down the sides of the peak at least as far as half maximum. On broad peaks, the points must be more widely spaced to encompass the peak, and the total count measured must be greater to achieve comparable accuracy in the *d*-spacing measurement. The above experiments and the argument that points measured on the steepest part of the peak, *i.e.*, the sides, will be most effective in pinning down the peak position, are consistent with this procedure.

Currently, measurements are made with the RU-200 rotating anode X-ray generator. X-ray flux is much higher with this source so somewhat shorter counting times are indicated but in most experiments peak counts of 30,000 or more are accumulated. This would seem unnecessary but experience indicates that some improvement in precision is obtained from the use of longer counting times. This may be partly due to greater fluctuations in the X-ray source. Both intensity changes and focal spot wandering may be involved.

The FACS-I system required manual adjustment of the tension between each scan and therefore placed a premium on efficient measurement. The inconvenience of longer counting times has been eliminated by the higher level of automation on the new system which allows program control of tension adjustment. Long runs are now possible without operator intervention since the only manual adjustment normally made during a measurement series is rotation of the FDD.

2θ Errors Due to Fiber Translation

An error in centering a sample in the diffractometer may cause an error in the measured 2θ for a Bragg reflection. Errors in 2θ are especially important in modulus studies because the determination of the large X-ray tensile modulus depends on an accurate detection of the very small 2θ shifts that are caused by the stress induced strain. Unfortunately, a device used to apply tension to the fibers may cause the fiber to shift toward or away from the X-ray tube as tension is applied. If such a shift occurs, the change in 2θ which is measured will be due partly to deformation of the crystallites and partly to the change in position of the fiber sample. It is therefore important to determine if a shift has taken place and to be able to estimate its magnitude. Shifts in the plane of the χ circle are easily observed with the telescope mounted on the Picker instrument, but shifts perpendicular to the χ circle are less easily seen and hard to quantitate. We now examine the relation between sample translation perpendicular to the χ plane and measured 2θ for a fiber sample.

The 2θ error introduced by a small translation of a fiber sample along the X-ray beam will be proportional to that translation, for a given reflection. This can be seen by consider-

ing the diffraction geometry for a fiber sample shown in Fig. 12. Here $\Delta x'$ is the apparent translation of the fiber sample; Δx, in mm, is the actual translation of the sample perpendicular to the plane of the χ circle and $\Delta 2\theta$ is the resulting error in 2θ. The relations are:

$$\Delta 2\theta = \frac{\Delta x'}{230}\ 57^{\circ}/\text{rad}\ ; \quad \text{where} \quad \Delta x' = \frac{\Delta x}{\cos\theta}\ \sin 2\theta$$

where 230 mm is the sample-to-detector distance. Note that a 1 mm displacement of the sample toward the X-ray beam will introduce an error of 0.3° if 2θ is 76°. The following experiment is an effort to place a limit on the magnitude of any undetected error in 2θ due to sample motion.

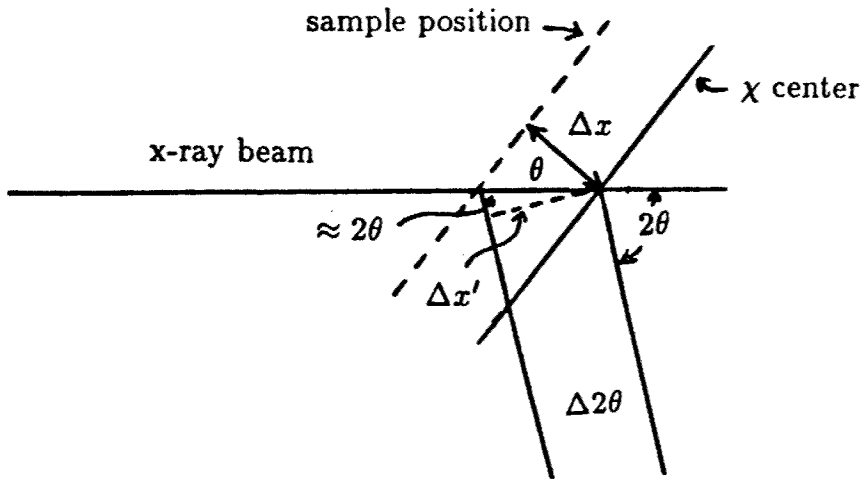

Figure 12. $\Delta 2\theta$ due to fiber sample translation perpendicular to the χ circle.

The first step in the experiment determines the motion of the sample that results from a given rotation of the translation screw on the lower sample mount holder of the modulus device. If the fiber is placed in a vertical orientation and translated in the χ plane, the microscope reticule can be used to measure the translation. The actual translation of the sample at the level of the incident X-ray beam will be less than the translation of the base mount because the opposite mount is approximately fixed, but, the fiber translation is *proportional* to the screw rotation. One turn of the translation screw moves the fiber in the beam by 0.57 mm.

The second step in the experiment determines the effect of known translation on the measured 2θ for an AFTECH II sample of 240 fibers. The sample was centered in the X-ray beam, then translated 3/8 screw revolution out of the center position toward the X-ray tube and then rotated to the diffracting position. The apparent 2θ value for the meridional peak at 76° 2θ was then determined by a step scan centered on the peak. The peak count rate was 14 cps and six steps 0.3° apart were counted for 400 s. The 2θ value was determined by least-squares fit of a Gaussian to the six observations. The translation screw was then advanced by 1/8 turn to move the sample back toward the center position and another scan was made. The result of six scans made in this manner is shown in Fig. 13 where 2θ is plotted *vs* the sample translation in mm. The slope of the line is $0.25 \pm 0.02^{\circ}$ per mm in reasonable agreement with the calculated value of 0.3° per mm.

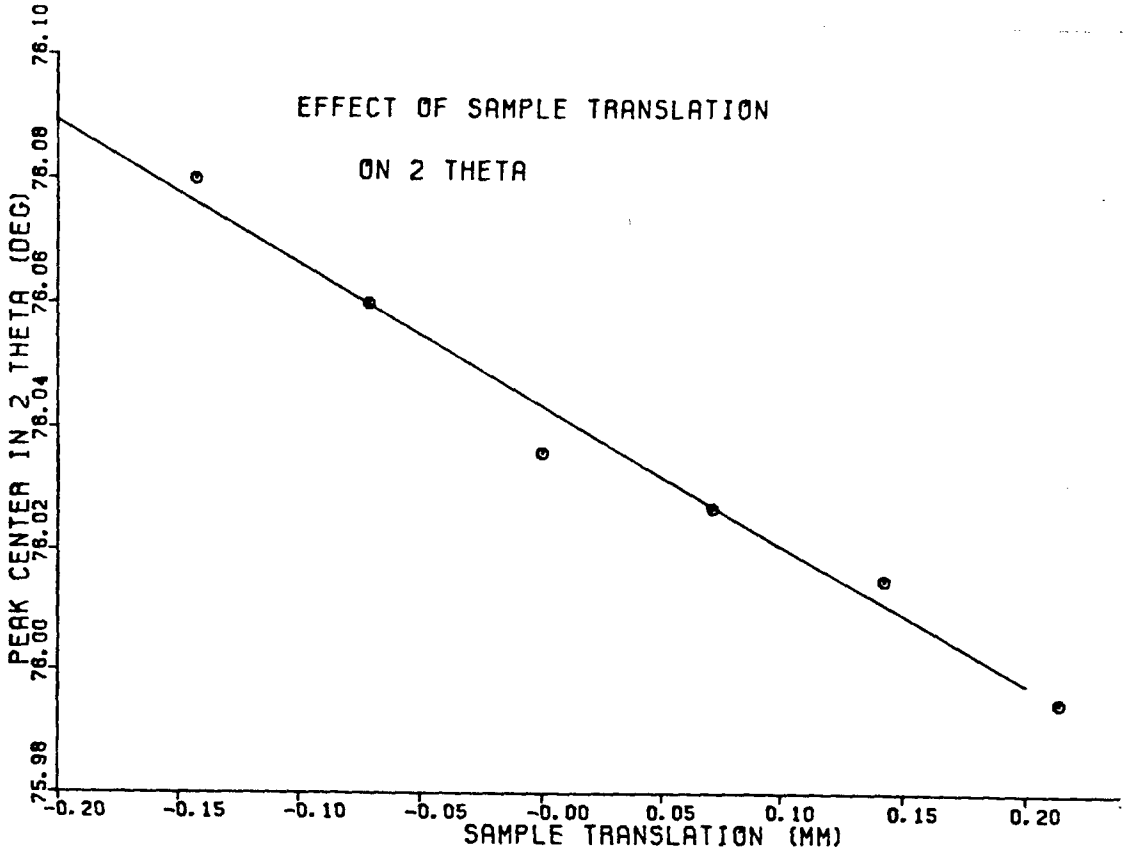

Figure 13. Relation between measured 2θ and sample position.

When the FDD is used, tension is applied to the sample by a cantilever arrangement operated by the micrometer screw. Motion of the cantilever may cause a small translation of the upper end of the sample perpendicular to the fiber axis. In normal use, this translation is minimal because only a few turns of the micrometer screw are required to produce the maximum tension needed. However, the FDD is sometimes mounted so that the expected translation, though small, will move the sample perpendicular to the plane of the χ circle. The resulting 2θ error will be positive or negative depending on the direction of the translation. If the modulus device is rotated 180° the direction of translation and therefore the sign of the 2θ error will reverse. Therefore, any errors in the calculated modulus can be eliminated by averaging modulus values obtained with the modulus device in each orientation.

In addition to sample translation introduced by movement of the tension arm there is also the possibility that applied tension will translate the sample because of compliance in other parts of the FDD. For example, if the lower sample mount holder is tipped slightly off the ϕ axis of the diffractometer, the application of large tensions will tend to straighten it and thereby translate the sample. If the FDD is rotated 180°, the error introduced by the compliant part of the device should change sign and averaging the two results should eliminate the error.

Multi-Fiber Samples with Non-Uniform Tension

It is fairly obvious that if some fibers in a sample are longer than others, the short fibers will bear the applied force first, be stretched as a result, and show an increase in *d*-spacing as compared to the longer fibers. This length distribution translates to a tension distribution, which results in a *d*-spacing distribution at any applied tension. It is not easy to see how large this effect will be, how it might be detected, and whether it will introduce an error in the X-ray modulus measurement. Since the problem is a relatively simple one to formulate (if the length distribution of the fibers is known) one should be able to calculate the result. This has been done as will now be explained.

The intensity of the diffraction peaks is easily expressed as a Gaussian function in terms of parameters that are obtained for each scan by least-squares fit. The expression,

$$I(x) = I_o \exp\left(\frac{-(x_o - x)^2}{a^2}\right),$$

can be applied to individual fibers in the sample. $I(x)$ will be the intensity of diffraction from a single fiber which has a peak intensity of I_o where the peak center is at x_o. The width parameter is a and the expression is a function of x where both x and x_o are in units of $2\sin\theta/\lambda$. With Bragg's Law, both x and x_o can also be expressed in terms of d which in turn can be related to the extension of the fiber.

If the specimen is unstressed, the diffraction peak will be centered at x_o. If tension is applied, x_o decreases as d increases and the increase in d can be related to tension if the modulus and the cross sectional area of the fiber are known. For the tensile modulus, Y_t, we have the relations between tension, F, area, A, unstressed length, l_o, and length, l, thus,

$$Y_t = \frac{F/A}{(l - l_o)/l_o} \quad \text{or} \quad F = Y_t A \frac{l - l_o}{l_o}.$$

For the X-ray tensile modulus, Y_x, we replace l by d, the crystal spacing, and then

$$F = Y_x A \frac{d - d_o}{d_o}$$

where we have written d_o for the fiber spacing at zero tension and d for the spacing when the fiber is stressed. Note that the replacement of d for l is valid even if Y_t and Y_x are not equal, so long as they are not functions of tension.

If sufficient stress is applied to stretch some fibers, but not others, then those which are not stressed have their unstressed length, l_o, and will diffract with the peak center at x_o. Those which are stressed will diffract with a peak center at x_{os}. For each individual fiber, the value of x_{os} will be determined by the tension on that fiber. We can thus distinguish two cases which we do in terms of the physical length of the sample, L. At zero tension, L is equal to l_o for the shortest fibers in the sample. As L increases, all fibers with l_o longer than L are unstressed and all fibers shorter than L are stretched so that their actual length, l, is equal to L. For these fibers the position of the diffraction peak shifts and the shift, in terms of d, is proportional to the physical extension of the fiber. Thus, we have two classes of fibers in our sample.

Case I. unstressed fibers with $l_o \geq L$

Case II. stressed fibers with $l_o < L$ and $l = L$.

For case II the position of maximum diffraction will be expressed as

$$x_{os} = \frac{l_o}{L\, d_o} \quad \text{since} \quad x_{os} = \frac{1}{d} \quad \text{and} \quad \frac{d}{d_o} = \frac{L}{l_o} .$$

Remember that l_o expresses the unstressed length of each fiber in the sample and that the numerical value of l_o, in general, differs for each. The intensity for any case II fiber will be given by

$$I(x) = I_o \exp\left(\frac{-(x_{os} - x)^2}{a^2} \right) .$$

The observed diffraction peak will be the sum of the intensities for the individual fibers and the shape of the peak, as well as its position in 2θ, can be expressed as a function of L or as a function of applied force, F.

The effect of non-uniform samples on an X-ray modulus experiment was studied by simulating the modulus experiment with a computer program prepared for this purpose. The program, called CALMF, calculates the diffraction peak profile for all fibers in the sample assuming the peak profile to be Gaussian. The individual diffraction profiles are summed to obtain the simulated diffractometer scan which is fit by least-squares to the usual Gaussian to find the peak center. The applied tension is calculated from the assumed mechanical tensile modulus and the sample strain, also by summing over the individual fibers. The X-ray modulus is then found by the usual linear least-squares fit of the tension *vs* *d*-spacing for the sample.

The X-ray modulus simulation is carried out by specifying the distribution of fiber lengths in the sample and the parameters of the material, the sample and the experimental conditions, *i.e.*, the strain, X-ray background, *etc*. The initial and final lengths of the sample are chosen and the change in length is divided into nine steps. The strain of each fiber in the sample is calculated in turn for each elongation step with the short fibers stressed first while longer fibers remain at their natural length. The increase in d is obtained from the assumed modulus of the material for those fibers that are elongated by the applied tension. The diffraction peak profile is calculated for the unstressed (case I) fibers and also for the stressed fibers (case II) which contribute at different diffraction angles, depending on their elongation. The composite diffraction peak for the stressed and unstressed fibers is fit to a Gaussian by least-squares using the same algorithm used in the X-ray modulus program, XRYMOD, which runs the actual diffraction experiment. The remainder of the calculation is also carried out by the XRYMOD subroutines to give an X-ray modulus value and a table of "observed" and calculated values for the simulated experiment.*

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* The simulation differs in two minor respects from the actual X-ray modulus experiment. The 2θ scan range in the simulation is fixed for all strain values. In the experiment, 2θ is adjusted so the scan "follows" the peak to a lower angle as the strain is increased. In the simulation, the sample length is increased in uniform steps, whereas, in the experiment, the tension is increased in uniform steps. It is judged that the effect of these differences is minor.

