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SEMIANNUAL PROGRESS REPORT

EFFECTS OF NEUTRON DAMAGE ON THE MECHANICAL PROPERTIES OF PYROLYTIC AND SINGLE CRYSTAL GRAPHITE

RELEASED FOR ANNOUNCEMENT

IN NUCLEAR SCIENCE ABSTRACTS

January 1, 1965 to June 30, 1965

Principal Investigator

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CARBON PRODUCTS DIVISION, TECHNICAL CENTER

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FOREWORD

This report summarizes the progress of an investigation of neutron damage on the mechanical properties of both graphite single crystals and pyrolytic graphite which has been compression-annealed. The work is jointly supported by the United States Atomic Energy Commission under Contract No. AT-(40-1)-3237 and Union Carbide Corporation, Carbon Products Division. The contract is administered by Dr. D. F. Cope, Director, Reactor Division, Oak Ridge Operations. The report covers the period January 1, 1965 to June 30, 1965.

The Project is under the general supervision of J. T. Meers. The graphite single crystal work has been carried out by R. Bacon, R. Sprague, D. E. Soule, and C. W. Nezbeda. The pyrolytic graphite work has been carried out by O. L. Blakslee, N. F. Graves, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng. This report was prepared by J. T. Meers with the active assistance of the participants in the program.

ABSTRACT

Pre-irradiation testing of compression-annealed pyrolytic graphite has been completed. A set of elastic compliance and stiffness constants has been obtained for compression-annealed pyrolytic graphite. In addition, the behavior of this material when subjected to shear is described and the stress-strain curve for shear is given. Values for shear strength of single crystal graphite are also given. Work has continued on the problem of measuring the tensile strength of single crystal graphites.

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1. INTRODUCTION

The general objective of the program is to determine the effects of neutron irradiation upon the mechanical properties of graphite single crystals and of highly ordered pyrolytic graphite. The specific objective of the work for the first year has been the production and pre-irradiation evaluation of these materials.

The first three quarterly progress reports^(1,2,3) describe the production of materials and the development of individual tests compatible with the severe anisotropy of the test specimens. Work during this semi-annual period has produced a reasonably consistent set of elastic constants for stress-annealed pyrolytic graphite. Measurements of the shear strength of single crystals have been made, and work has been initiated to obtain the stress-strain curve in shear for single crystals. Curves of torque versus angular deformation in torsion for stress-annealed pyrolytic graphite have been obtained. The experimental results during this period have been reviewed, and it is possible now to plan a specific irradiation program.

2. SUMMARY

The recovery of graphite crystals from the Essex County, New York calcite has been completed. Only a few of these crystals are of sufficient quality to be used for mechanical property determinations. An experiment to isostatically compression-anneal pyrolytic graphite was conducted, but the temperature attained was too low to achieve plastic flow; hence, the results were inconclusive. A sufficient quantity of compression-annealed pyrolytic graphite was produced for pre-irradiation testing. Several specimens of compression-annealed pyrolytic graphite have been examined with optical and electron microscopes and a number of structural features associated with the processing have been observed.

The shear strengths of several natural graphite crystals have been measured. The values were found to be in good agreement with Gillin and Kelly's quoted value of 3.9 to 4.9×10^6 dynes/cm². Several specimens of compression-annealed pyrolytic graphite were tested in the single crystal shear apparatus. The values obtained were in good agreement with those found with the torsion apparatus and the shear wedges.

Static compression tests of compression-annealed pyrolytic graphite have yielded values of $1/s_{33}$ ranging from 3.3 to 4.4×10^{11} dynes/cm². The best value, $1/s_{33} = 3.65 \pm .07 \times 10^{11}$ dynes, was obtained for a sample which exhibited a perfectly linear stress-strain curve with no hysteresis loop and behaved like a perfectly elastic material until failure.

Static torsion tests were performed on compression-annealed pyrolytic graphite. The shear modulus $1/s_{44}$ ranged from 0.018 to 0.031×10^{11} dynes/cm² with an average of 0.025×10^{11} dynes/cm². The stress-strain relation in torsion exhibits anelastic behavior and upon cycling the torque, there are narrow hysteresis loops and some residual strain.

The compliance constants $1/s_{11}$ and $1/s_{44}$ have been calculated from Timoshenko's equations by using the appropriate frequency of a resonant bar and c_{66} as measured ultrasonically. The program for the compound torsion oscillator (CTO) was modified so that computations could be made for the compound longitudinal oscillator (CLO). Values of $1/s_{44}$ in good agreement with static and resonant bar measurements were obtained from CTO data, but reasonable values of $1/s_{33}$ were not obtained using the CLO method. A series of tests was made in which several different materials were used as inertial masses in combinations with each other to form compound longitudinal oscillators. It was found that a CLO made of lead-steel-lead yielded a value of $1/s_{11}$ for steel which was approximately 10 per cent low. The value of $1/s_{11}$ for compression-annealed pyrolytic graphite as determined by a steel-graphite-steel oscillator was 85.7×10^{11} dynes/cm², compared with $1/s_{11} = 95 \times 10^{11}$ dynes/cm² as given by the free-free flexural resonance of the same specimen.

The change of the elastic stiffness constant c_{33} was measured as a function of c-axis compressive stress. The fractional change in c_{33} per unit stress σ is given by $\frac{1}{c_{33}} \frac{dc_{33}}{d\sigma} = \frac{d \ln c_{33}}{d\sigma}$. The calculated value of $\frac{d \ln c_{33}}{d\sigma}$ for one specimen was 9.1×10^{-11} cm²/dyne, which expressed in another set of units is .63 per cent per 1000 lb/in². A set of elastic constants for compression-annealed pyrolytic graphite has been obtained by analyzing all the static, sonic resonant bar, and ultrasonic test results. The results are given below where the c_{ij} and $1/s_{ij}$ are in 10¹¹ dynes/cm² and s_{ij} are in 10⁻¹¹ cm²/dyne.

$c_{11} =$	106 ± 2	$1/s_{11} =$	101.5 ± 3
$c_{12} =$	18 ± 2	$s_{12} =$	$-.0015 \pm .0004$
$c_{13} =$	$2.72 (x 2^{\pm 1})$	$s_{13} =$	$-.0063 (x 2^{\pm 1})$
$c_{33} =$	3.6 ± 1	$1/s_{33} =$	$3.48 \pm .2$
$c_{44} = 1/s_{44} = .018 \text{ to } .035$			

3. MATERIALS PREPARATION

Materials preparation methods have been described in the previous quarterly reports. ^(1,2,3) During this period, enough pyrolytic graphite was produced for the pre-irradiation testing. A new technique, hot isostatic annealing, was tried, but the temperatures attained were too low to anneal the samples effectively.

3.1. Recovery of Graphite Single Crystals

C. W. Nezbeda

Approximately 300 pounds of calcite was acid leached for graphite crystals. After the calcite was digested, the remaining sludge was washed, and the graphite crystals were removed with a wet camel hair brush. Although a large number of crystals have been recovered, only a very few are of sufficient quality to be used for mechanical property determinations.

3. 2. Isostatic Pressure Annealing of Pyrolytic Graphite*

Several experiments were conducted in which pyrolytic graphite specimens were annealed under a hot-isostatic-pressing process. Bare and tantalum-clad pyrolytic graphite samples were isostatically pressed at 2650°C and 13000 lb/in² for one hour. The experimental results for two samples are given in Table I.

TABLE I
HOT-ISOSTATIC GAS-PRESSED PYROLYTIC GRAPHITE

Specimen No.	Average Diameter in.	Average Diameter Expansion, %	Average Thickness, in.	Average Thickness Contraction, %	Weight, gm	Weight Loss, %	Approximate Density, gm/cc	Density Increase, %
<u>Canned</u>								
IV Before	1.2442		0.4757		20.7626		2.18	
IV After	1.2458	0.129	0.4591	3.57	20.2411	2.51	2.22	1.83
<u>Uncanned</u>								
V Before	1.2446		0.4700		20.4302		2.14	
V After	1.2484	0.305	0.4600	2.13	20.1877	1.118	2.18	1.87

The plasticity of graphite is very low at 2650°C; hence, the changes effected by these conditions are small but measurable. The method appears promising. A very interesting material should be produced by isostatically pressing pyrolytic graphite at 2800-3000°C under pressures similar to that used in these experiments.

3. 3. Compression Annealing of Pyrolytic Graphite

Sixteen of the twenty-five plates of 3.5-inch diameter pyrolytic graphite deposited from methane and designated M301 to M325 have been compression-annealed in the first half of this year at the Advanced Materials Laboratory in Lawrenceburg, Tennessee. The annealing conditions of 2800°C and 4000 lb/in² which were established for the propane deposited pyrolytic graphite

* At the suggestion of J. G. Conner, this work was performed at Battelle Memorial Institute by P. D. Ownby and D. C. Carmichael.

have also proved to be suitable for the methane deposited pyrolytic graphite. The as-deposited plates had excellent internal structure, but they were, unfortunately, slightly bowed with convex curvature on the substrate side. The roughly conical substrate face of as-deposited plate M301, which is believed to be typical of the group, showed a misalignment of approximately 2 degrees from one side of center to the other. This geometrical defect in the as-deposited plates caused some difficulties in the compression-annealing process.

Some of the as-deposited plates were machined flat on both surfaces; these plates showed evidence of side slipping during compression-annealing, probably because the layer planes were slightly inclined to the surfaces of the plate. Best results were obtained by compression-annealing plates, the surfaces of which retained their curvature, but which were of uniform thickness. Since there is a tendency for imperfections on the surfaces of either the specimen or mold to be propagated through the material during compression-annealing, some plates were first compression-annealed at 1500 or 2000 lb/in² pressure to make them relatively flat, the surfaces were retouched by stripping or machining, and, finally, the plates were compression-annealed again at higher pressure and/or temperature. Pressures ranging from 1500 to 5000 lb/in², and temperatures of 2800°C and 2900°C have been used. Under the best processing conditions, these methane deposited pyrolytic graphite plates yielded good quality compression-annealed pyrolytic graphite. However, attempts will be made in future production of pyrolytic graphite to eliminate or reduce the curvature in the as-deposited plates.

4. MATERIAL CHARACTERIZATION

A hydrostatic method of weighing was chosen for the measurement of the density of the pyrolytic graphite. This technique has an advantage over other methods, in that the dimensions of samples do not enter the calculations; hence, odd shapes, fragments, or broken samples can be used for the measurement. The density variations noted for the several samples could not be related to a quantity such as crystallite orientation as measured by optical reflectivity.

Optical reflectivity has continued to be the method by which sample crystallite orientation has been monitored. The orientation of the sample as a function of distance from the surface shows that the best alignment of crystallites usually occurs in a layer at or near the center of the sample.

Several structural features of compression-annealed pyrolytic graphite have been observed using the optical and electron microscopes. Although most of the structural variations observed have not been studied extensively, work is reported on lenticular twins and upon the polygonal structure noted in previous work.

4.1. Density by Hydrostatic Weighing

O. L. Blakslee

A hydrostatic weighing technique was used for determining the density of compression-annealed pyrolytic graphite. Carbon tetrachloride was chosen as the working fluid because: (1) it wets graphite, (2) it does not absorb contaminants from its environment, (3) its density dependence on temperature is well known, and (4) it has a relatively high density. The experimental procedure was to weigh the sample in air and then weigh it immersed in carbon tetrachloride, noting both the initial weight and the steady state weight. (The weight changes as the carbon tetrachloride soaks into surface cracks. This operation may take 20 to 30 minutes). The temperature of the carbon tetrachloride is recorded.

The density is calculated from the following equation:

$$\rho_g = \frac{M\rho_f}{M-M'} - \frac{M'\rho_a}{M-M'},$$

where ρ_g = density of graphite,

ρ_f = density of fluid,

ρ_a = density of air,

M = weight mass necessary to balance graphite in air,

and M' = weight mass necessary to balance graphite in fluid.

The term $\frac{M'\rho_a}{M-M'}$ corrects for air buoyancy and is about equal to

0.0005 g/cc.

The term $M-M'$ is calculated by subtracting the combined weight of the sample and the holding basket in the fluid from the total of the basket in the fluid plus the weight of the sample in air.

The fluid density (ρ_f) at a temperature T ($^{\circ}\text{C}$) is equal to $1.6326 - 1.911T \times 10^{-3} - 0.690T^2 \times 10^{-6}$. ⁽⁴⁾

Table II shows the density of several samples determined by this technique.

TABLE II
DENSITIES OF COMPRESSION-ANNEALED PYROLYTIC GRAPHITES

Sample	ρ^*	ρ^{**}
M 106-12	2.2457	2.2573 g/cc
M110-5	2.2600	2.2600
M111-1	2.2609	2.2616
P202-1C	2.2561	2.2567
P210-5	2.2578	2.2579
P210-6	2.2614	2.2614
P211-1	2.2522	2.2530
P211-2	2.2516	2.2526
P213-2-RB	2.2553	2.2567
M302-2	2.2596	2.2613
M304-C	2.2602	2.2603
M305-US	2.2601	2.2608
M308-C	2.2605	2.2609

* From initial weight in fluid.

** From steady state weight in fluid.

4.2. Optical Reflectivity

O. L. Blakslee

Table III gives the results of all of the optical reflectivity measurements made during this period. The minimum and maximum half-width values $\theta_{\frac{1}{2}}$ are given for all samples, and a weighted average is given for those samples, the measurements for which were sufficient in number and scope to be representative of the block.

TABLE III
CRYSTALLITE ORIENTATION OF COMPRESSION-
ANNEALED PYROLYTIC GRAPHITE

Sample	No. of Measurements	Min.	$\theta_{1/2}$ Max.	Avg.*	Sample	No. of Measurements	Min.	$\theta_{1/2}$ Max.	Avg.*
C5	32	0.15*	1.32*	0.37*	P207-1	4	0.19*	0.32*	
C103-1	5	.37	.83		P207-3	4	.25	.32	
C103-2	2	.40	.97		P207-4	4	.26	.38	
M101-1	9	.55	1.01		P207-9	1	.26		
M103	16	.32	.88	.64	P207-10	2	.29	.48	
M106	18	.40	1.34	.52	P207-11	2	.30	.40	
M107-1	6	.20	.63		P207-12	6	.16	.20	
M107-2	7	.30	4.4		P207-13	7	.20	.37	
M107-3	8	.25	3.0		P207-15	4	.16	.21	
M107-4	10	.32	2.5		P207-17	7	.29	1.4	
M107-6	2	.29	.49		P210-3	10	.17	.25	.21
M107-7	2	.22	.27		P210-4	9	.21	.65	.51
M108-22	2	.32	1.44		P210-5	2	.17	.27	
M108-23	2	.62	1.11		P211-1	1	.29		
M108-25	2	.28	.75		P211-2	2	.35	.43	
M108-27	2	.66	.67		P211-3	10	.64	.91	.79
M108-28	6	.32	.50		P213-2	11	.68	2.3	1.8
M109-1	4	.55	.65		M304	27	.08	.78	.13
M110-2	19	.16	.88	.47	M305	4	.31	1.15	.46
M110-3	61	.13	2.7	.60	M307	72	.11	.75	.21
M110-4	7	.31	.57		M308	27	.09	.70	.19
M110-5	2	.39	.49		M309	7	.33	1.18	.54
M111	4	.51	.52		M311	29	.22	1.12	.38
M112-14	4	.73	.91		M312	13	.15	.28	.19
P202-1	11	.30	1.9	.62	M313	4	.20	.28	
P205-2	2	.59	1.8		M314	6	.33	1.04	
P205-3	2	.61	2.3		M315	6	.20	.38	

* Measurements made on the surfaces grossly misoriented by the ram faces are excluded from the average.

There have been indications that the crystallite orientation distribution varies significantly with position in the block, especially that the material near the ram faces during annealing is more disordered than that in the middle. During this period, optical reflectivity surveys were made along the c and a-axes of several blocks. Figure 1 shows $\theta_{1/2}$, the halfwidth at half maximum intensity, along the c-axis for four representative blocks. Figure 2 shows a similar survey along the diameter of disk M304.