The simulation program was used to study eight samples with different length distributions. All eight samples confirm the result that X-ray modulus measurements on non-uniform samples will give an X-ray tensile modulus that is independent of the fiber lengths in the sample. The result for some of these simulations is shown in Table 10.

Table 10. *Summary of simulated X-ray modulus experiments. Sample parameters for PBZT are used for all entries below with an assumed X-ray modulus of 400 GPa and an assumed mechanical tensile modulus of 300 GPa. All simulated samples have 300 fibers.*

Samples	initial & final length (cm)	Tension (mv)	width param. x10^5	peak height	2θ range (°)	Modulus (GPa)
A	2.50 - 2.52	0.0 - 3.7	658 - 658	300 - 300	76.10 - 75.57	401.2±0.0
B	2.50 - 2.52	0.0 - 1.8	658 - 756	300 - 264	76.10 - 75.83	401.0±0.1
B	2.51 - 2.53	0.9 - 3.7	680 - 754	290 - 264	75.97 - 75.57	400.8±0.3
C	2.51 - 2.53	0.5 - 3.7	672 - 699	292 - 282	76.03 - 75.57	398.4±0.3
D	2.51 - 2.53	1.2 - 4.9	669 - 676	295 - 292	75.92 - 75.40	400.7±0.2

A Uniform sample. All fibers are 2.500 cm long

B 150 fibers, 2.500 cm; 150 fibers; 2.520 cm

C Gaussian distribution of fiber lengths. Minimum length, 2.49 cm (one fiber), ave. length 2.510 cm (17 fibers), Maximum length, 2.53 cm (one fiber)

D 150 fibers, 2.500 cm; 100 fibers, 2.505 cm; 30 fibers, 2.510 cm; 20 fibers, 2.515 cm. This distribution of fiber lengths is judged to be reasonable for a normal modulus sample.

Consider first sample A, with all fibers of equal length. The ten points on the simulated modulus curve covered a range of lengths from 2.50 cm to 2.52 cm, *i.e.*, all fibers were stretched by 0.02 cm to give a maximum strain of 0.8% which for the 300 fibers in the sample gave a maximum tension of 3.7 mv or 97 N. For this uniform sample, the width parameter and the Bragg peak height were constant, the 2θ for the peak changed from 76.10° to 75.57°. The calculated modulus of 401.2 GPa differs slightly from the assumed value of 400 GPa, probably due to rounding errors in the calculations.

Sample B illustrates all the essentials of a non-uniform sample. In the first of the two listed experiments in Table 10, there are, in effect, two samples, one strained and the other unstrained. Both diffract simultaneously to give a combined Bragg peak. The composite peak has one part which shows no change in diffraction angle, the other part moves with tension. The change in diffraction angle for the second part is larger than the nominal tension value suggests since this tension is applied to only half of the sample fibers. The composite peak, then, is made up of two peaks, one stationary, the other shifted by approximately twice the expected amount. When the composite peak is subjected to the least-squares fit, its center is found to shift by the expected amount for a uniform sample where the total tension is divided equally between all fibers. The width parameter for the composite peak will be larger and the peak height smaller because the peak is a composite of two peaks at slightly different values of 2θ. The peak height drops from 300 cps to 264 cps at maximum tension while the width parameter increases from 0.00658 at zero tension to 0.00754 at maximum tension.

Samples with various length distributions, subjected to different strains, have been studied. The principle illustrated by the dual sample, B, applies to all non-uniform samples and produces the same result, *i.e.*, an X-ray tensile modulus value independent of the length distribution of the fibers in the sample. The variation in strain for the individual fibers in the sample is measured by the increase in the width parameter and the decrease in the peak height.*

The above examples suggest that one should expect no problems from a fiber sample which has a non-uniform length distribution. There is, in fact, one serious problem with such a sample. If the tensile strength of the shorter fibers is exceeded, they will break. Depending on the length distribution in the sample, fibers may break before maximum tension has been applied. Fewer fibers then remain to carry the load and if more break, the entire sample may be destroyed even though only a fraction of the nominal breaking tension has been applied. This result is more likely with high modulus fibers which may stretch very little before breaking.

G30 Scan Error Experiment

In X-ray modulus measurements made on G30 carbon (modulus sample G30a), the σ's for the individual modulus values are quite large (9 to 30 GPa) due to the difficulty of making precise 2θ determinations for the peak. The peak count for the reflection used is 460 to 480 CPS and the FWHM is about 4.2° 2θ and the center of the 2θ diffraction peak is 43.23°. These three factors, a relatively weak, broad, low angle peak, make it difficult to determine 2θ values accurately. Note that if one counts for 400 s on each step, the σ for each count will be 0.7 CPS for the end points of the scan. The X-ray intensity from the generator has been observed to vary by nearly 1% between adjacent 400 s counts (see **RU-200 X-ray Stability Test**, below), which is a count rate variation of two CPS or more. If the 2θ value determined by fitting a scan is compared to the 2θ value obtained from the same scan with the end points of the scan changed by +3 and -3 CPS, 2θ for the peak center will change by 0.008° and the corresponding *d*-spacing will change by 0.00038. Errors of this magnitude are comparable to the largest deviations observed on the *d*-spacing *vs* tension plots for the G30a sample.

An experiment was performed to determine the statistical error in the *d*-spacing when this peak is scanned in the mode used for modulus measurements. The tension was set at 0.5 mv and 28 scans were made with a counting time of 400 s per step and another series of 33 scans was run with a counting time of 1000 s per step. The usual least-squares algorithm in PKFIT was used to find *d* for each scan. The average *d* and σ_d were calculated for each of the series. The results are displayed in Fig. 14.

The standard deviations, calculated from the scatter of the *d* values are similar for both series. They are: 0.00015 and 0.00016 Å respectively. Increasing the counting time from 400 s per step to 1000 s per step does not appear to increase the precision of the *d*-spacing values. It may be that the fluctuation in X-ray intensity observed in a separate experiment (see below) sets the effective limit on the precision of this measurement.

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* A caution is necessary here since real fibers can undergo structural changes as tension is applied which will change the shape and height of the Bragg peak. These changes could be opposite to those observed in the simulation studies.

The *d*-spacing *vs* tension curves from which the modulus values for G30 carbon are calculated show deviations of the individual measurements in *d* comparable to the σ's observed in this experiment. The conclusion suggested is that random errors in the modulus values are the minimum that can be obtained with this material and the equipment available. Improved precision in the modulus measurements could come from a larger number of measurements or an increase in the tension range used. It is also important to note that the relatively large error in *d* observed for G30 carbon should not be present when materials with sharper peaks are studied.

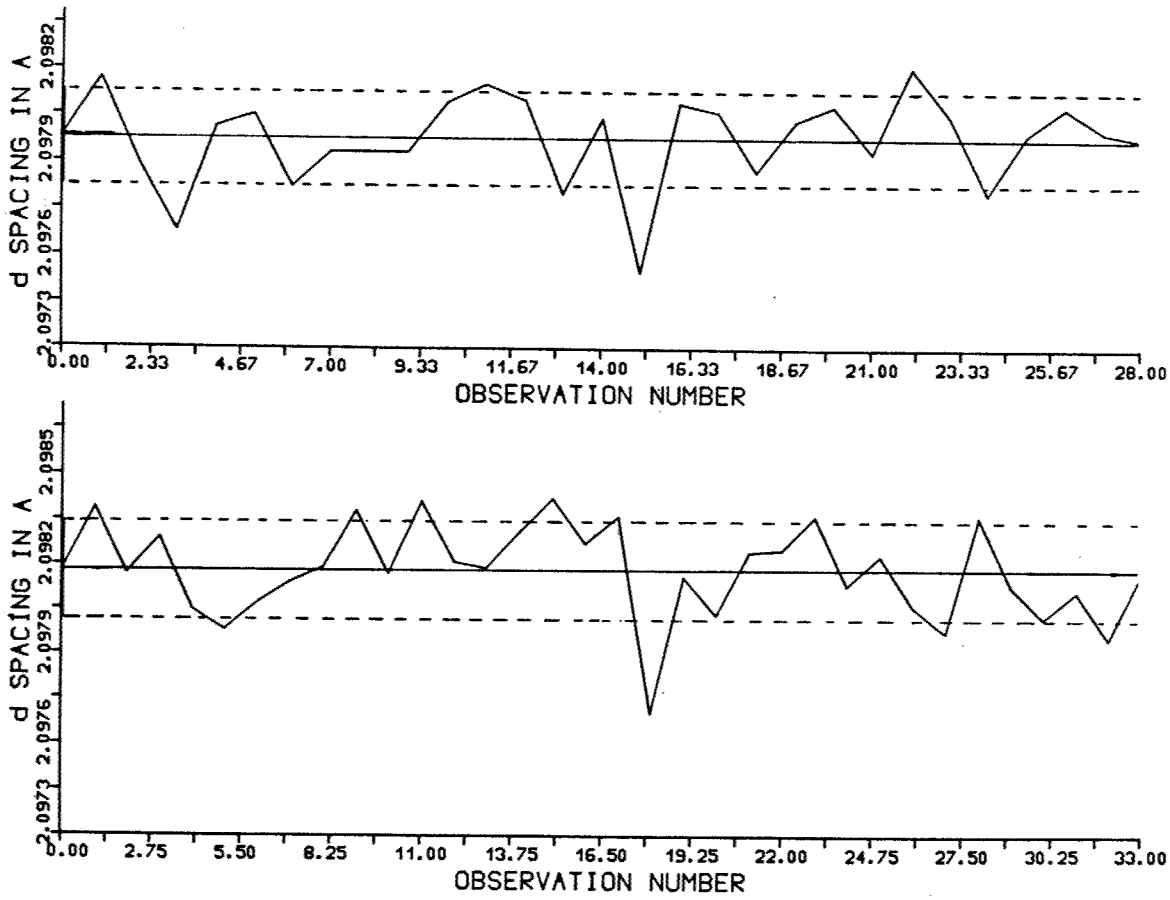

Figure 14. G30 carbon *d*-spacing for repeated measurement of the (100) reflection. The solid line is the average *d* for the series, the dashed line shows $d+\sigma_d$ and $d-\sigma_d$. Upper plot shows the result with 400 s step count, lower shows 1000 s counts.

RU-200 X-ray Stability Test

The difficulty of obtaining consistent scan results for G30 carbon prompted an investigation of the X-ray output stability. As noted above, fairly small fluctuations in the X-ray intensity on a time scale comparable to the scan time for a single scan can introduce a noticeable error in the X-ray modulus values.

Two experiments were run. Both used the diffracted intensity from the 43.25° peak of G30 carbon (modulus sample G30a) with instrument settings of: SVA 3x6 mm, collimators; 1.0 mm incident, 1.5 mm diffracted, 45 Kv, 70 ma, no filter. The count rate was

about 480 CPS. The program STABLE was used to measure repeated counts for a fixed time interval. In the first experiment, the counting time was 400 s, the time for each of the steps in the G30 modulus scans. Over a period of 19 hr. 168 measurements were made. The results are plotted in Fig. 15 which shows the total count accumulation in 400 s plotted against observation number. The standard deviation, based on counting statistics, is 430 counts, a little less than the distance between tick marks on the count axis in the figure. Fig. 16 shows the results for the second experiment where the result for the 175 measurements were made with counting times of 1000 s over a period of 49 hr. In this figure, the COUNTS scale is shortened by a factor of 2.5 so that a given percent change in counts is represented by the same distance on each plot. Here the standard deviation is 680 counts, less than half the distance between the tick marks.

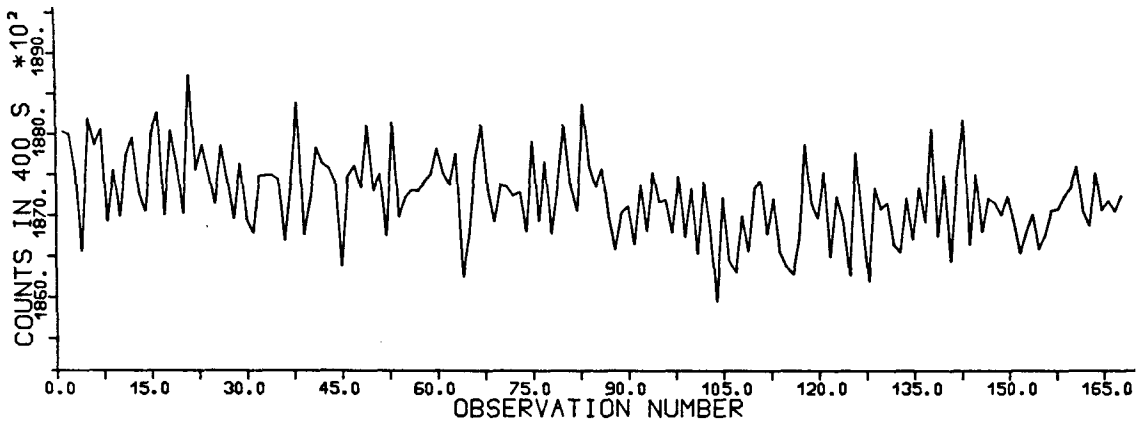

Figure 15. Stability experiment for RU 200 unit, intensity from (100) G30 carbon peak; 400 s counting time gives a standard deviation of 430 counts.

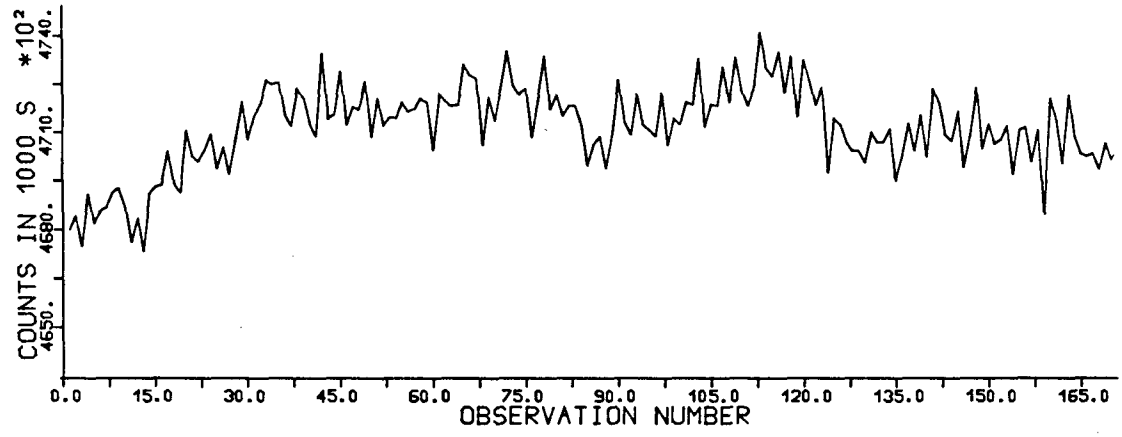

Figure 16. Same as Fig. 15 with 1000 s counting time. Here the standard deviation is 680 counts. COUNTS axis shortened by a factor of 2.5 to adjust for greater counting time.

In both figures, the apparent count rate frequently changes by several standard deviations over a time scale of a few observations, *i.e.*, less than the time required to scan one modulus data point with either a 400 s or 1000 s step count time. The cause of this variation in apparent X-ray output is not known.

8. EXAMPLES OF X-RAY MODULUS MEASUREMENTS

General Comments on the Results

The following pages show examples of X-ray modulus measurements made with the materials mentioned in the introduction. These materials illustrate the problems encountered and the results obtained to date with the automated FDD and the analysis methods employed, *i.e.*, those described in the preceding sections of this report. The modulus values given with any example are for that particular measurement and they may differ significantly from values determined by averaging measurements taken with the FDD and the diffractometer in all of the eight positions used for a complete modulus series.

Each example shows two 2θ scans of the reflection used for a modulus measurement. One scan is made at minimum tension and one at maximum tension. They are plotted together to show graphically the fit and the shift in 2θ obtained. The printed summary given in the first table for each example shows the observed and calculated counts for the Gaussian fit as carried out by PKFIT along with the calculated *d*-spacing and other Gaussian parameters. The second graph, a *d*-spacing *vs* tension plot, is made with scans at each tension in the modulus run including the maximum and minimum tension scans shown in the first plot. The graph is produced by CALMOD in the X-ray modulus program, XRYMOD. The printed summary for the data in this graph is shown in the second table.

The following table summarizes parameters from the examples which are expected to be relevant to the design of X-ray modulus experiments. In Table 11, ΔT is the difference between the maximum and minimum tension applied, %BStr is the ratio of maximum tension to the breaking strength, Δ2θ is the change in 2θ resulting from the applied tension, FWHM is the full width at half maximum for the reflection used and the %error column gives the observed percent error (from the least-squares calculation of the modulus), an average value from repeated runs.

Table 11. *Parameters characterizing the X-ray modulus measurement examples.*

Material	*h k l*	ΔT (mv)	%BStr	Δ2θ°	FWHM°	Δ2θ/FWHM	%error	Δd/d
PBZT	0 0 10	2.90	25	0.172	0.863	0.199	1.6	0.0019
KEV149	0 0 4	0.81	44	0.113	0.545	0.207	1.6	0.0040
KEV149	0 0 6	0.79	44	0.172	0.633	0.272	1.5	0.0040
G30	1 0 0	3.03	21	0.095	4.215	0.023	3.7	0.0021
T50	1 0 0	3.02	38	0.070	1.090	0.064	2.7	0.0016
T50	1 1 0	3.03	38	0.136	1.085	0.125	2.2	0.0015
Silk	0 0 2	0.67	59	0.182	0.978	0.186	1.3	0.0071
Silk	0 0 6	0.67	59	0.592	1.956	0.303	1.4	0.0059

Inspection of the scan plots shown below for PBZT, KEVLAR 149 (both reflections) and Silk (both reflections) will show symmetrical curves which are well fit by the Gaussian model. The 2θ separation resulting from the applied tension is relatively large. In Table 11

and in the discussion of these examples, the $\Delta 2\theta$/FWHM values are seen to be in the range of 0.2 to 0.3 and the resulting modulus values have errors of 1.3 to 1.6%. The only irregularity noted appears in the plot (Fig. 29) for the degummed silk (002) reflection where the high tension scan is reduced in height. The explanation for this appears to be that the peak is broadened by tension. One also notes that, contrary to expectations, the observed modulus is smaller for the (002) reflection than for the (006) reflection. The meridional reflections of silk, and the (002) in particular have high background scattering and this may, in some way affect the peak fit and consequently the observed 2θ values. The effect deserves more study.

Unlike this result for Silk, the modulus values for the Kevlar reflections (004) and (006) agree well as one would expect. Generally, when the reflections are fairly sharp and symmetrical, good agreement is found between modulus values for different orders of the same reflection. Earlier X-ray modulus measurements reported for heat treated PBZT (650° C) were made with the (007), (0 0 10) and (0 0 12) reflections. These gave modulus values of 390, 394 and 396 GPa respectively with estimated errors of about 7 GPa (Lenhert and Adams, 1985).

It should also be noted that silk has a tendency to relax when it is stretched so that when the sample is stretched with the FDD, tension increases to a maximum value. Over time the tension is seen to drop as the sample relaxes. The data shown in the silk example was measured by setting the tension, repeating the tension reading at intervals and starting the scan only after tension decay had effectively stopped. The tension used in the plots and the calculations is the tension measured at the time of the scan.

The KEVLAR and Silk experiments used 44% and 59%, respectively, of the tension expected to break the samples. Experience shows that 50% is a safe tension to use. The PBZT experiment used only 25% of the breaking tension. This measurement could be improved by using a smaller sample and the same tension range, thus increasing the $\Delta 2\theta$/FWHM ratio with an expected reduction in the error. Larger samples of KEVLAR 149 and Silk would allow an increase in tension range, facilitating improved tension measurements with the FDD. Although this would not change the $\Delta 2\theta$/FWHM ratio, a small reduction in the modulus error would be expected.

Scans of the T50 carbon sample are slightly asymmetrical and not exactly Gaussian in shape. The $\Delta 2\theta$/FWHM ratio is significantly smaller than observed for the first three materials, partly because the X-ray modulus is higher and partly because the optimum tension range has not been used for this sample. The difference between the X-ray modulus value obtained for the (100) and the (110) reflections needs further study. Partial overlap of the (100) reflection with the (101) reflection may contribute to the apparent difference in the measured modulus, especially since the sample is from a twisted yarn.

Measurement of the G30 carbon X-ray modulus was undertaken as a test of the method. The (100) reflection is broad and non-Gaussian. The $\Delta 2\theta$/FWHM ratio is very small, mostly because of the large FWHM (about 4.2°) for the reflection. Only 21% of the breaking tension was applied since the only material available consisted of a yarn of 3000 fibers. (The problem of enumerating the small carbon fibers deterred us from separating the yarn.) This combination of factors along with the high modulus is responsible for the large statistical error in the modulus value reported. Because of the peak width, asymmetrical shape and the long counting times used, the result may also include significant systematic errors.

Example I. PBZT (0 0 10) Reflection at 2θ = 75.14° (d = 1.2501 Å)

This sample contains 700 fibers with a diameter of 13.1μ. The mechanical tensile modulus is 293 GPa and the tensile strength 3.88 GPa. The maximum tension applied corresponds to approximately 25% of the breaking strength. A 2θ shift of 0.172° results from an increase in tension of 2.90 mv (75.3 N). The FWHM is 0.863°; Δ2θ/FWHM is 0.199. The $\Delta d/d$ ratio is 0.0019.

Figure 17. (top right) Plot of experimental points for PBZT (0 0 10) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 12.

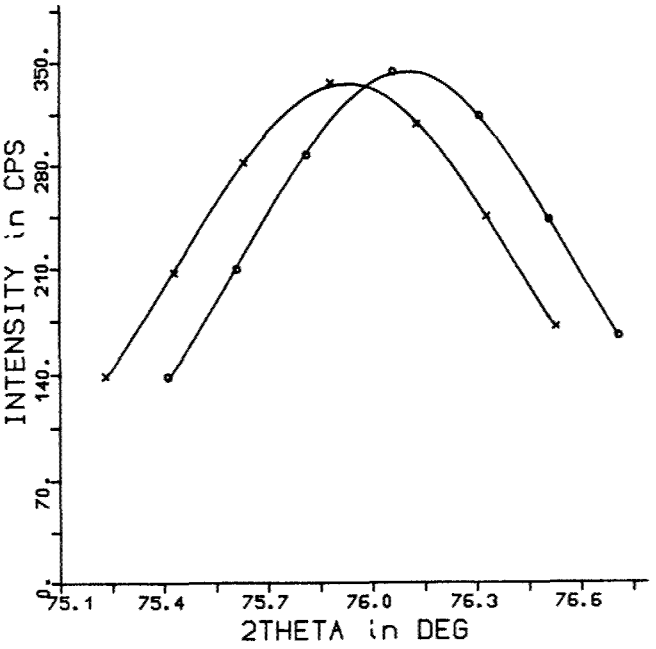

Figure 18. (lower) Plot of *d*-spacing *vs* tension for a PBZT (0 0 10) modulus run including the two points in Fig. 17. Data points for this plot are in Table 13. The modulus shown, 405.1±7.3 GPa, compares to the value of 394 GPa previously reported.

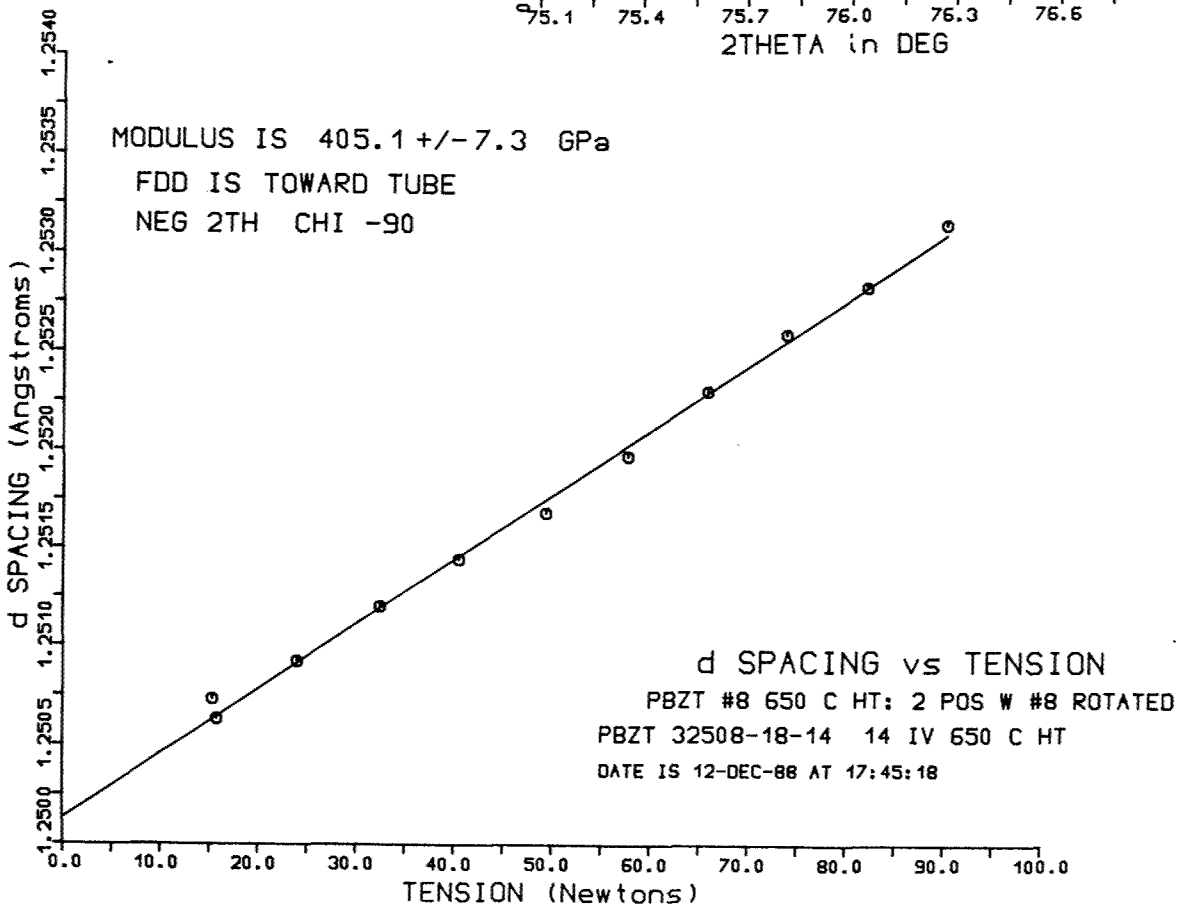

Table 12. *Summary of the Gaussian least-squares fits for 2θ scans of the (0 0 10) reflection of PBZT. The first scan is at the minimum tension of 0.593 mv (15.4 N), the second at the maximum tension of 3.488 mv (90.6 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 17.*

```
 PBZT #8  0.593  and  3.488 mv  12-DEC-88  40 Kv 80 ma
 -2T -CH90  TUBE  100s  No FILT  3.0 mm SVA
BKG
2TH = 74.10  CPS =    39.4
2TH = 78.10  CPS =    36.4

2TH OBS   75.41  75.61  75.81  76.06  76.31  76.51  76.71
OBS CPS   138.3  209.4  287.3  343.2  313.5  242.4  164.4
CLC CPS   136.5  210.6  288.2  342.3  313.1  243.0  164.4
DELTCPS     1.8   -1.2   -0.9    0.9    0.4   -0.6    0.0
     2TH     d       Io        a         SIG      BKG
  76.100 1.25075  305.6  0.005786  0.000073   37.9

2TH OBS   75.23  75.43  75.63  75.88  76.13  76.33  76.53
OBS CPS   138.7  206.9  281.5  336.0  307.6  244.6  170.5
CLC CPS   137.5  208.4  281.8  334.0  309.3  244.8  169.7
DELTCPS     1.2   -1.5   -0.3    2.0   -1.7   -0.2    0.8
     2TH     d       Io        a         SIG      BKG
  75.928 1.25316  297.4  0.005953  0.000128   37.9
PLOT MADE DATE IS 13-MAR-90 AT 14:12:48
```

Table 13. *Summary of modulus calculation for the (0 0 10) reflection of PBZT as plotted in Fig. 18. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig. 17.*

```
   Y-INTERCEPT =   1.250132 +/-0.33131E-04
         SLOPE = 0.85444E-03 +/-0.15447E-04

X-OBS      Y-OBS      Y-CALC      Y-DELT     2 TH-OBS   2 TH-DELT
0.589    1.25073    1.25064     0.00009      76.102      -0.007
3.472    1.25315    1.25310     0.00005      75.929      -0.004
2.842    1.25259    1.25256     0.00003      75.968      -0.002
2.219    1.25197    1.25203    -0.00006      76.013       0.004
1.557    1.25144    1.25146    -0.00002      76.051       0.002
0.922    1.25092    1.25092     0.00000      76.088       0.000
1.250    1.25120    1.25120     0.00000      76.068       0.000
1.898    1.25168    1.25175    -0.00007      76.034       0.005
2.533    1.25230    1.25230     0.00000      75.989       0.000
3.159    1.25283    1.25283     0.00000      75.951       0.000
0.606    1.25063    1.25065    -0.00002      76.109       0.001

   MODULUS IS 405.1 +/-  7.3 GPA
```

Example II. KEVLAR 149 (004) Reflection at 2θ = 27.59° (d = 3.2332 Å)

This sample contains 233 fibers with a diameter of 11.8μ. The mechanical tensile modulus is 149 GPa and the tensile strength 2.34 GPa. The maximum tension applied corresponds to approximately 44% of the breaking strength. A 2θ shift of 0.113° results from an increase in tension of 0.81 mv (20.9 N). The FWHM is 0.545°; Δ2θ/FWHM is 0.207. The $\Delta d/d$ ratio is 0.0040.

Figure 19. (top right) Plot of experimental points for KEVLAR 149 (004) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 14.