It is worthy of note that the optical reflectivity measurements are somewhat dependent upon surface preparation, i. e., whether it is cleaved with either a razor blade or scotch tape, sheared, or twisted off in torsion, and whether or not it had been swabbed with acetone. It also appears that a freshly cleaved surface may yield a narrower half-width than one exposed for several weeks.

Figure 1

Half-Width $\theta_{\frac{1}{2}}$ vs. Position Along C-Axis
as Determined by Optical Reflectivity

N-7231

Figure 2

Half-Width $\theta_{\frac{1}{2}}$ vs. Position Along A-Axis
as Determined by Optical Reflectivity (M304)

N-7230

4.3. Electron and Optical Microscopy

N. F. Graves

The electron and optical microscopes reveal a number of structural features which are present on the polished or cleaved surfaces of compression-annealed pyrolytic graphite. Remnants of cone structure and a type of basal slip, for example, are clearly observed under polarized light; several types of surface imperfections are discernible with incident light; and internal structure is visible through the electron microscope. Additional features are brought out by etches which selectively attack graphite at particular crystallographic sites. Most observations described in this report were made on surfaces etched by argon ion bombardment.

Mechanical Lenticular Twins

Compression-annealed pyrolytic graphite contains deformed areas which resemble the mechanical lenticular twins or kink bands formed by shear stresses in some metals. Bowed or S-shaped marks are visible without etching on cleaved c-surfaces where they reflect light in a completely different direction from that reflected over the general area. The deformations are not so easily identified at the a-face and require etching. The marks may occur singly, but often several are aligned to form a distinctive pattern. Sizes range from microscopic to those large enough to be seen without optical aid. One was observed by successive cleavages to extend at least $\frac{1}{4}$ inch through the lamellar planes.

The outline of the deformation mark on the c-surface (Figure 3) indicates that it is mechanically introduced as a result of stress. The direction of deformation appears to follow that resulting from a stress pattern rather than from a crystallographic direction. At the a-surface, however (Figure 4), the basal slip lines of the band intersect those on either side at approximately the $20^{\circ} 48'$ angle expected of graphite twins. The same type of deformity occurs in thermally annealed pyrolytic graphite (Figure 5). Without compressive forces, deformation was limited to comparatively thin lamellae, as evidenced at the cleavage fracture in the foreground.

Figure 3

A Mechanical Lenticular Twin in Compression-Annealed,
Propane Deposited Pyrolytic Graphite, c-Surface

N-8002

Figure 4

A Mechanical Lenticular Twin in Compression-Annealed,
Propane Deposited Pyrolytic Graphite, a-Surface

N-8003

Figure 5
Mechanical Twins or Kink Bands in Thermally Annealed,
Propane Deposited Pyrolytic Graphite, c-Surface

N-8004

Polygonal Structure

A cathodically etched, cleaved surface of a specimen from piece C5 showed a grain-like structure which was described in a previous report. ⁽²⁾ The grains of the etch pattern were found to be approximately the same size as the crystallites, about 30 microns. Since spectroscopic analysis revealed the presence of vanadium in C5, it seemed possible that the impurity had migrated to the crystallite boundaries during strain-anneal and was subsequently the source of pits during the etching process.

A technique to outline crystallite boundaries would provide a convenient microscopic method for determining grain size. Therefore, a series of experiments was performed in an attempt to duplicate the etch pattern of C5. Vanadium was added to other starting material at several stages of the strain annealing process. Representative specimens from each stage were etched by ion bombardment. None of the prepared specimens displayed the characteristic grain-like structure, even though crystallites were larger than those in C5. A specimen cut from piece C5 was then chlorine treated to remove vanadium, but re-etching produced the same type of network.

These experiments indicate that an impurity is not required in this case to initiate the etching process. Instead, etch pits may be formed at polygonal boundaries. It is not certain whether the boundaries coincide with crystallite boundaries or are superimposed through the crystallite network.

5. STATIC TESTS ON SINGLE CRYSTALS

5.1. Tensile Tests of Graphite Single Crystal

R. Sprague

Specimen Preparation

In the preparation of a tensile specimen from a graphite crystal, a crystal is first mounted in a thermoplastic "dop stick", and one side of the crystal is cleaved, using scotch tape, until a monoreflectant, unstepped surface is obtained. A drop of polyvinyl alcohol (PVA) is then applied to the prepared surface. After the PVA solidifies, a piece of scotch tape is placed over the PVA; the tape is then used to strip the PVA and a thin (5 to 20 μ) crystal from the part of the crystal which remains on the dop

stick. The tape is then dissolved with acetone, and the PVA and thin crystal are placed in a steel mask which is in the dog bone shape desired for a tensile specimen. The mask holds the crystal rigidly while the unprotected crystal area is sand-blasted away by an airbrasive machine.

The dog bone shaped crystal and PVA mount is handled with tweezers and transferred to filter paper in a covered petrie dish. The filter paper is wetted with water, but not so much that the crystal floats. Complete dissolution of the water soluble PVA requires a day or more; but when this operation is completed, the filter paper may be air dried, leaving the crystal free on its surface. The crystal must then be carefully handled with the hairs of a fine brush and transferred to the tensile mount.

The tensile mount consists of two surface ground steel bars held in a jig. One end of the tensile specimen is cemented to the upper support bar with a thin layer of DuPont conductive silver paint. This operation is accomplished by positioning the crystal and flowing a drop of acetone into the interface between the crystal and the previously applied paint. The jig is used to transfer the support bars and crystal to the tensile machine, where they are clamped rigidly in place. The jig is then removed, leaving the crystal supports in the desired alignment. The lower end of the specimen is then cemented to the lower bar in the same manner as described above for the upper end.

Instrumentation of Microtensile System

The microtensile machine was described in the previous progress report.

The force transducer was calibrated with standard weights, and the extension transducer was calibrated by a micrometer, using a 50:1 displacement lever.

System Proving

The compliance of the microtensile machine, defined as all the compliance other than that attributed directly to the specimen, has been measured. In one experiment, a solid steel bar was substituted for specimen and supports, giving only the compliance of the machine. In a second experiment, the machine compliance was measured with the specimen supports in place and

a steel bar cemented to and connecting the supports; the cemented area was equivalent to the normal crystal grip area. Hence, the machine compliance and the compliance of the cement were measured. The compliance of the machine was measured with several cements: Duco cement, Courtright cement, Eastman 910 epoxy cement, and DuPont conductive silver paint. The silver paint gave the lowest compliance and was also the easiest to use in this specimen.

Many tests were made with metal foils of known elastic modulus to check the accuracy of the tester. Foils of titanium, aluminum, and tungsten were mounted by using silver paint, and the modulus was measured in the microtensile machine. Aluminum appeared to be so compliant that the yield point was reached in an indeterminate part of the stress-strain curve. This result was confirmed by testing on a larger Instron machine.

Titanium foil of about $1/4$ mil thickness was air-abrasive machined in the steel mask to the same size and shape as that used for graphite specimens and subsequently tensile tested. The modulus obtained with the microtensile machine was about 10×10^6 lb/in², whereas that furnished by the manufacturer is about 5×10^6 lb/in². This same specimen was then removed from the supports, and the area of the grip was trimmed in successive stages to determine whether the measured compliance was a function of grip area. The grip area was reduced from about five times that of the gage area to an area nearly equal to that of the gage area with no change in sample compliance.

Modulus values obtained with the microtensile machine using a tungsten ribbon as test specimen have ranged between 43.7×10^6 lb/in² and 57.7×10^6 lb/in². The handbook value is 51.5×10^6 lb/in². Much of the scatter in the values of these preliminary experiments with tungsten can be attributed to irregularities in the thickness of the specimen.

Results with Graphite Crystals

Preliminary results using cleaved compression-annealed pyrolytic graphite crystals have given moduli much lower than those obtained in the static, sonic, and ultrasonic tests on larger specimens. Since these experiments were completed, several changes have been made in the

microtensile machine and the machine tests described above have been conducted. Experiments are at present aimed toward establishing reproducibility of values and toward the determination of the effect of gage length on the measured modulus. The greatest scatter of measurements in past experiments has been with short specimens, with gage lengths 6mm and lower. Most natural graphite experiments must be made with gage lengths below 3mm, due to the small size of available samples.

5.2. Shear Tests of Graphite Single Crystal

C. W. Nezbeda, D. E. Soule

An apparatus has been designed to measure shear strength in both single crystal and pyrolytic types of graphite and is shown schematically in Figure 6. The main shearing carriage consists primarily of a $1\frac{1}{2}$ inch,

Figure 6
Single Crystal Shear Apparatus

N-6839

60-case hardened rod traveling in special adjustable split ball bushings with a tolerance of less than .005 inch. This rod is kept from rotating by a $\frac{1}{4}$ inch outrigger arm traveling in a resiliently mounted ball bushing. The static friction of this entire carriage arrangement is on the order of 17 grams.

Perpendicular to the shearing carriage movement is mounted a normal displacement carriage containing four ball bushings riding on two $\frac{1}{4}$ inch, 60-case hardened rods. This movement can also be actuated by a pulley arrangement and the shear studied as a function of normal force, if so desired.

The detachable shearing heads, shown in the inset, vary in diameter from 2 to 8 mm, thus accommodating a wide range in sample areas.

Because of the exceedingly low shear strengths of the small single crystals measured, the shearing force on the sample is provided by the weight of water flowing into a container which is connected to the shearing carriage. In this manner, the shear force can be continuously increased at almost any desired rate from a lower limit of about $\frac{1}{2}$ gram per second.

For future modulus measurements, a differential transformer core of the Schaevitz shielded type has been attached to the shearing carriage and will be used in conjunction with a Daytronic 201 AH transducer-exciter-demodulator and a Mosely 2D X-Y recorder with time drive.

Figure 7 shows an overall view of the entire apparatus, and Figure 8 shows a closeup view of the shearing and displacement carriages with a sample in position for shearing. The natural single crystals were attached to the shearing heads with Eastman 910 epoxy cement. For maximum adherence, the crystals were first lightly etched with a gentle sand blast. Alignment of the crystals on the shear heads was carefully controlled, the cementing carried out in situ, and the cemented sample left in place for the actual shear.

Figure 7
Overall View of Single Crystal Shear Apparatus

N-7307

Figure 8
Closeup View of Shearing and Displacement Carriages

N-6924

The compression-annealed pyrolytic samples were cut from specific locations in the original compression-annealed block, cleaved, and then turned down to the desired diameter on a lathe. These samples were also lightly etched by sand blasting to obtain sufficient adherence to the shear heads.

Typical results of the measurements on single crystal and pyrolytic samples are shown in Figure 9.

Figure 9

Typical Shear Strength Results for Pyrolytic and Single Crystal Graphite

N-7233

For single crystals, a generally expected initial increase in shear strength is common to all of the crystals measured. This condition is undoubtedly due to the occurrence of initial structural weak points, such as edge imperfections or partial internal delamination.

This assumption of initial imperfections is strengthened by the fact that the shear strength values saturate, becoming asymptotic to a value most representative of the true shear strength of the entire sample. Accordingly, an average taken (omitting the first shear) from a total of 20 shears on 9 crystals gives a shear strength of $4.2 \pm 0.8 \times 10^6$ dynes/cm². This value is corroborated by the value of 4.3×10^6 dynes/cm² as obtained from the shear of a highly annealed and uniform crystal ECP-1, shown in Figure 10.

Figure 10
Uniform and Extended Shear of Single Crystal ECP-1

N-6998

In the shearing of this crystal, an extreme and rather unique example of plastic slip was obtained. When this crystal began to shear, no further increase of stress was applied. The crystal, however, continued to slip until the shearing carriage hit the stop, a distance of 5.5mm, whereas the diameter of the crystal was only 4mm. The crystal had still not fractured at this point, and the two halves had to be separated manually. The slip steps can clearly be seen in Figure 10 forming a "deck of cards" effect. This crystal was evidently very homogeneous, since over 125 uniformly spaced slip steps can be seen. In other cases, crystals did show partial individual slips, but these were pinned before the actual fracture point was reached.

The average value for the shear strength in single crystal graphite is also in good agreement with the value of 3.9 to 4.9×10^6 dynes/cm² quoted by Gillin and Kelly⁽⁵⁾ obtained by extrapolation to zero normal force from diagonal shear measurements.

In the case of compression-annealed pyrolytic graphite, the results are considerably more dependent upon the initial fabrication conditions of the particular sample measured. Results of measurements on pyrolytic sample 3-M304-E indicate the somewhat erratic behavior of successive shear values. This characteristic was present in all of the pyrolytic samples measured.

The magnitudes of the pyrolytic graphite shear strengths are also much higher than those of the single crystals, as seen in Table IV. The higher shear strengths of the pyrolytic samples were to be expected, since pyrolytic graphite is polycrystalline and the grain boundaries undoubtedly act as pinning points for dislocation movement along the basal planes of individual crystallites. In addition, the degree of preferred orientation of compression-annealed pyrolytic graphite, although good and less than one degree, is not perfect; thus, additional bonding forces are operative.

TABLE IV
INDIVIDUAL SHEAR STRENGTHS OF SINGLE CRYSTAL
AND PYROLYTIC GRAPHITE SAMPLES IN UNITS OF 10^6 DYNES/CM²

<u>THERMALLY ANNEALED SINGLE CRYSTALS</u>				
Sample	Area (mm ²)	Shear Strength	Gillin & Kelly	
EC-3*	13.4	4.8, 4.2		
EP-74	5.74	4.6, 4.1		
ECP-1	12.6	4.3		
ECP-2	12.6	4.6		
EP-84	12.8	2.8	~4-5	
ECPA-6	7.74	6.8		
ECPA-5	6.52	3.7		
<u>COMPRESSION-ANNEALED PYROLYTIC</u>				
			Seldin (Extrapolated)	Half- Width $\theta_{\frac{1}{2}}$
C-5	71.1	8.3 ± 1.4	8.9 ± 1.1	0.45°
2-M305-PS	50.2	12.4 ± 2.6	15.7 ± 5.4	0.19°
3-M304-E	33.1	9.2 ± 2.6		

* For single crystals, type and order of preparation methods are indicated by the prefix letters, i. e., E, Essex County; C, cut; P, purified and annealed at 3000°C; and A, additional anneal at 3100°C.

6. STATIC TESTS ON PYROLYTIC GRAPHITE

E. J. Seldin and T. Weng

Tensile tests have been made on specimens of compression-annealed pyrolytic graphite mounted in metal end pieces. The testing was performed on the Instron machine, using the load cell on the Instron to detect the stress; pairs of strain gages on the specimen measured the longitudinal and transverse strains. Experimental values of the compliances s_{11} , s_{12} , and s_{13} have been obtained. The longitudinal strains have been measured on both the a- and c-faces of several specimens to check the uniformity of the stress distribution. The effect of a kink in the material on the stress-strain curves has also been investigated.

Compression tests have been made on small cylindrical specimens of compression-annealed pyrolytic graphite held in a compression cage, using the compression load cell on the Instron machine to detect the stress; a pair of strain gages on the specimen measured the longitudinal strain. The problems of compression testing small cylinders were studied, using both compression-annealed pyrolytic graphite and steel specimens. The longitudinal modulus $1/s_{33}$ was determined for several specimens, and the problem of determining the compliance s_{13} in a compression test was investigated.

The torsion apparatus was used to test several specimens of compression-annealed pyrolytic graphite and one specimen of as-deposited pyrolytic graphite. Curves of torque-vs. -angular deformation to failure were obtained, and the shear modulus $1/s_{44}$ was determined from the slope in the limit of zero strain.

Shear tests were made on specimens from neighboring regions of a layer of compression-annealed pyrolytic graphite in order to investigate reproducibility of the shear strength, the dependence of the strength on the specimen size, and the variation of shear strength with successive shears.