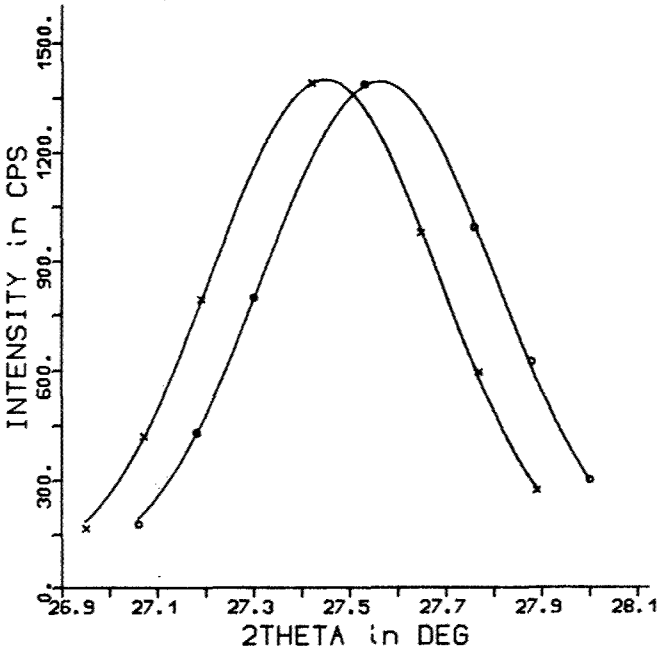

Figure 20. (lower) Plot of *d*-spacing *vs* tension for a KEVLAR 149 (004) modulus run including the two points in Fig. 19. Data points for this plot are in Table 15. The modulus shown, 203±2.9 GPa, compares to the value previously determined, 207.8 GPa, which was obtained by averaging measurements taken on both the (004) and (006) reflections.

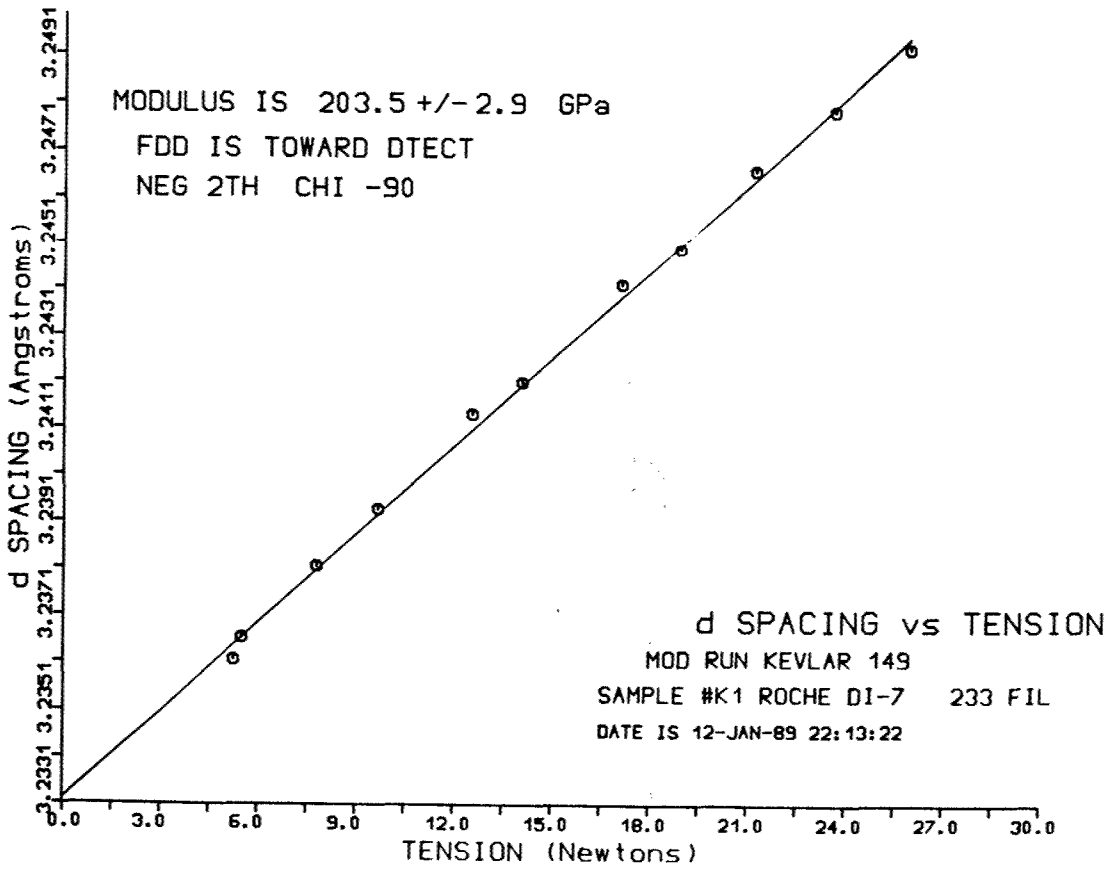

Table 14. *Summary of the Gaussian least-squares fits for 2θ scans of the (004) reflection of KEVLAR 149. The first scan is at the minimum tension of 0.204 mv (5.3 N), the second at the maximum tension of 1.009 mv (26.2 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 19.*

```
 KEVLAR 149   0.204 and  1.009 mv  12-JAN-89
 -2T -CH90  DET  100s  No FILT  1.5mm SVA
BKG
2TH = 25.86  CPS =    48.4
2TH = 29.46  CPS =    33.1

2TH OBS   27.06  27.18  27.30  27.53  27.76  27.88  28.00
OBS CPS   179.6  428.8  796.3 1385.9  990.7  622.4  299.9
CLC CPS   197.4  427.4  791.2 1382.7 1006.2  606.8  299.1
DELTCPS   -17.8    1.4    5.1    3.2  -15.5   15.6    0.8
     2TH     d       Io        a         SIG     BKG
  27.562 3.23620 1353.3  0.003746  0.000457   40.8

2TH OBS   26.95  27.07  27.19  27.42  27.65  27.77  27.89
OBS CPS   166.3  419.2  793.2 1389.0  976.1  593.2  270.6
CLC CPS   188.0  416.0  785.6 1390.3  985.4  578.0  276.1
DELTCPS   -21.7    3.2    7.6   -1.3   -9.3   15.2   -5.5
     2TH     d       Io        a         SIG     BKG
  27.449 3.24927 1358.8  0.003666  0.000481   40.8
PLOT MADE DATE IS 13-MAR-90 AT 14:41:17
```

Table 15. *Summary of modulus calculation for the (004) reflection of KEVLAR 149 as plotted in Fig. 20. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å obtained from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig. 19.*

```
Y-INTERCEPT =   3.233219 +/-0.14658E-03
      SLOPE = 0.16348E-01 +/-0.23531E-03
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.202	3.23616	3.23652	-0.00036	27.562	0.003
0.994	3.24924	3.24947	-0.00023	27.449	0.002
0.814	3.24668	3.24653	0.00015	27.471	-0.001
0.657	3.24420	3.24396	0.00024	27.493	-0.002
0.482	3.24139	3.24110	0.00029	27.517	-0.003
0.299	3.23815	3.23811	0.00004	27.545	0.000
0.371	3.23937	3.23928	0.00009	27.535	-0.001
0.540	3.24208	3.24205	0.00003	27.511	0.000
0.726	3.24498	3.24509	-0.00011	27.486	0.001
0.907	3.24794	3.24805	-0.00011	27.460	0.001
0.211	3.23663	3.23667	-0.00004	27.558	0.000

```
MODULUS IS 203.5 +/-  2.9 GPA
```

Example III. KEVLAR 149 (006) Reflection at 2θ = 41.92° (d = 2.1550 Å)

This sample contains 233 fibers with a diameter of 11.8μ. The mechanical tensile modulus is 149 GPa and the tensile strength 2.34 GPa. The maximum tension applied corresponds to approximately 44% of the breaking strength. A 2θ shift of 0.172° results from an increase in tension of 0.79 mv (20.5 N). The FWHM is 0.633°; Δ2θ/FWHM is 0.272. The $\Delta d/d$ ratio is 0.0040.

Figure 21. (top right) Plot of experimental points for KEVLAR 149 (006) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 16.

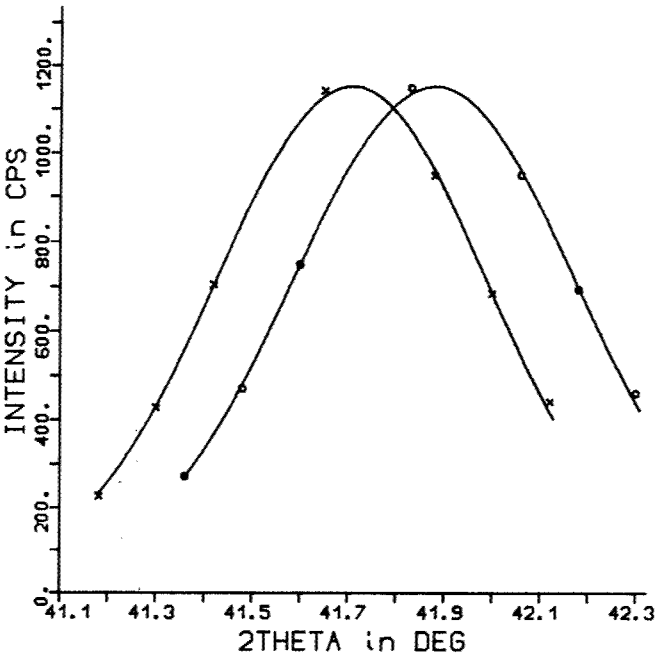

Figure 22. (lower) Plot of *d*-spacing *vs* tension for a KEVLAR 149 (006) modulus run including the two points in Fig. 20. Data points for this plot are in Table 17. The modulus shown, 206.1±2.5 GPa, compares to the value previously determined, 207.8 GPa, which was obtained by averaging measurements taken on both the (004) and (006).

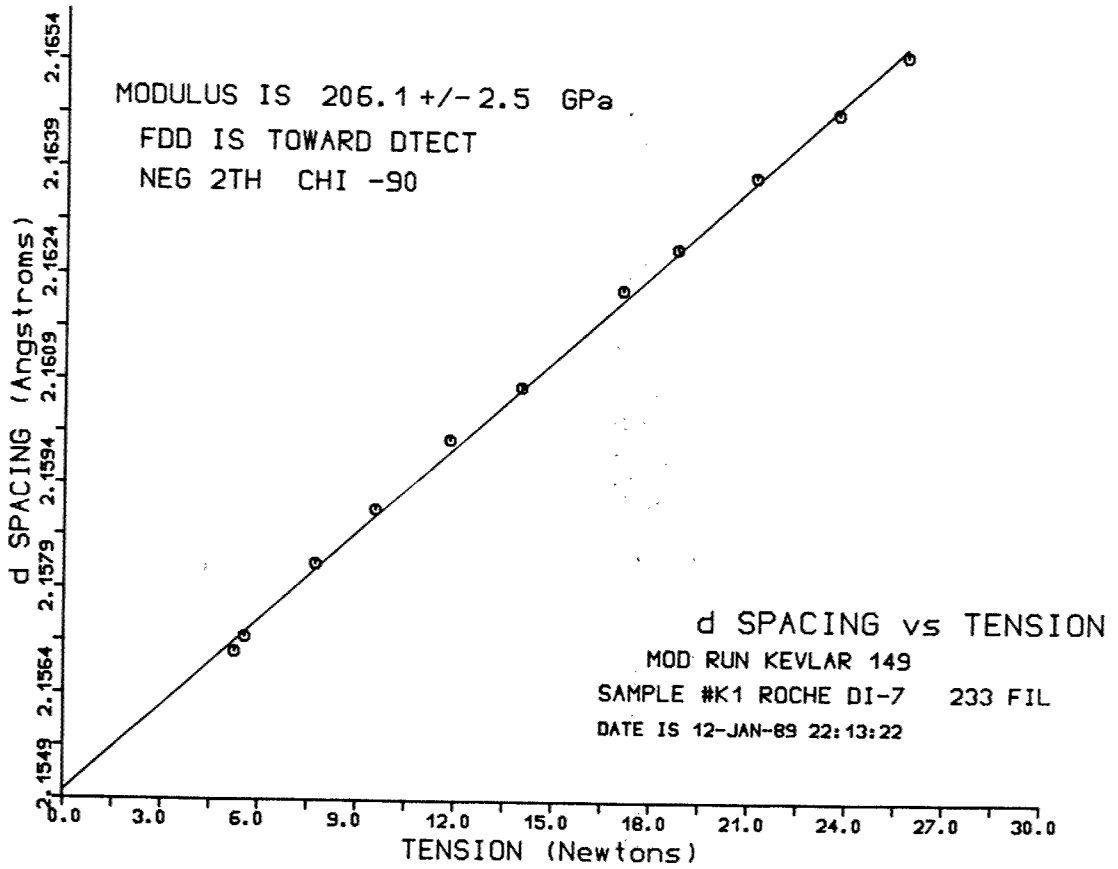

Table 16. *Summary of the Gaussian least-squares fits for 2θ scans of the (006) reflection of KEVLAR 149. The first scan is at the minimum tension of 0.203 mv (5.3 N), the second at the maximum tension of 0.991 mv (25.7 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 21.*

```
 KEVLAR 149   0.203 and  0.991 mv  12-JAN-89
 -2T -CH90  DET  100s  No FILT  1.5mm SVA
BKG
2TH = 40.17  CPS =    46.2
2TH = 43.77  CPS =    32.3

2TH OBS   41.36  41.48  41.60  41.83  42.06  42.18  42.30
OBS CPS   273.0  471.2  748.2 1149.2  947.1  691.7  459.1
CLC CPS   272.8  480.4  746.5 1136.9  961.7  699.6  439.0
DELTCPS     0.2   -9.2    1.7   12.3  -14.6   -7.9   20.1
     2TH     d        Io        a         SIG      BKG
  41.880 2.15702 1113.2  0.004390  0.000744   39.3

2TH OBS   41.18  41.30  41.42  41.65  41.88  42.00  42.12
OBS CPS   226.4  427.1  702.4 1142.3  946.6  681.9  440.6
CLC CPS   233.8  431.2  701.3 1130.3  962.3  688.4  419.8
DELTCPS    -7.4   -4.1    1.1   12.0  -15.7   -6.5   20.8
     2TH     d        Io        a         SIG      BKG
  41.708 2.16554 1112.9  0.004211  0.000759   39.3
PLOT MADE DATE IS 13-MAR-90 AT 14:41:41
```

Table 17. *Summary of modulus calculation for the (006) reflection of KEVLAR 149 as plotted in Fig 22. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig. 21.*

```
Y-INTERCEPT =   2.155014 +/-0.81235E-04
      SLOPE = 0.10757E-01 +/-0.13125E-03
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.202	2.15700	2.15719	-0.00019	41.881	0.004
0.988	2.16552	2.16564	-0.00012	41.708	0.002
0.812	2.16380	2.16375	0.00005	41.743	-0.001
0.656	2.16220	2.16207	0.00013	41.775	-0.003
0.454	2.16005	2.15990	0.00015	41.819	-0.003
0.297	2.15826	2.15821	0.00005	41.855	-0.001
0.367	2.15904	2.15896	0.00008	41.839	-0.002
0.538	2.16081	2.16080	0.00001	41.803	0.000
0.720	2.16278	2.16276	0.00002	41.763	0.000
0.908	2.16469	2.16478	-0.00009	41.725	0.002
0.214	2.15722	2.15732	-0.00010	41.876	0.002

```
MODULUS IS 206.1 +/-  2.5 GPA
```

Example IV. G30 Carbon (100) Reflection at 2θ = 43.26° (d = 2.0915 Å)

This sample contains 3000 fibers with a diameter of 6.9μ. The mechanical tensile modulus is 234 GPa and the tensile strength 3.78 GPa. The maximum tension applied corresponds to approximately 21% of the breaking strength. A 2θ shift of 0.095° results from an increase in tension of 3.03 mv (78.9 N). The FWHM is 4.215°; Δ2θ/FWHM ratio of 0.023. The $\Delta d/d$ ratio is 0.0021.