6. 1. Tensile Tests on Compression-Annealed Pyrolytic Graphite

A. Apparatus

Figure 11 is a drawing of a compression-annealed pyrolytic graphite tensile specimen mounted in metal end pieces. The specimen has straight shoulders with angles matched to those of the end pieces. The specimen and end pieces were aligned in a special fixture: while the assembly was kept under a small tensile stress of 30 to 50 lb/in², epoxy cement was used to fill the gap between the end of the specimen and the metal, and the cement was also used along the edges of the specimen as a fillet material. After hardening, the epoxy maintained the alignment of the specimen in the end pieces and reduced the tendency for the layer planes to delaminate and fold back along the steel during the tensile test. Two specimens with round shoulders, of the type used with epoxy end pieces, ^(1,2,3) were also tested in tension using metal end pieces designed to fit the specimens; but this design was subsequently abandoned in favor of the configuration shown in Figure 11. The tensile tests were performed on an Instron machine, using the same techniques for obtaining stress-strain curves and elastic constants as described in the preceding Quarterly Reports. ^(1,2,3)

Figure 11

B. Results

In previous tensile tests on specimens of compression-annealed pyrolytic graphite potted in epoxy end pieces, the strains measured on the c-faces of the specimen were higher than those measured on the a-faces. This result was due to a nonuniform stress distribution across the width of the specimen, caused by constraint of the c-faces within the epoxy end pieces. The metal end pieces were introduced in order to correct this difficulty by giving more uniform support to the ends of the specimen.

The uniformity of the stress distribution was checked by running tensile tests on several specimens in which pairs of gages were mounted on the a- and c-faces. The results are given in Table V. For some of the specimens, more than one test was performed, and Table V indicates whether the gages were the same as those used in the previous test or new gages. The measurements on the a- and c-faces did not agree as well as one might wish, but the strains were no longer consistently higher on the c-faces. In addition, reproducibility from test to test was good in some cases and poor

in others. The material also varied in quality. Since M304 was judged to be the best material because it was flat and straight and had low optical reflectivity, tests on specimens M304-1 and M304-3 using transverse gages were also conducted. In contrast, since specimen P213-2 was badly bowed and had high optical reflectivity, it was judged to be of relatively poor quality.

TABLE V
RESULTS OF STATIC TENSILE TESTS ON COMPRESSION-ANNEALED
PYROLYTIC GRAPHITE SPECIMENS MOUNTED IN METAL END PIECES

Specimen	Young's Modulus $1/s_{11}$ (10^6 lb/in ²)		Compliances s_{11}		(10 ⁻¹¹ cm ² /dyne)		Optical Reflectivity $\theta_{\frac{1}{2}}$ (deg)
	c-face	a-face	c-face	a-face	s_{12}	s_{13}	
C5-2*	131	126	.0111	.0115			.22
C5-4	108	154	.0134	.0094			.27
C5-5	94	86	.0154	.0169			.35
	100≡	86≡	.0145	.0169			
C5-6*	151	157	.0096	.0093			.19
C5-7	120	92	.0121	.0158			.17
M109-1	147.5	126.5	.0098	.0115			.61
M112-14	149	105	.0097	.0138			.82
	125.8≡	105≡	.0116	.0138			
P213-2	64.3	63.8	.0226	.0227			1.80
	100≡	63.1≡	.0145	.0230			
	106#	63#	.0137	.0230			
	74.5#	46.8#	.0195	.0310			
	76.8#	47.2#	.0189	.0308			
M304-1	138.4	113.1	.0105	.0128			.11
	138.3≡	118	.0105	.0123	-.0019	-.0029	
M304-3	108	135	.0134	.0108			.14
	108.9≡	126.8≡	.0133	.0115	-.0017		
	105.8≡	129.1≡	.0137	.0112		-.0034	
M308-1	105.8		.0137				.20
	118#		.0123				

* Round-shouldered specimens of type used with epoxy end pieces

≡ Same gages as in previous test

New Gages

Table VI summarizes the moduli and longitudinal and transverse compliances obtained from tensile tests on specimens from block M307; the longitudinal strains in these tests were all measured on the c-faces. Each of the first three specimens in Table VI had a clearly visible kink across the middle of the gage section. For specimen M307-1, the first and last tests were made with strain gages over the kink. The longitudinal stress-strain curves in these tests were nonlinear and showed residual strains and hysteresis loops when the stress was cycled, much like the stress-strain curves obtained from measurements of polycrystalline graphite. The Young's moduli, which were obtained from the slopes of the curves in the limit of zero strain, are low because of the large strain in the kinked region of the specimen. The stress-strain curves which were obtained with gages alongside, but not covering, the kinks were linear, showed no hysteresis, and yielded considerably higher values for Young's modulus. Specimens M307-6 and M307-7 had no clearly visible kinks.

TABLE VI
RESULTS OF STATIC TENSILE TESTS ON COMPRESSION-ANNEALED
PYROLYTIC GRAPHITE SPECIMENS MOUNTED IN METAL END PIECES

Specimen	Young's Modulus Compliances (10^{-11} cm ² /dyne)				Optical Reflectivity θ , ν_r (deg.)
	$1/s_{11}$ (10^6 lb/in ²)	s_{11}	s_{12}	s_{13}	
M307-1	43.6*	.0333			.145
	111.5#	.0130			.145
	114.0#	.0127			
	41.0#*	.0353	-.00247		
M307-2	107.1	.0136	-.00185		.12-.19
	105.5≡	.0138			.11-.15
	102.6#	.0142			
M307-3	69.0	.0210	-.0030		.18-.22
	68.9≡	.0210	-.0031≡		.15-.21
M307-6	140.0	.0104	-.00146	-.00378	.14-.18
	118.0#	.0123	-.0012≡	-.00308#	.27-1.24
	141.6#	.0103	-.00120≡	-.00247#	
	155.2≡	.0093	-.0012≡	-.00444≡	
M307-7	128.0	.0113	-.00130		.15-.26
	122.8#	.0118	-.00135		.15-.24

* Gages covering Kink

≡ Same gages as in previous test

New gages

6.2. Compression Test

A. Apparatus and Experimental Techniques

The elastic modulus $1/s_{33}$ for compression-annealed pyrolytic graphite has been determined from the stress-strain curves obtained in compression tests on cylindrical specimens. Some exploratory compression tests were first run on cylinders of steel, arbitrarily chosen as a representative well-behaved elastic material, in order to investigate the influence of specimen size and geometry on the results and to check the apparatus and testing techniques. Since the compression-annealed pyrolytic graphite is made in plates approximately 0.3-inch thick, several steel cylinders were made with this length and with diameters of $1/2$, $3/8$, $5/16$, and $1/4$ inch; in addition, two $1/2$ inch diameter steel cylinders were made with lengths of $1/2$ and 1 inch. The cylinders were tested on the Instron machine, using the compression load cell for the measurement of stress. The strains were measured by pairs of strain gages, and the techniques used for recording the stress-strain curves were identical to those used in the tensile tests. Two methods were used for supporting the cylinders: either the cylinder was placed at the center of a self-aligning table on top of the compression load cell, or it was placed in a compression cage between two plane-parallel steel faces. The tests on the 0.3-inch length steel cylinders were duplicated on compression-annealed pyrolytic graphite specimens with the same diameters.

The 1 inch long steel cylinder yielded a linear stress-strain curve when the specimen was tested both on the self-aligning table and in the compression cage, but the quality of the stress-strain curves for the $1/2$ inch diameter steel cylinders worsened as the length of the cylinder decreased. For the $1/2$ inch long cylinder, the stress-strain curve was nonlinear at low stress and then became linear as the stress was increased. For the 0.3-inch long cylinder, the stress-strain curve was even more nonlinear and contained large hysteresis loops when the stress was cycled.