Figure 23. (top right) Plot of experimental points for G30 Carbon (100) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 18.

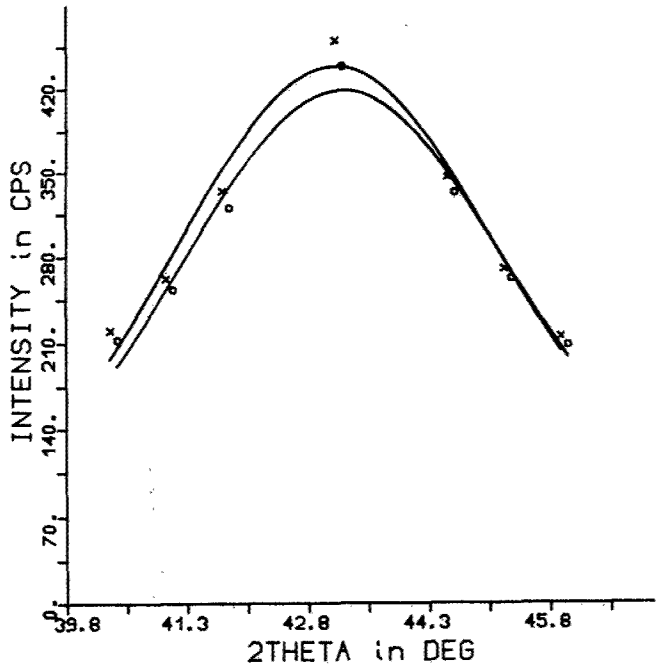

Figure 24. (lower) Plot of *d*-spacing *vs* tension for a G30 Carbon (100) modulus run including the two points in Fig. 23. Data points for this plot are in Table 19. The modulus shown, 343.1±8.8 GPa, compares to the value previously determined, 376.1 GPa, which was obtained by the usual averaging procedure of eight FDD and diffractometer positions.

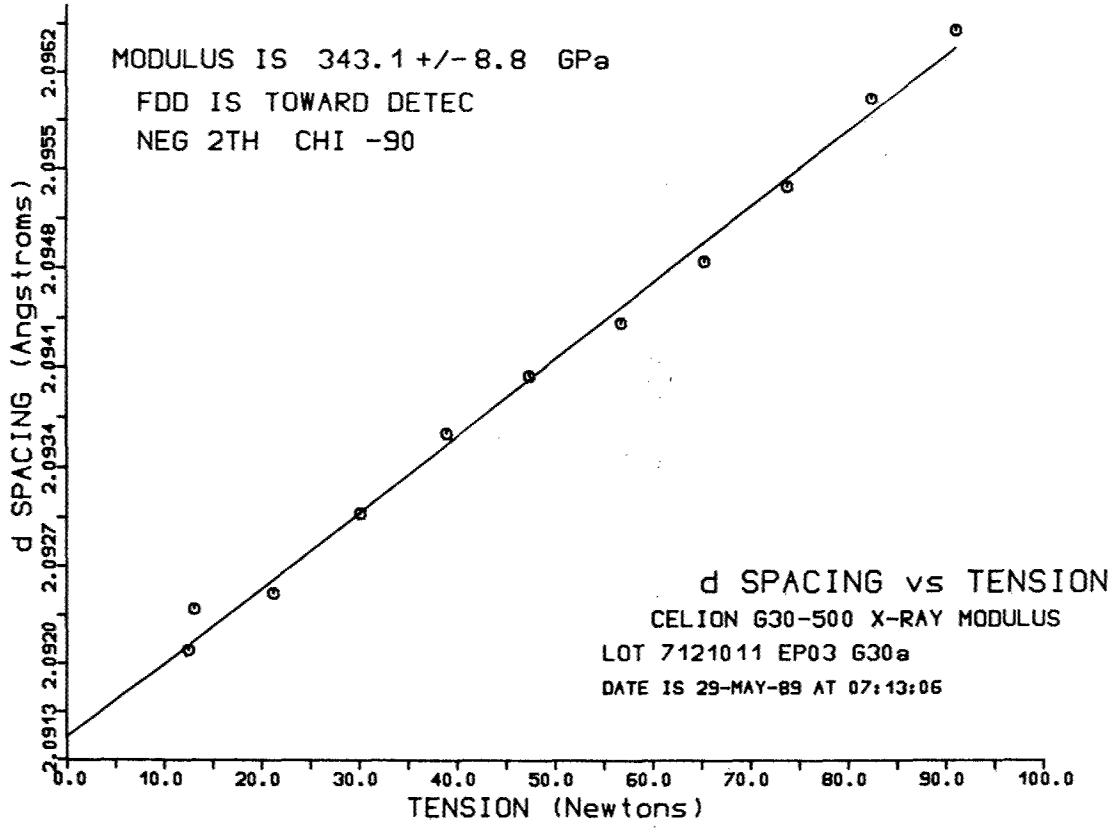

Table 18. *Summary of the Gaussian least-squares fits for 2θ scans of the (100) reflection of G30 Carbon. The first scan is at the minimum tension of 0.476 mv (12.4 N), the second at the maximum tension of 3.510 mv (91.3 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 23.*

```
 G30a 0.476 and 3.510 mv  28-MA7-89
 -2T -CH90  DET   400s  No FILT  3.0 mm SVA
BKG
2TH = 32.25  CPS =    71.1
2TH = 53.25  CPS =    78.0

2TH OBS   40.43  41.13  41.83  43.23  44.63  45.33  46.03
OBS CPS   211.9  252.6  319.6  437.9  331.7  261.1  207.1
CLC CPS   191.4  262.0  336.8  418.5  341.2  268.0  198.2
DELTCPS    20.5   -9.4  -17.2   19.4   -9.5   -6.9    8.9
     2TH     d       Io        a         SIG      BKG
  43.244 2.09210  343.8  0.028730  0.011810   74.6

2TH OBS   40.34  41.04  41.74  43.14  44.54  45.24  45.94
OBS CPS   219.3  261.6  333.4  459.3  344.8  269.0  213.6
CLC CPS   197.1  272.0  351.7  438.4  355.2  277.1  203.2
DELTCPS    22.2  -10.4  -18.3   20.9  -10.4   -8.1   10.4
     2TH     d       Io        a         SIG      BKG
  43.149 2.09650  363.7  0.028570  0.012487   74.6
PLOT MADE DATE IS 13-MAR-90 AT 14:40:36
```

Table 19. *Summary of modulus calculation for the (100) reflection of G30 Carbon as plotted in Fig. 24. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig 23.*

```
Y-INTERCEPT =   2.091473 +/-0.76111E-04
      SLOPE = 0.14064E-02 +/-0.35979E-04
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.480	2.09210	2.09215	-0.00005	43.244	0.001
3.492	2.09651	2.09638	0.00013	43.148	-0.003
2.828	2.09538	2.09545	-0.00007	43.173	0.002
2.180	2.09442	2.09454	-0.00012	43.194	0.003
1.495	2.09364	2.09358	0.00006	43.211	-0.001
0.815	2.09251	2.09262	-0.00011	43.235	0.002
1.156	2.09308	2.09310	-0.00002	43.223	0.000
1.817	2.09404	2.09403	0.00001	43.202	0.000
2.505	2.09485	2.09500	-0.00015	43.184	0.003
3.160	2.09601	2.09592	0.00009	43.159	-0.002
0.504	2.09240	2.09218	0.00022	43.237	-0.005

```
MODULUS IS 343.1 +/-  8.8 GPA
```

Example V. T50 Carbon (100) Reflection at 2θ = 42.69° (d = 2.1179 Å)

This sample contains 3000 fibers with a diameter of 6.5μ. The mechanical tensile modulus is 390 GPa and the tensile strength 2.42 GPa. The maximum tension applied corresponds to approximately 38% of the breaking strength. A 2θ shift of 0.070° results from an increase in tension of 3.02 mv (78.6 N). The FWHM is 1.090°; Δ2θ/FWHM ratio of 0.064. The $\Delta d/d$ ratio is 0.0016.

Figure 25. (top right) Plot of experimental points for T50 Carbon (100) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 20.

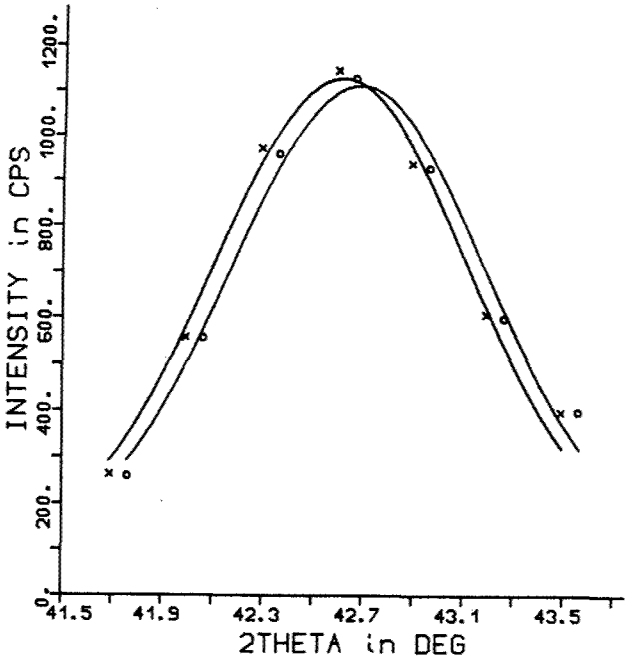

Figure 26. (lower) Plot of *d*-spacing *vs* tension for a T50 Carbon (100) modulus run including the two points in Fig. 25. Data points for this plot are in Table 21. The modulus shown, 486.9±14.4 GPa, compares to the value previously obtained, 593 GPa, which was obtained by the usual averaging procedure.

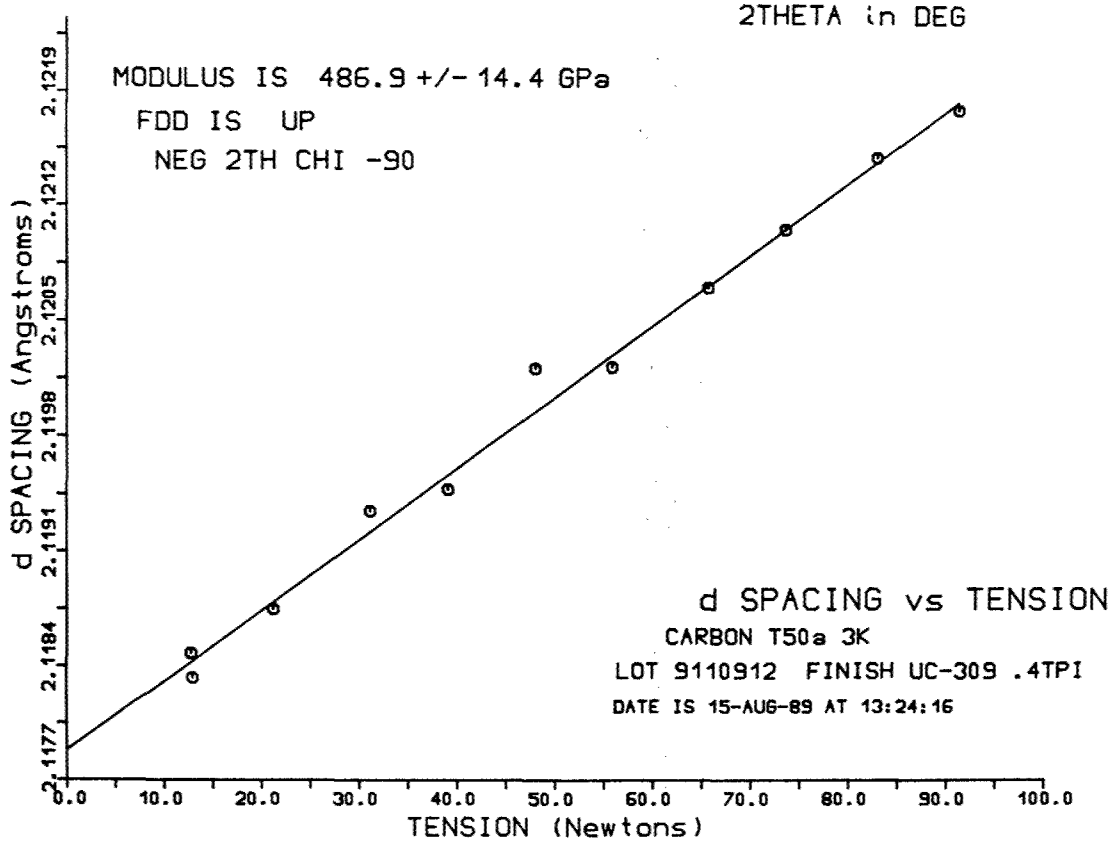

Table 20. *Summary of the Gaussian least-squares fits for 2θ scans of the (100) reflection of T50 Carbon. The first scan is at the minimum tension of 0.480 mv (12.5 N), the second at the maximum tension of 3.502 mv (91.1 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 25.*

```
T50a 3K  0.480 and 3.502 mv  15-AUG-89
-2T -CH90  UP   80s  No FILT  3.0 mm  SVA
BKG
2TH = 40.17  CPS =   110.1
2TH = 45.67  CPS =   115.1

2TH OBS   41.76  42.06  42.36  42.66  42.96  43.26  43.56
OBS CPS   258.7  554.3  959.2 1128.0  927.3  597.2  397.2
CLC CPS   292.4  572.5  926.3 1111.8  965.6  619.6  322.9
DELTCPS   -33.7  -18.2   32.9   16.2  -38.3  -22.4   74.3
     2TH     d        Io        a          SIG      BKG
  42.679 2.11848 1000.2  0.007421  0.010291  112.6

2TH OBS   41.69  41.99  42.29  42.59  42.89  43.19  43.49
OBS CPS   261.5  555.3  971.0 1145.2  938.0  605.8  396.2
CLC CPS   292.4  576.5  937.6 1127.9  978.5  625.2  323.7
DELTCPS   -30.9  -21.2   33.4   17.3  -40.5  -19.4   72.5
     2TH     d        Io        a          SIG      BKG
  42.609 2.12178 1016.3  0.007392  0.009763  112.6
PLOT MADE DATE IS 13-MAR-90 AT 13:26:15
```

Table 21. *Summary of modulus calculation for the (100) reflection of T50 Carbon as plotted in Fig. 26. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig. 25.*

```
Y-INTERCEPT =   2.117886 +/-0.70855E-04
      SLOPE = 0.11289E-02 +/-0.33480E-04
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.489	2.11848	2.11844	0.00004	42.679	-0.001
3.494	2.12178	2.12183	-0.00005	42.609	0.001
2.815	2.12105	2.12106	-0.00001	42.625	0.000
2.138	2.12022	2.12030	-0.00008	42.642	0.002
1.498	2.11948	2.11958	-0.00010	42.658	0.002
0.811	2.11875	2.11880	-0.00005	42.673	0.001
1.193	2.11935	2.11923	0.00012	42.661	-0.002
1.837	2.12021	2.11996	0.00025	42.642	-0.005
2.511	2.12070	2.12072	-0.00002	42.632	0.000
3.174	2.12149	2.12147	0.00002	42.615	0.000
0.495	2.11833	2.11844	-0.00011	42.682	0.002

```
MODULUS IS 486.9 +/- 14.4 GPA
```

Example VI. T50 Carbon (110) Reflection at 2θ = 77.93°(d = 1.2259 Å)

This sample contains 3000 fibers with a diameter of 6.5μ. The mechanical tensile modulus is 390 GPa and the tensile strength 2.42 GPa. The maximum tension applied corresponds to approximately 38% of the breaking strength. A 2θ shift of 0.136° results from an increase in tension of 3.03 mv (78.8 N). The FWHM is 1.085°; Δ2θ/FWHM ratio of 0.125. The $\Delta d/d$ ratio is 0.0015.