The nonlinearity and hysteresis loops in the stress-strain curves for the 0.3-inch long steel cylinders was reduced as the diameter of the cylinder was reduced. However, the position of the cylinder relative to the center

of the self-aligning table became more critical as the diameter of the cylinder decreased; a $1/64$ inch displacement of one of the smaller diameter cylinders from the center of the table caused a definite increase in the nonlinearity of the stress-strain curve. The stress-strain curve obtained with a steel cylinder in the compression cage was comparable to the best curve obtained by very careful positioning of the cylinder on the self-aligning table, and the stress-strain curve was not sensitive to the position of the cylinder within the cage. Similar tests with 0.3-inch long cylinders of compression-annealed pyrolytic graphite having the same range of diameters gave comparable results. Therefore, the compression cage was chosen in preference to the self-aligning table as the apparatus to be used for the testing of graphite. In addition, a specimen diameter of $1/4$ inch was chosen as a standard for future tests; with this diameter, the specimen has a sufficiently high length-to-diameter ratio and sufficient surface area for the application of strain gages..

The compression stress-strain curves for both steel and compression-annealed graphite were highly sensitive to the condition of the end faces of the specimen. The curve for one of the $1/4$ inch diameter steel cylinders was, on first testing, nonlinear with increasing slope to a stress of 3000 lb/in² and then linear at higher stresses. When the end faces were very carefully ground and polished, the region of nonlinearity was reduced to stresses below 500 lb/in². On the other hand, the graphite specimens had, for the most part, naturally cleaved end faces which were not perfectly plane parallel. This condition caused the initial parts of the stress-strain curves to be nonlinear. The nonlinearity was reduced, but not entirely eliminated, in two ways: first, the end faces were sanded on fine emery paper while the specimen was held in the core of a steel cylinder with a squared end; secondly, the graphite cylinders were cemented with epoxy cement between two steel cylinders (which had carefully ground plane parallel end faces) while the assembly was aligned in a V-block, the objective of this method being to fill in the surface irregularities of the graphite with epoxy.

B. Results of Compression Tests on Compression-Annealed Pyrolytic Graphite

A total of 6 specimens with $1/4$ inch diameter and a total of 12 specimens with $5/16$ or $3/8$ inch diameter were tested in compression, using the compression cage on the Instron machine. Most of the stress-strain curves were nonlinear at low stress, with slopes either increasing or decreasing as the stress increased and with no hysteresis loops when the stress was cycled. When the specimens were cemented with epoxy to steel end pieces, the region of nonlinearity was reduced, but some hysteresis loops appeared as a result of the constraint of the specimen at the ends. The modulus was determined from the linear regions of the curves at high stress, and values of $1/s_{33}$ ranging from 3.3 to 4.4×10^{11} dynes/cm² were obtained. One well-aligned $1/4$ inch diameter cylindrical specimen of compression-annealed pyrolytic graphite (M311-CC3) with naturally plane-parallel end faces was tested in the compression cage without end pieces. This specimen yielded a perfectly linear stress-strain curve with no hysteresis loop and behaved like a perfectly elastic material until failure; the average modulus for several tests was $1/s_{33} = 3.65 \pm .07 \times 10^{11}$ dynes/cm².

The compliance s_{13} cannot be determined from measurements with strain gages along the transverse direction in our compression test. Because of the extremely low Poisson ratio- s_{13}/s_{33} , a gage aligned in the transverse direction experiences a small strain along the gage axis and a very large strain in the transverse gage direction. By using the transverse sensitivity coefficient of the type FAP-06-12 gages^(6, 7) one obtains a calculation which shows that the longitudinal and transverse strains in the gage almost exactly compensate for each other in their effect on the gage resistance.

The equation used in the calculation was

$$\epsilon_a = (1 - \mu k) \epsilon_c - k \epsilon_n,$$

where

ϵ_a = true strain along gage axis

ϵ_c = apparent strain along gage axis (change in resistance divided by gage factor, as given by manufacturer)

ϵ_n = true strain transverse to gage axis

$\mu = .285$ = Poisson ratio of steel (gages are calibrated by manufacturer on steel).

k = transverse sensitivity coefficient (equal to 0.12 for type FAP-06-12 gages, according to Wu⁽⁷⁾).

In two compression tests where transverse strain gages were actually used, the apparent strain measured in the transverse direction was zero for one test and very slightly positive in the other test. We conclude that the compliance s_{13} cannot be measured accurately in a compression test unless the transverse sensitivity coefficient of the strain gage is accurately known (it is not), or unless a gage with drastically lower transverse sensitivity can be obtained. Therefore, s_{13} should be measured only in a tensile test.

Most of the compression specimens were taken to failure. The maximum stress sustained by the specimens fell within the range of 36,000 to 59,000 lb/in², and failure always occurred by shear along layer planes. Sometimes a specimen sheared along only one plane, but there were several cases where a thin layer of the material sheared out of position. Figure 12 shows one such case, where a thin layer sheared almost halfway out of the center of the specimen, while the piece as a whole remained intact. The maximum compressive stress at failure is, therefore, more a measure of the degree of alignment of the layers in the material than a measure of compressive strength.

Figure 12
Compression Specimen M304-B2 After Failure

N-7072

6.3. Torsion Tests

A. Apparatus

The torsion apparatus is shown in Figure 13. The $\frac{1}{2}$ inch diameter specimen was cemented between steel end pieces with Eastman 910 cement. The lower end piece was held fixed by means of set screw, and the upper end piece was attached to the lower end of the torsion shaft. The torque was applied through a 2-inch diameter wheel on top of the torsion shaft by means of a pair of strings and pulleys and fixed weights. The rotation of the upper end piece was communicated to the core of a linear variable differential transformer (LVDT) by a bar which was attached to a ring around the upper end piece. The distance between the center of the specimen and the axis of the LVDT core was 5 inches. Since the rotation of the specimen was extremely small, the linear motion of the LVDT core was directly proportional to the angular rotation of the specimen. In the torsion test, the torque was increased and decreased in uniform increments by changing the weights on the weight hangers, and the LVDT output was detected on a strip chart recorder. The LVDT was calibrated by means of a micrometer screw.

Figure 13
Static Torsion Apparatus

N-6759

B. Equations

For a linearly elastic material, the modulus of rigidity G of a solid cylinder of radius R and length L subjected to a torque T about its longitudinal axis is given by

$$G = 2TL / \pi R^4 \theta, \quad (1)$$

where θ is the angle of rotation. The shear stress σ within the cylinder varies linearly with the radius r according to the relationship

$$\sigma = 2Tr / \pi R^4. \quad (2)$$

The maximum shear stress at failure $\sigma_{\max}$ due to a maximum torque $T_{\max}$ occurs at the periphery of the cylinder and is given by the equation

$$\sigma_{\max} = 2T_{\max} / \pi R^3. \quad (3)$$

Since the initial part of the curve of torque-vs. -angular deformation for compression-annealed pyrolytic graphite is linear, Equation (1) accurately gives the shear modulus $G = 1/s_{44}$. Nadai⁽⁸⁾ has shown that, when the curve of torque vs. angular deformation is nonlinear, Equations (2) and (3) are no longer accurate; and he gives geometrical transformation formulae for obtaining a curve of $\sigma_{\max}$ -vs. -angular deformation from the curve of torque-vs. -angular deformation. Nadai's correction, when applied to the torsion data for compression-annealed pyrolytic graphite, causes the true maximum shear stress at failure to be about 15 per cent lower than that given by Equation (3).

C. Results of Torsion Tests on Pyrolytic Graphite

Figure 14 is a representative plot of torque-vs. -angular deformation per unit length for a specimen of compression-annealed pyrolytic graphite tested in torsion to failure. The initial slope of the curve is linear to a torque of approximately 1 in. lb. To obtain the shear modulus $1/s_{44}$, the initial slope was corrected to take account of the deformation of the steel end pieces and the cement joints. The correction was determined from tests on steel cylindrical specimens in which the deformation calculated from the known modulus of rigidity of steel was subtracted from that which was actually observed. In the test shown in Figure 14, the torque was cycled once; a narrow hysteresis loop and some residual strain were observed.

Figure 14
Torque vs. Angular Twist per Unit Length for Compression-Annealed
Pyrolytic Graphite Specimen

Tables VII and VIII summarize the static torsion tests conducted on the compression-annealed pyrolytic graphite specimens. A series of tests was usually run on a given specimen by using the successively smaller pieces which remained after each test; the starting piece was labeled A, and the pieces which were generated by successive shear breaks in the torsion tests were labeled in alphabetical order. Tables VII and VIII list the thickness of each piece, the shear modulus determined from the initial slope of the curve of torque-vs. -angular deformation, the maximum shear stress at failure as determined from Equation 3, the previous maximum shear stress to which the specimen was subjected, and the optical reflectivity measurements which were made after each test on the surfaces along which shear failure occurred. The values of $1/s_{44}$ fall within the

range of 0.018 to 0.031×10^{11} dynes/cm², with an average value of about 0.025×10^{11} dynes/cm². There is no apparent correlation between the value of $1/s_{44}$ and the flatness of the material as given by the optical reflectivity. The true shear strengths are approximately 15 per cent lower than those given in Tables VII and VIII; Nadai's⁽⁸⁾ correction was not made, for it is a laborious process and we were interested more in comparing the relative stresses at which successive breaks occur than in measuring shear strengths. The shear strength usually increased with successive shear tests, but there were a few exceptions. The shear modulus showed no tendency to either increase or decrease with successive tests.

TABLE VII
STATIC TORSION TESTS

Specimen	Test No.	Piece	Thickness (in)	Previous Max. Shear Stress * (lb/in ²)	Max. Shear Stress at Failure * (lb/in ²)	Initial Modulus $1/s_{44}$ (10^{11} dynes/cm ²)	Pieces After Test	Optical Reflectivity θ_{ν} (degrees)
C5	1	A	.0535	0	40		B	
							C	
	2	B	.0362	40	125	.0219	D	.35
							E	
	3	D	.0303	125	198	.0216	F	.22-.27
M110-2							G	
	4	F	.0267	198	162	.0249	H	.29
							J	
	1	A	.0933	0	189	.0286	B	.18
							C	.19
M110-3	2	B	.0365	189	364	.0272	D	.195
							E	.21
	1	A	.1395	0	45		B	.17
							C	.17
	2	B	.0749	45	36		D	.18
M110-3							E	.14
	3	D	.0353	45	360	.0238	F	.18
							G	.20
	4	E	.0396	45	328	.0224	H	.16
							J	.18
	5	H	.0139	328	390	.0198	K	.22
							L	.23
	6	F	.0331	360	278*	.0223	M	.17
							N	.17
	7	C	.0649	45	202	.0225	O	.17
M110-3							P	.21
	8	O	.0349	202	193	.0211	Q	.16
M110-3							R	.19

* Torque was reversed in this test to -45 lb/in², which may have caused decrease in shear stress at failure.

* Shear stress is uncorrected value as calculated from equation 3.

TABLE VIII
STATIC TORSION TESTS

Specimen	Test No.	Piece	Thickness (in)	Previous Max. Shear Stress * (lb/in ²)	Max. Shear Stress at Failure * (lb/in ²)	Initial Modulus 1/s ₄₄ (10 ¹¹ dynes/cm ²)	Pieces After Test	Optical Reflectivity θ _{1/2} (degrees)
M304A	1	A	.3887	0	4		B	.14
							C	.20
	2	B	.2959	4	20	.0256	D	.09
							E	.08
	3	D	.201	20	346	.0248	F	.09
							G	.09
	4	E	.0965	20	229	.0243	H	.10
							J	.09
M108-25	1	A	.3557	0	175	.0258	B	.75
							C	.62
	2	C	.3169	175	202	.0267	D	.37
							E	.27
M108-27	1	A	.3484	0	310	.0225	B	.66
							C	.62
M108-28	1	A	.3752	0	220	.0282	B	.42
							C	.30
	2	B	.1107	220	166	.0244	D	.44
							E	.60
P207-1	1	A	.2437	0	36	.0196	B	.19
							C	.24
	2	C	.1228	36	130	.0175	D	.32
							E	.29
P207-3	1	A	.2528	0	139	.0236	B	.27
							C	.26
	2	C	.1047	139	229	.0264	D	.32
							E	.25
P207-4	1	A	.2537	0	112	.0228	B	.30
							C	.34
	2	C	.1711	112	185	.0235	D	.37
							E	.37
P210-3C	1	A	.1310	0	337	.0293	B	.24
							C	.20
	2	B	.0710	337	395	.0310	D	.21
							E	.195
	3	D	.0588	395	409	.0288	F	.19
							G	.21

* Shear stress is uncorrected value as calculated from equation 3.

One specimen of as-deposited pyrolytic graphite (M301) was tested in static torsion. The shear modulus 1/s₄₄ was determined from the initial slope of the curve of torque-vs. -angular deformation to be 0.13 x 10¹¹ dynes/cm².

6.4. Results of Shear Tests on Compression-Annealed Pyrolytic Graphite

Shear tests were made on specimens of compression-annealed pyrolytic graphite taken from a single 1.5mm thick layer of plate M305, using both large and very small compression-shear fixtures of the type described in the Second Quarterly Progress Report. ⁽²⁾ The shear faces of the large fixtures measured 1/2 x 1/4 inch and made an angle θ of 45° with the horizontal. Three sets of very small fixtures were used; the shear faces of these fixtures measured 2 x 2mm and made an angle θ with the horizontal of 15°, 30°, and 45°, respectively.

Figure 15 is a plot of the shear stress at failure-vs. -the normal stress for the tests made with the very small fixtures; the numbers next to the data points indicate the order in which the points were obtained. The numerical average values and the extreme values are extrapolated linearly to obtain the shear strength in the limit of zero stress. The values of shear strength which were obtained varied from 140 to 305 lb/in², with an extrapolated average of 230 lb/in².

Figure 15

Shear Stress at Failure vs. Normal Stress for Compression-Annealed Pyrolytic Graphite M305-Very Small Shear Fixtures

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Two series, each consisting of ten consecutive tests, were also made with the large shear fixtures on specimens taken from positions in the layer adjacent to each other and to the specimens used with the very small fixtures. The average values of shear strength obtained in the two series of tests were 245 and 253 lb/in², respectively. These values may be compared with the average value of 256 lb/in² obtained with the very small shear fixtures having $\theta = 45^\circ$. The spread of values obtained with the large fixtures was comparable to that obtained with the very small fixtures, and the values obtained on successive breaks also fluctuated in a random manner. We conclude that the shear strength measured with the compression shear fixture is independent of the size of the fixture. In addition, some tests in pure shear were made on one other specimen from the same layer, and the values of shear strength which were measured were compatible with the linearly extrapolated values obtained with the compression shear fixtures.

7. ULTRASONIC AND RESONANT BAR TESTS OF PYROLYTIC GRAPHITE

O. L. Blakslee and D. G. Proctor

7.1. Resonant Bar Results

Table IX gives the results of the resonant bar measurements made during this period. The analysis given in the Third Quarterly Report⁽³⁾ was used for the calculation of the moduli shown. As described earlier,* a flexural vibration has both a shear and a longitudinal contribution; from a flexural frequency and one modulus (shear or Young's), the other modulus can be calculated. The $1/s_{11}$ was calculated from the c_{66} measured by ultrasonics and the fundamental flexural resonance parallel to the basal plane (FFT). The $1/s_{44}$ was found by two methods: (1) the flexural resonances perpendicular to the basal plane (FFD) and the $1/s_{11}$ measured by FFT, and (2) the fundamental torsional resonance and the c_{66} measured ultrasonically. The Timoshenko shear equivalence constant k used in the flexural calculations was 0.85.

Specimens M106-1 and M106-2 consisted of two bars cut from disk M106. Specimens M106-2A, 2B, 2C were three separate bars cleaved from M106-2. Specimen P211-3RB1 was cleaved from P211-3RB. Specimens

* Third Quarterly Report, Page 24.

P213-2-RB1 and RB2 were two bars cleaved from P213-2. All the M304 specimens were cleaved from M304-C:

M311-RB1 and RB2 were cleaved from M311-RB.