Figure 27. (top right) Plot of experimental points for T50 Carbon (110) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 22.

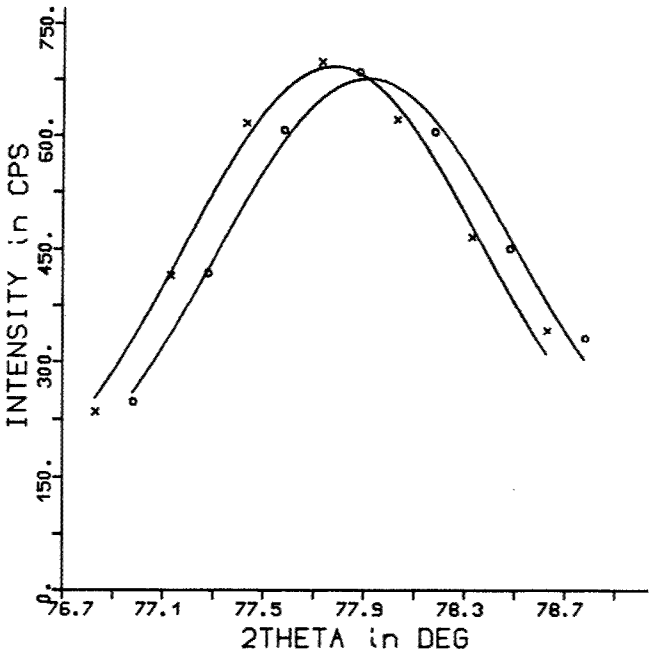

Figure 28. (lower) Plot of *d*-spacing *vs* tension for a T50 Carbon (110) modulus run including the two points in Fig. 27. Data points for this plot are in Table 23. The modulus shown, 531.1±7.4 GPa, compares to the value previously reported, 622 GPa, which was obtained by the usual averaging procedure.

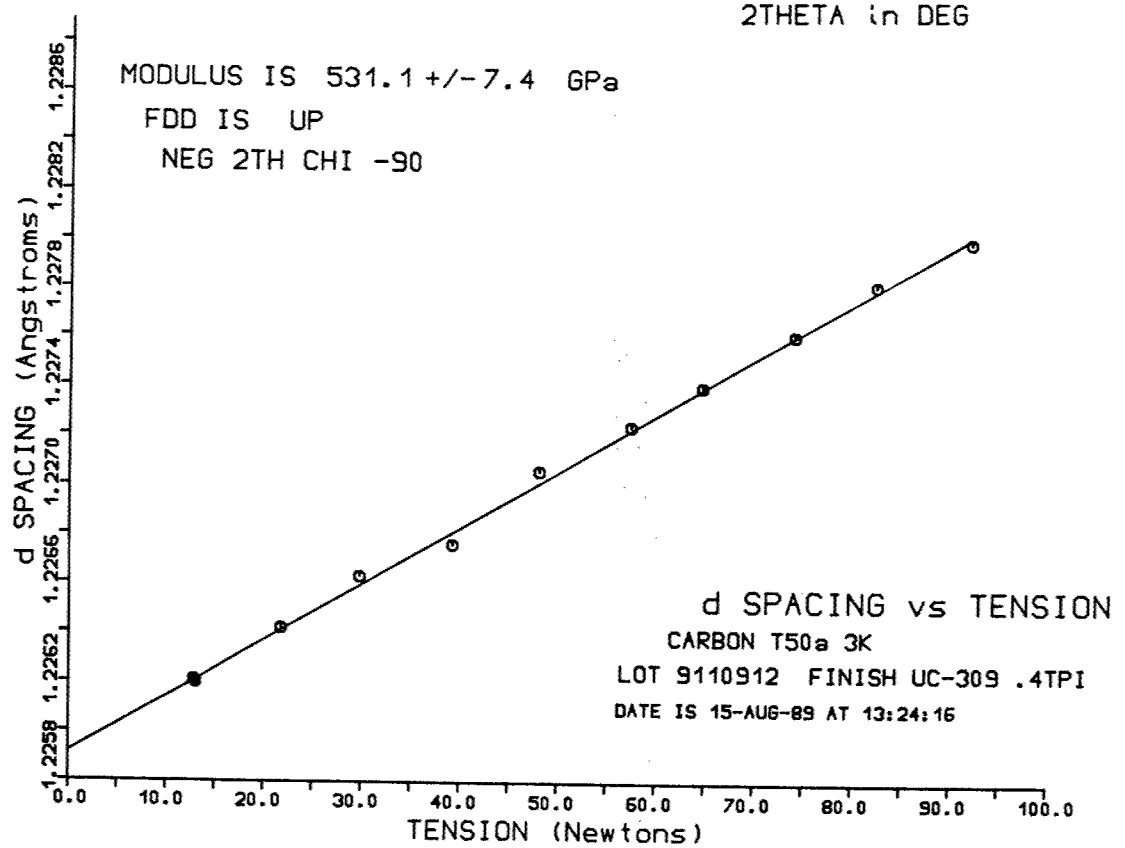

Table 22. *Summary of the Gaussian least-squares fits for 2θ scans of the (110) reflection of T50 Carbon. The first scan is at the minimum tension of 0.490 mv (12.7N), the second at the maximum tension of 3.519 mv (91.6 N). The observed points (2TH OBS and OBS CPS) are plotted along with the calculated curves in Fig. 27.*

```
T50a 3K  0.490 and 3.519 mv  15-AUG-89
-2T -CH90  UP   80s  No FILT  3.0 mm  SVA
BKG
2TH = 75.40  CPS =    75.7
2TH = 80.90  CPS =   119.9

2TH OBS    76.98   77.28   77.58   77.88   78.18   78.48   78.78
OBS CPS    247.0   418.6   607.2   684.6   604.8   450.0   331.3
CLC CPS    260.0   423.7   592.6   675.7   620.8   466.4   302.2
DELTCPS    -13.0    -5.1    14.6     8.9   -16.0   -16.4    29.1
      2TH      d        Io         a          SIG      BKG
   77.907 1.22621   580.7   0.007412   0.005505    97.8

2TH OBS    76.83   77.13   77.43   77.73   78.03   78.33   78.63
OBS CPS    234.1   414.7   616.7   698.2   621.0   465.6   341.1
CLC CPS    252.7   419.3   597.2   690.7   639.8   481.3   309.8
DELTCPS    -18.6    -4.6    19.5     7.5   -18.8   -15.7    31.3
      2TH      d        Io         a          SIG      BKG
   77.771 1.22800   597.7   0.007344   0.006670    97.8
PLOT MADE DATE IS 13-MAR-90 AT 13:28:01
```

Table 23. *Summary of modulus calculation for the (110) reflection of T50 Carbon as plotted in Fig. 28. X-OBS is the measured tension in millivolts, Y-OBS is the d-spacing in Å from the Gaussian least-squares fit. The scan data and fitting parameters for the first two points appear in the Table above and in Fig. 27.*

```
Y-INTERCEPT =   1.225918 +/-0.17599E-04
      SLOPE = 0.59897E-03 +/-0.83102E-05
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.492	1.22621	1.22621	0.00000	77.906	0.000
3.517	1.22800	1.22802	-0.00002	77.771	0.002
2.832	1.22761	1.22761	0.00000	77.801	0.000
2.195	1.22724	1.22723	0.00001	77.829	-0.001
1.500	1.22676	1.22682	-0.00006	77.865	0.004
0.832	1.22642	1.22642	0.00000	77.890	0.000
1.139	1.22663	1.22660	0.00003	77.875	-0.002
1.838	1.22706	1.22702	0.00004	77.842	-0.003
2.473	1.22740	1.22740	0.00000	77.817	0.000
3.147	1.22782	1.22780	0.00002	77.785	-0.001
0.498	1.22620	1.22622	-0.00002	77.907	0.001

```
MODULUS IS 531.1 +/-  7.4 GPA
```

Example VII. Silk (002) Reflection at 2θ = 25.44° : (d = 3.5012 Å)

This sample contains 880 fibers with a diameter of 11.9μ. The mechanical tensile modulus is 10 GPa and the tensile strength 0.33 GPa. The maximum tension applied corresponds to approximately 59% of the breaking strength. A 2θ shift of 0.182° results from an increase in tension of 0.67 mv (17.4 N). The FWHM is 0.978°; Δ2θ/FWHM is 0.186. The $\Delta d/d$ ratio is 0.0071.

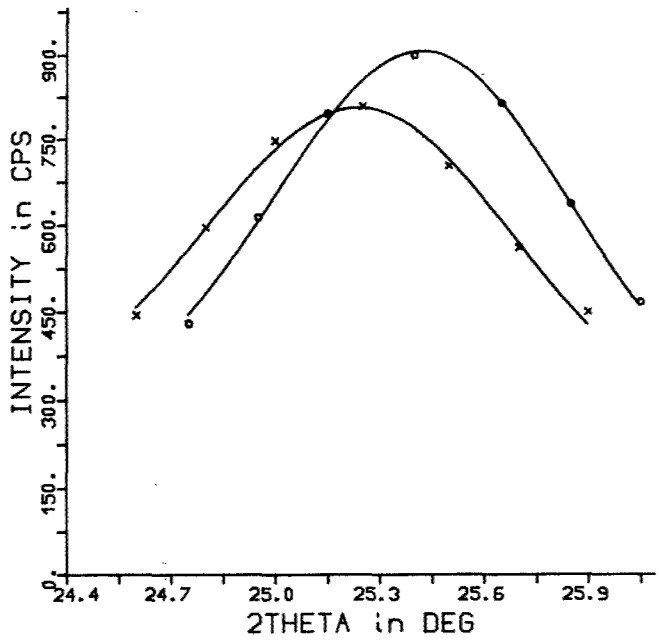

Figure 29. (top right) Plot of experimental points for silk (002) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 24.

Figure 30. (lower) Plot of *d*-spacing *vs* tension for a silk (002) modulus run including the two points in Fig. 29. Data points for this plot are in Table 25. The modulus shown, 24.7±0.2 GPa, differs from the value obtained with the (006) reflection from the same sample.

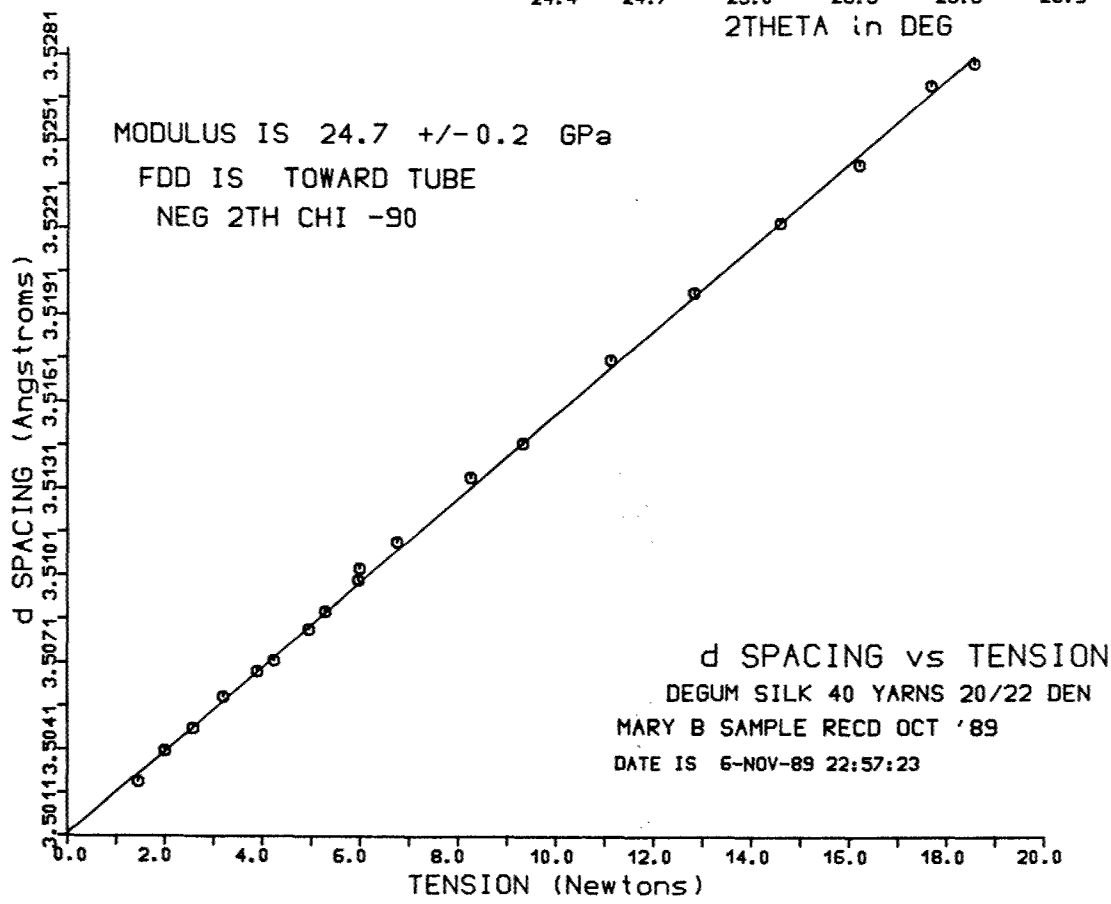

Table 24. *Gaussian least-squares fits for 2θ scans of the Silk (002) reflection at minimum and maximum tension. The first at 0.059 mv (1.5 N), the second at 0.727 mv (18.9 N). The observed points (2TH OBS & OBS CPS) and calculated curves are plotted in Fig. 29.*

```
 DEGUM SILK II 0.059 and 0.727 mv  6-NOV-89
 -2T -CH90  TUBE 60s  No  FILT  3.0 mm SVA
BKG
2TH = 23.87  CPS =   291.5
2TH = 28.22  CPS =   207.0

2TH OBS    24.75  24.95  25.15  25.40  25.65  25.85  26.05
OBS CPS    429.7  612.7  794.9  899.1  813.5  636.0  466.5
CLC CPS    446.7  605.9  784.6  906.0  815.5  637.5  459.3
DELTCPS    -17.0    6.8   10.3   -6.9   -2.0   -1.5    7.2
      2TH     d        Io        a          SIG      BKG
   25.426 3.50301   645.5  0.006500  0.001310   249.3

2TH OBS    24.60  24.80  25.00  25.25  25.50  25.70  25.90
OBS CPS    443.7  595.0  746.6  808.1  702.7  560.0  449.1
CLC CPS    458.4  595.3  732.5  806.4  715.5  569.0  426.3
DELTCPS    -14.7   -0.3   14.1    1.7  -12.8   -9.0   22.8
      2TH     d        Io        a          SIG      BKG
   25.244 3.52787   541.7  0.006800  0.004035   249.3
PLOT MADE DATE IS 26-MAR-90 AT 16:12:07
```

Table 25. *Modulus calculation for the Silk (002) reflection as plotted in Fig. 30. X-OBS, measured tension in millivolts; Y-OBS, d-spacing in Å from the Gaussian least-squares fit.*

```
   Y-INTERCEPT =   3.501203 +/-0.91876E-04
         SLOPE = 0.37859E-01 +/-0.24611E-03
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.056	3.50300	3.50332	-0.00032	25.426	0.002
0.077	3.50407	3.50412	-0.00005	25.418	0.000
0.099	3.50486	3.50495	-0.00009	25.412	0.001
0.123	3.50595	3.50586	0.00009	25.404	-0.001
0.150	3.50683	3.50688	-0.00005	25.398	0.000
0.163	3.50720	3.50737	-0.00017	25.395	0.001
0.190	3.50826	3.50840	-0.00014	25.387	0.001
0.203	3.50887	3.50889	-0.00002	25.383	0.000
0.230	3.51033	3.50991	0.00042	25.372	-0.003
0.229	3.50992	3.50987	0.00005	25.375	0.000
0.259	3.51123	3.51101	0.00022	25.366	-0.002
0.317	3.51350	3.51320	0.00030	25.349	-0.002
0.358	3.51468	3.51476	-0.00008	25.340	0.001
0.427	3.51756	3.51737	0.00019	25.319	-0.001
0.492	3.51990	3.51983	0.00007	25.302	-0.001
0.559	3.52231	3.52237	-0.00006	25.284	0.000
0.621	3.52434	3.52471	-0.00037	25.270	0.003
0.677	3.52710	3.52683	0.00027	25.250	-0.002
0.711	3.52787	3.52812	-0.00025	25.244	0.002

```
   MODULUS IS  24.7 +/-  0.2 GPA
```

Example VIII. Silk (006) Reflection at 2θ = 83.10° (d = 1.1622 Å)

This sample contains 880 fibers with a diameter of 11.9μ. The mechanical tensile modulus is 10 GPa and the tensile strength 0.33 GPa. The maximum tension applied corresponds to approximately 59% of the breaking strength. A 2θ shift of 0.592° results from an increase in tension of 0.67 mv (17.4 N). The FWHM is 1.956°; Δ2θ/FWHM is 0.303. The *Δd/d* ratio is 0.0071.

Figure 31. (top right) Plot of experimental points for silk (006) 2θ scans at minimum and maximum tension. Solid curves are calculated from Gaussian least-squares fit. See Table 26.

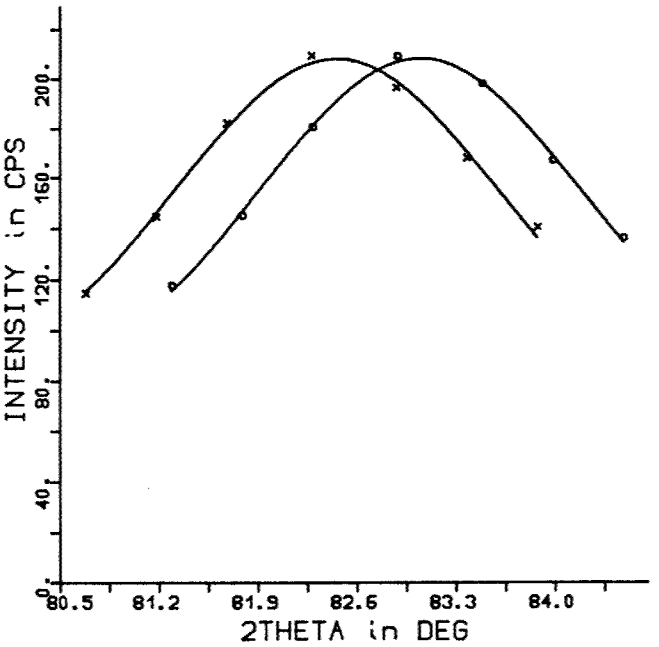

Figure 32. (lower) Plot of *d*-spacing *vs* tension for a silk (006) modulus run including the two points in Fig. 31. Data points for this plot are in Table 27. The modulus shown, 29.9±0.3 GPa, differs from the value obtained with the (002) reflection from the same sample.

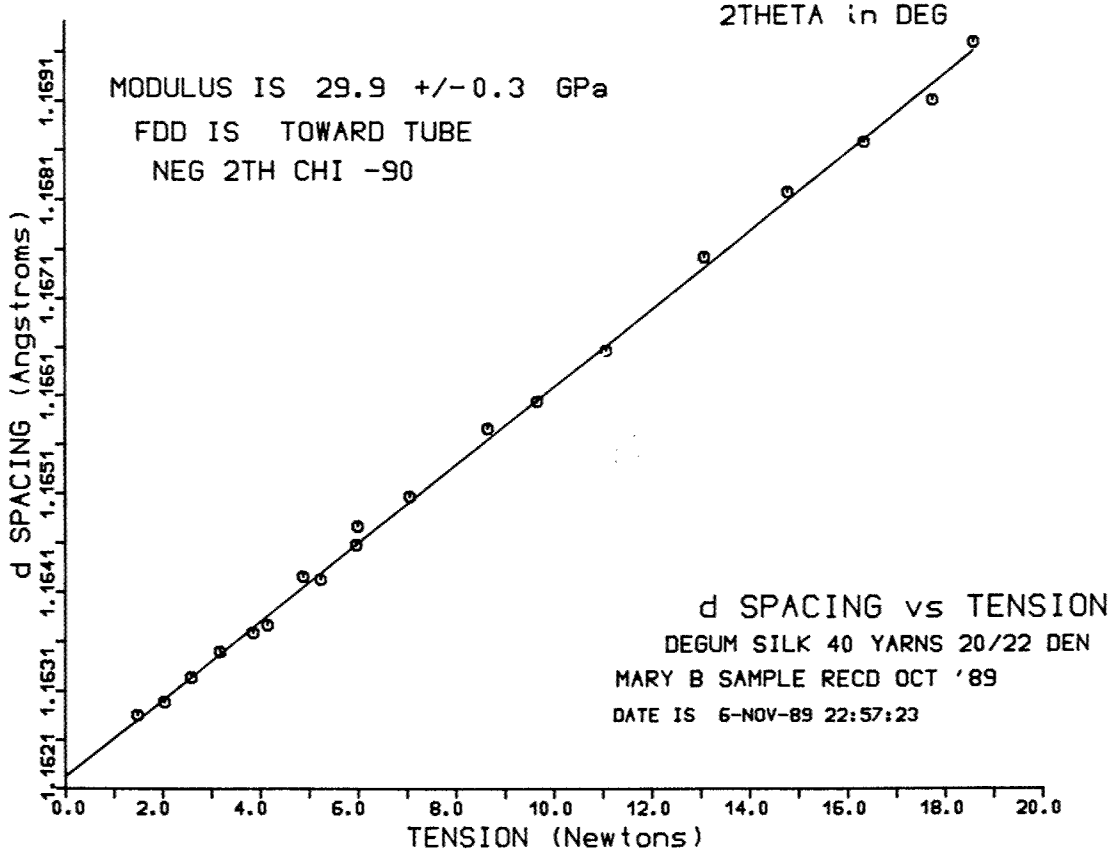

Table 26. *Gaussian least-squares fits for 2θ scans of the Silk (006) reflection at minimum and maximum tension. The first at 0.060 mv (1.6 N), the second at 0.725 mv (18.9 N). Observed points (2TH OBS & OBS CPS) are plotted with the calculated curves in Fig. 31.*

```
 DEGUM SILK II 0.060 and 0.725 mv  6-NOV-89
 -2T -CH90  TUBE  150s  No  FILT  3.0 mm SVA
BKG
2TH = 78.25  CPS =    81.3
2TH = 87.65  CPS =    77.8

2TH OBS   81.29  81.79  82.29  82.89  83.49  83.99  84.49
OBS CPS   117.6  145.0  180.5  209.1  197.8  166.9  135.9
CLC CPS   115.7  146.8  181.3  207.0  198.2  168.8  134.3
DELTCPS     1.9   -1.8   -0.8    2.1   -0.4   -1.9    1.6
     2TH     d       Io        a         SIG      BKG
  83.048 1.16286  128.7  0.013223  0.001093   79.6

2TH OBS   80.68  81.18  81.68  82.28  82.88  83.38  83.88
OBS CPS   114.4  144.4  182.1  209.2  196.2  167.8  140.2
CLC CPS   115.5  146.1  180.5  206.6  199.0  170.4  136.1
DELTCPS    -1.1   -1.7    1.6    2.6   -2.8   -2.6    4.1
     2TH     d       Io        a         SIG      BKG
  82.456 1.16970  128.4  0.013368  0.002724   79.6
PLOT MADE DATE IS 26-MAR-90 AT 16:12:52
```

Table 27. *Modulus calculation for the Silk (006) reflection as plotted in Fig. 32. X-OBS, measured tension in millivolts; Y-OBS, d-spacing in Å from the Gaussian least-squares fit.*

```
   Y-INTERCEPT =   1.162230 +/-0.36402E-04
         SLOPE = 0.10357E-01 +/-0.96520E-04
```

X-OBS	Y-OBS	Y-CALC	Y-DELT	2 TH-OBS	2 TH-DELT
0.057	1.16286	1.16282	0.00004	83.048	-0.003
0.078	1.16299	1.16304	-0.00005	83.037	0.004
0.099	1.16324	1.16326	-0.00002	83.015	0.001
0.122	1.16350	1.16349	0.00001	82.992	-0.001
0.148	1.16369	1.16376	-0.00007	82.976	0.006
0.159	1.16377	1.16388	-0.00011	82.969	0.009
0.187	1.16426	1.16417	0.00009	82.926	-0.008
0.201	1.16423	1.16431	-0.00008	82.929	0.007
0.229	1.16458	1.16460	-0.00002	82.898	0.002
0.230	1.16477	1.16461	0.00016	82.882	-0.014
0.271	1.16507	1.16504	0.00003	82.856	-0.003
0.332	1.16576	1.16567	0.00009	82.796	-0.008
0.371	1.16604	1.16607	-0.00003	82.772	0.003
0.425	1.16657	1.16663	-0.00006	82.726	0.005
0.502	1.16752	1.16743	0.00009	82.644	-0.008
0.567	1.16817	1.16810	0.00007	82.588	-0.006
0.627	1.16868	1.16872	-0.00004	82.544	0.004
0.681	1.16911	1.16928	-0.00017	82.507	0.015
0.713	1.16970	1.16962	0.00008	82.456	-0.007

```
   MODULUS IS  29.9 +/-  0.3 GPA
```

9. A CRITIQUE OF THE DEVICE AND METHOD

FDD Critique and Improvements

Fabrication of the FDD is described in **Construction, Wiring and Drive Characteristics**. In use, the device has proved serviceable and it gives reproducible results with good precision. It may be useful, however, to comment on several points where improvements could be made if another unit were to be constructed.

Fabrication of the present FDD was not always held to appropriate tolerances. Improvements at the points mentioned in the **Construction** section above would further reduce unwanted motion. In addition, the following points should receive special attention. The upper sample holder as received from the shop did not have the knife edge exactly perpendicular to the instrument axis. The dimensions of the sample end pieces were not uniform. Some end pieces fit into the upper and lower sample holders snugly but a few were too large. This was discovered, in one case, after a valuable sample had been prepared and the only solution was to slightly enlarge the holes in the sample holders. In the first batch of sample end pieces, the center hole was not well centered in some pieces. This was improved in later batches after the importance of centering was emphasized.

Some of the difficulties discussed in the section **Sample Translation and the Lower Sample Holder** could be eliminated by redesign of the lower sample mount holder, goniometer head base and mount. As noted, introduction of shims for alignment, and metal shims to allow the length adjustment screws to be tightened, reduced sample translation so that this problem appears to be solved, at least when the FDD is in the "Tube" or "Detector" positions. Rigidity of this assembly could be improved by fabricating the goniometer head base and the mount which attaches it to the diffractometer as one piece. The translation adjustments could be provided with larger surfaces for the sledges. The sample mount holder itself should have a larger base to give a larger area of contact with the top sledge. The top of the lower sample mount holder should be made smaller to increase the maximum 2θ available for modulus measurements.

Mounting the holder on the diffractometer should be made more reproducible by improving the fit of the base plate to the mounting surface on the diffractometer. A pin to allow mounting in only one position should also be provided.

The strain gauge bridge works well, gives readings proportional to tension and is stable. Overall, the tension measuring and electrical aspects are fully satisfactory. Two possible improvements in this area come to mind. The 10 turn potentiometer, used to adjust the bridge input, might be replaced by a unit designed for low voltage operation. This might improve the wiper contact and facilitate voltage adjustments. The amplifier (Omega unit) used for the strain gauge output must be set at a high gain and as a result, noise problems require that ten readings be averaged to get satisfactory tension values. Better amplifiers are available and, in fact, the one originally used, a part of the Keithley 177 DVM, had no noise problem. Its use was discontinued when readings became erratic.

If samples of lower modulus are to be measured routinely, it would be advisable to use a thinner, more flexible tension arm. This would improve the accuracy of the low tension measurements. However, at low tensions, the tendency of the upper sample holder to sag would be a problem. This is not a serious problem with the FDD in the "Tube" and

"Detector" positions but it is noticeable at low tensions in the "Up" and "Down" positions because the sample holder "hinges" on the knife edge.

Determination of *d*-Spacing

In a few cases (noted earlier in this report) problems were encountered when diffraction peaks were broad or subject to overlap from nearby peaks on the same layer line. Unsymmetrical peaks, such as those of carbon fibers do not fit the Gaussian model well. Further study is needed to determine how much, if at all, the *d*-spacing measurements are affected by these factors. The modulus values obtained will only be in error if the *d*-spacing error changes with tension. Peaks which sit on a high background may also be subject to *d*-spacing errors. The analysis used assumes the background is linear and is not a function of tension. These assumptions should be satisfactory for materials which give sharp peaks, but they may introduce some error in cases of unsymmetrical or broad peaks.

If the degree of order in the sample is changed by the application of tension, the shape of the diffraction peak will be expected to change also. If the symmetry of the peak also changes, the *d*-spacing as determined by the Gaussian model may be affected. Further study is needed and, in some cases, another model for relating the measured scan to the *d*-spacing may be required.

Improved precision in the *d*-spacing measurements might also result from improved stability in the X-ray output from the RU-200. The tests reported above suggest that under some conditions the fluctuation in X-ray intensity and perhaps source motion relative to the diffractometer affects the *d*-spacing measurements. Again, further study of this effect is needed to determine its magnitude and suggest corrective action.

Further Work

Future work using the FDD should include measurements at increased and reduced temperature. One of the low temperature devices available in the laboratory could be adapted to deliver a stream of cold gas onto the portion of the sample in the X-ray beam. The cold stream delivery tube would eliminate the automatic measurement of *d vs* tension curves at both $+\chi_{90}$ and $-\chi_{90}$ in a single run but otherwise the measurements could be made in the usual manner. Similarly, several devices are available which could be adapted to provide a stream of hot gas from below the sample to allow *d*-spacing measurements at increased temperature.

Measurements on a single crystal under tension, another research area of interest, would require major redesign of the FDD and some modification of the diffractometer. Measurements on a single crystal fiber require that angles about the ϕ axis be set under program control. This must be done without torsional strain on the sample while the fiber is under tension, therefore, both the upper and lower parts of the FDD must be driven by the ϕ motor. Because of the limited space available in the χ circle of the diffractometer, the drive motor for tension adjustment must be smaller than the one currently used and the mechanism for applying tension to the sample must be redesigned. Both the design and fabrication problems appear to be demanding.

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11. APPENDIX

A. XRYMOD Data Analysis Programs

Plotting Step Scans, PKFTPL

In a preliminary assessment of the experimental parameters for a modulus run it is useful to examine a plot of the experimental and calculated curve for step scans made at minimum and maximum tension. PKFTPL accepts data from step scans at two tensions, makes a least-squares fit of the Gaussian parameters to the experimental points and then plots the calculated curve for both scans. This gives a graphic display of the fit and shows the peak shift which results from the maximum application of tension. The Gaussian fit is carried out by the XRYMOD subroutine PKFIT and the plotting is done by a modified version of the subroutine PLOTEM from the program FIT. The Calcomp subroutines in CCM88 are used to generate the plot.

Input from the file PK., as specified in the program comments, consists of a two line title which should include the important experimental parameters such as sample data, tension data, diffractometer configuration, counting time, filter, SVA settings, *etc.* The next lines give the 2θ and counts for the background, plot size parameters and 2θ & CPS data for the step scan. An example of PK. is shown in Table 28.

Output, to the file PKOUT., is similar to the peak fit display written by XRYMOD. The plotter output is written in PLOT.PLT. For examples see Table 5 and Fig. 11 above.

Table 28. *Example input files, PK., for PKFTPL (left) and REPLOT. (right).*

```
PBZT #8  0.593  and  3.488 mv  12-DEC-88  40 Kv 80 ma
-2T -CH90  TUBE  100s  No FILT  3.0 mm SVA
 74.1  39.4
 78.1  36.4
  75.1
75.41  138.3
75.61  209.4
75.81  287.3
76.06  343.2
76.31  313.5
76.51  242.4
76.71  164.4
 -1    -1
75.23  138.7
75.43  206.9
75.63  281.5
75.88  336.0
76.13  307.6
76.33  244.6
76.53  170.5
 -1    -1
```

```
PBZT #8 650 C HT: 2 POS W #8 ROTATED
PBZT 32508-18-14  14 IV 650 C HT
DATE IS 12-DEC-88 AT 17:45:18
TOWARD TUBE
NEG 2TH  CHI -90
700 1.57 1.896 2650.
1
.589 1.25073
3.472 1.25315
2.842 1.25259
2.219 1.25197
1.557 1.25144
.922 1.25092
1.250 1.25120
1.898 1.25168
2.533 1.25230
3.159 1.25283
.606 1.25063
-1 -1
```

Replotting Tension *vs* *d*-spacing Data, REPLOT

The program REPLOT allows data from modulus runs to be combined or modified before plotting. The program generates the usual modulus plot and prepares a summary of the observed and calculated values similar to the one written by XRYMOD. Subroutines CALMOD and GRAPH (slightly modified) from XRYMOD are used.

Input is from the file REPLOT. as given by comments in the program and shown in Table 28. Output is to XRYMOD.TMP and PLOT.PLT.

B. Shop Drawings

Sample End Piece Shop Drawing

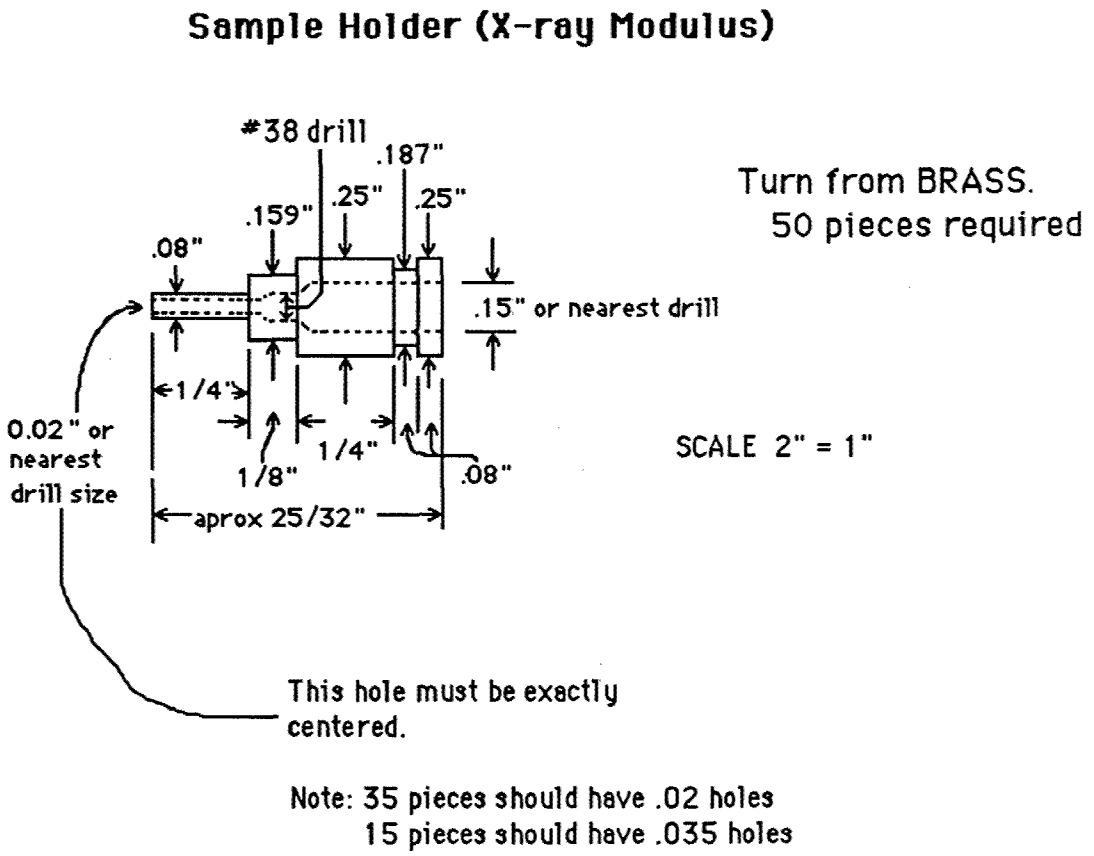

Figure 33. Shop drawing of sample end piece. The hole in the left end can be varied in size as required for the samples to be used.

C. MATERIALS LAB X-RAY MODULUS HISTORY

1981

WWA talked to Mauritz Northolt at ACA Meeting, Ottawa, Canada about doing X-ray modulus on high E fibers.

The following events are recorded in PGL's lab notebook. They have been edited to make them suitable for use in this format. Most apply to the X-ray modulus device or measuremens. Some relate to the Picker diffractometer or diffractometer software.

1982

July 28	Talked with Wade about stress experiment set-up.
August 2	Discussed tension device with Wade.
August 4	Discussed stress apparatus with Jones and others.

1983

Mark I FDD constructed by Bill Click. Titanium arm with two strain gauges, no rotation of sample, no adjustment for length of sample. Early use by Viswanathan and Joe O'Brian.

1984

May 7	Started on least-squares peak fit program for 2θ scans. Check papers on equi-tension fibers.
May 9	PDP-8 version of Peak Fit.
May 14	Working on equi-tension sample.
June 4	Hang weights on fiber bundle.
June 5	Peak Fit working. Wade impressed by fibers with weights.
June 8	Rotated tension device so micrometer adjustment is toward tube. Prepare paper tape input for statistics run on weekend. Equi-tension bundle had 73 wts, 146 fibers.
June	Step scan study for scan accuracy.
June 27	Started modulus run on AFTECH II equi-tension sample using 1000 s 7 point scans.
June 30	Made nonequi-tension AFTECH II sample under tension (all wts. on main loop).
July 3	Cut several #20 hypodermic needles on lathe to make better mounts. Used grinding tool, diamond saw and lathe. Adjusted modulus device and rechecked calibration 0, 500, 1000, 2000 got 57.5 gm/deg. Samples of new design should be 46 mm shoulder to shoulder.
July 4	Began analysis of nonequi-tension sample effect on modulus. Worked on program to calculate modulus for a distribution of fiber lengths.
July 6	Worked on peak calculation program. Results now seem independent of length distribution of fibers in the sample!

July 9 Translated modulus sample to discover how reproducible modulus results are.

July 13 Worked on new equi-tension sample of PBT, Sample #3.

July 30 Worked on modulus device design modifications. Got Delco New Departure bearing to make rotatable FDD.

August 6 Cut lead block to make calibration weights.

August 8 Found modulus device needs more work. Cut base to change micrometer travel.

August 14 Used IBM card to prevent rotation with bearing installed. Nylon lock screws added a few days later.

1985

Jan. 1-18 Discussed strain gauges with Bob McReynolds at Vanderbilt. He gave me technical reports with strain gauge bridge circuits.

April 1 Made centering weight.

May 1 Overnight run confirms electrical stability of strain gauges on modulus device.

May 7 Finished drawing of new suspension and arm for modulus device. Still some stability problems, was advised by Measurement Group people that 1% change is too large.

May 21 Started to assemble improved power supply with adjustable driving voltage and switch to read both input and output on digital meter. Used old FACS-I Mag. tape power supply from Vanderbilt.

May 28 Picked up modified device, new arm with knife edge.

May 30 Got adjustment screws for upper sample holder. Variation in sample length can now be compensated.

June 4 Cemented strain gauges on new arm.

July 1 Heated modulus samples in vacuum oven to cure epoxy.

July 12 Picked up 10 turn potentiometer for strain gauge input adjustment.

August Reported modulus device and results at Stanford meeting of American Crystallographic Association.

1986

May 2 Tested bridge input voltage *vs* mv reading for wt. #1 and #3. Found driving voltage with old power supply was changing.

May 8 Found old Picker X-ray tube tower at Vanderbilt and brought it to WPAFB for use with Picker when it is put on the RU-200.

May 15 Modified lower sample holder to allow scans in any ϕ position. Now possible for FDD to go from micrometer in tube-detector position to up-down position w/o releasing tension.

May & June Reworked Strouse Programs for Picker and Huber and worked on elementary polymer programs and got ready to move Picker to new lab.

June 30 Stripped Picker and moved her to Bldg. 654.

July Worked to get Picker up and FORTRAN program for modulus working.

August	Continued to work on software and hardware for updated diffractometer.
August 15	Installing *Crystal Logic* FDD interface and testing.
Nov. 20,	Put in overprinting for updating counts as they accumulate. Old power supply for strain gauge bridge scrapped, went to Omega power supply. Modulus hardware working and ready to repackage.
Nov. 26	DIFF. file for storage of angles perfected.

1987

Feb. 28	Backlash jumpers were removed on Picker and Huber. Phi software backlash was also removed.
March 4	Minor modification to FDD because of adding micrometer motor.
May 4	Took metal off Picker microscope mount to allow modulus device with motor to rotate.
May 5	Made circuit diagram for FDD.
May 7	Worked on FDD software and forward limit problems. Ran tests on step size *vs* tension when FDD is driven.
May 8	Modified motor screw driving surface with sheet of stainless steel.
May 12	Working to get XRYMOD running.
May 20	Got center reflection program working for use in diffractometer alignment.
June 10	K177 DVM "acts up" and gives wrong tension readings causing FDD to destroy sample. Switched DVM to display only and used Amplifier in Omega amp-power supply. This required averaging of 10 tension reads because of "noise" in amplification.
June 12	Wrote CKFDD to check stability of tension of FDD readings.
June 24	General program to make modulus plots with titles finished and incorporated into XRYMOD.
July 2	FDD forward limit problem again. Programmed retrys and got around it.
August	Did modulus measurements on three PBO samples.
Sept.	Wrote first version of Picker, Huber and FDD User's Manual.

1988

July	Chi scan centering software added to PICKER.
August 17	Time estimates in PICKER for TH and CH scans.
Aug., Sept.	Worked out curve fit and data reduction for equatorial fiber scans.
Sept. 9	Another fix in Peak centering subroutine - OMPEAK
Sept. 22	Reworked upper sample holder on modulus Device. Put in larger screws and lapped them.
Sept. 26	Modified PKFIT in XRYMOD to use measured background to fit peaks.
Sept. 28	Data shows variation in modulus values -- too much play somewhere.
Oct. 19	Modified XRYMOD to allow $\pm\chi 90$ and $\pm 2\theta$ scans.

Dec. 1	Modulus paper given at MRS meeting in Boston.
Dec. 12	Four nylon lock screws on FDD.

1989

Jan. 9	XRYMOD will now do up to 10 tension series.
Feb. 17	Worked on Dead time correction for Picker.
Feb. 21	Put dead time correction in subroutine COUNT.
March 7	Working on Fourier fold-unfold for χ scans.
March 20	Made least-squares polynomial fit program to do interpolation, works great.
April 7 & 8	Tried to come up with FDD design for single crystal tension work. There just isn't enough space for everything when both ϕ drives are used.
April 18	Modified bearing connection for FDD to make it more stable.
May	G30 carbon modulus: investigated problems of modulus measurement on broad peaks in high modulus materials.
May 24	Had bearing part of FDD redone by shop to get rid of play.
May 31	Lower FDD holder returned to shop to be redone, too much play.
July 24	Tests of modified FDD with PBT #8 sample.
July 31	Coded OMSCAN program and fit to find ω peak center.
August 17	XRYMOD can now use different scan parameters for different peaks in a multi-reflection scan.
August 22	Relaxation version of XRYMOD coded.
Sept. 15	Worked up LLPLOT to plot layer line scans. Made LLSCAN & LLPLOT compatible.
Oct. 2	Improved clearance on top part of FDD for full rotation.
Oct. 3	Made gauge rod "sample" for testing FDD translation as a function of tension.
Oct. 10	Spent several days making measurements of translation *vs* tension with gauge rod "sample". Used shims to true up lower sample holder and eliminate translation.
Oct. 14	Running SILK II samples, wait for relaxation but don't reset. Four tension ranges -- two up and two down.
Dec. 8	After fixing χ drive problem on Picker and realigning instrument, mounted FDD and used "gauge rod sample" to test translation *vs* tension. Translation measured at 0.0012 in with tension range of 0.2 to 3.0 mv.

1990

Feb. 13	Fixed time-delay feature was added to XRYMOD.
March 8	Made new alignment tool for FDD with well centered gauge rod.
April 10	Gave poster paper on modulus results to date at ACA meeting in New Orleans.
April 23	Tested new, longer, upper sample holder. Added a shim to true up knife edge.

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