TABLE IX
MODULI OF COMPRESSION-ANNEALED PYROLYTIC GRAPHITE

		M106-1	M106-2	M106-2A	M106-2B	M106-2C	P202-1-C	P211-3-RB	P211-3-RB1	P213-2-RB1	P213-2-RB2
$\frac{1}{2}E_{11}$	FFT-1	-----	-----	38.7	46.2	-----	53.6	73.1	89.0	43.7	54.5
$\frac{1}{2}E_{33}$	FFD-1	.0196	.0180	.0188	.0188	.0209	.0219	.0277	.0302	.0210	.0222
	2	200	190	189	179	163	228	307	313	224	231
	3	201	194	196	185	180	233	313	320	231	235
	4	204	197	206	-----	185	235	320	324	234	238
	5	204	199	209	193	179	235	316	327	235	239
	6	205	201	209	192	181	238	321	329	237	240
	7	206	202	218	196	186	240	323	331	239	241
	8	202	194	212	192	181	240	327	332	270	244
	9	207	201	-----	200	183	240	327	334	-----	243
$\frac{1}{2}E_{33}$	FT 1	206	202	214	198	180	238	360	327	235	238

		M304-C	M304-C1	M304-C11	M304-C111	M304-C112	M304-C2	M307-RB	M311-RB	M311-RB1	M311-RB2
$\frac{1}{2}E_{11}$	FFT-1	92.6	95.1	99.0	98.6	89.2	91.3	69.9	82.1	93.0	68.0
$\frac{1}{2}E_{33}$	FFD-1	.0247	.0256	.0252	.0250	.0222	.0246	.0208	.0303	.0326	.0334
	2	259	278	263	259	246	271	224	333	338	335
	3	262	282	264	263	252	269	233	344	343	341
	4	263	282	269	266	-----	267	234	348	347	342
	5	265	276	270	268	258	261	236	345	348	345
	6	304	277	273	270	259	260	236	348	350	345
	7	291	279	273	271	262	263	240	352	351	347
	8	-----	281	275	272	263	266	-----	358	353	348
	9	-----	280	275	273	-----	264	-----	356	353	349
$\frac{1}{2}E_{33}$	FT 1	261	278	270	270	258	259	226	360	354	354

Units are 10^{11} dynes/cm²

In calculating $1/s_{44}$ from the flexural resonant frequencies, thick specimens (low L/D) and high harmonics are less affected by changes of assumed $1/s_{11}$ than thin specimens and low harmonics.* Slight errors in the T or D dimensions cause approximately the same per cent error in the calculated modulus, and in the same direction. Errors in L cause two or three times as much error in the calculated modulus, but in the opposite direction. The same doubts expressed in an earlier report⁽³⁾ about the $1/s_{44}$ calculated from torsional resonance apply to those data reported in Table IX.

7.2. Compound Oscillator Results

Table X gives the results of the compound torsion oscillator (CTO) measurements made during this period. The value of $1/s_{44}$ measured by ultrasonics on the same specimen is also given. It appears that there is a systematic discrepancy between the ultrasonic and CTO results. The ultrasonic technique has been carefully checked and is regarded as accurate; even so, it is not completely clear that the CTO measurement is in error, because the ultrasonic wave averages the elasticity values of the material through which it is propagated in one way, whereas the compound oscillator averages elasticity values in a different way. It is possible, however, that the discrepancy is an error accruing from the quality of the glue joints; the analysis assumes perfect junctions.

TABLE X
VALUES OF $1/s_{44}$ BY CTO METHOD COMPARED WITH
 c_{44} BY ULTRASONIC MEASUREMENTS

	CTO (10^{11} dynes/cm ²)	Ultrasonic
M108-25	0.0266	0.0271
M108-28	.0267	.0272
M110-2C	.0273	.0288
M110-3C	.0221	.0231
P207-3	.0230	.0236
P207-4	.0226	.0230
P210-3C	.0289	.0297
M304-A	.0234	.0244

* Increasing the input $1/s_{11}$ decreases the calculated $1/s_{44}$. If one calculates $1/s_{11}$, decreasing the input $1/s_{44}$ increases the calculated $1/s_{11}$; but the low harmonics are then affected less than the high.

The equations for the CTO computer program⁽²⁾ were modified; with the new equations, the compound torsion oscillator (CTO) and the compound longitudinal oscillator (CLO) with either round or square cross-section can be analyzed. In addition, the cross-sections of the specimen and inertia masses (weights) can be of different shape and area. It should be emphasized, however, that the equations used in this program are not rigorously correct for any conditions except those employing round compound torsion oscillators in which the specimen and weights are of the same diameter.

The new equations for the compound oscillators are:

For odd harmonics

$$X \tan X = \frac{M}{2M'} \cdot \frac{Y}{\tan Y},$$

and for even harmonics

$$\frac{X}{\tan X} = \frac{-M}{2M'} \cdot \frac{Y}{\tan Y},$$

where

$$X = \pi f l \sqrt{\rho/E}$$

$$Y = 2\pi f l' \sqrt{\rho'/E'}$$

$$f = \text{resonant frequency}$$

$$l = \text{specimen length}$$

$$l' = \text{length of individual inertia mass}$$

$$\rho = \text{specimen density}$$

$$\rho' = \text{density of inertia masses}$$

$$E = \text{specimen modulus}$$

$$E' = \text{modulus of inertia masses}$$

$$M = \text{mass of specimen, and}$$

$$M' = \text{mass of individual inertia mass}$$

The inertia masses are assumed to be identical.

Several experiments to check the suitability of the techniques and of the program for the calculation by means of the CLO of $1/s_{11}$ on stress-annealed pyrolytic graphite were conducted; brass, steel, and lead weights and compression-annealed pyrolytic graphite, steel, and brass specimens were used. There were several lengths of both weights and specimens (1, 1.5, 2, 2.5 cm), and all length combinations of steel-brass-steel and brass-steel-brass were made.

Oscillators composed of lead-steel-lead were the most appropriate means (with respect to density and moduli ratios) for checking the accuracy of steel-graphite-steel oscillators, and the former gave answers for $1/s_{11}$ of steel which were about nine per cent low; the steel-graphite-steel oscillators gave values of $1/s_{11}$ for the graphite of 85.7×10^{11} dynes/cm² as compared with 95×10^{11} dynes/cm² given by free-free flexural resonance (parallel to the basal plane) on the same specimen. The implication is that 95×10^{11} dynes/cm² is the actual value of $1/s_{11}$ for that specimen, since the value measured by the CLO is lowered by the same per cent that the value for steel was lowered when measured by the lead-steel-lead CLO. The measured values of $1/s_{11}$ for the central piece of the CLO's in the less extreme cases of brass-steel-brass and steel-brass-steel ran 2 to 9 and 1 to 7 per cent low, respectively.

Generally speaking, as the specimen length became shorter and the lengths of the weights became longer, and as the ratios of weight density to specimen density and weight modulus to specimen modulus became smaller, the moduli measured tended to be lowered. In no case was the modulus found by the compound longitudinal oscillator greater than the actual modulus.

The approximate densities and moduli for the materials which were used and one other appropriate material are shown in Table XI.

TABLE XI
MODULI AND DENSITIES OF WEIGHTING MATERIALS
FOR COMPOUND OSCILLATOR

	E (10^{11} dynes/cm ²)	ρ (g/cm ³)
Compression-Annealed Pyrolytic Graphite	100	2.26
Steel	20	8
Brass	10	8
Lead	2.3	11
Tungsten	40	19

Tungsten would be a far better material than steel to use as weights, because it has both a high density and a high modulus. The problem of availability and machining of tungsten has thus far prevented its use.

7.3. Specimen Size Effects

Some experiments were performed on stress-annealed pyrolytic graphite to determine the possible effects of wave guiding on the ultrasonic measurement of c_{11} . Specimen M304 was measured at 1 mc as an 8 cm diameter disk 1 cm thick (wave propagation along the diameter of the disk). A rectangular bar 0.8 cm wide (still 1 cm thick) was then cut from the disk and measured at 1 mc. The velocity measured on the 8 cm disk was 21.71×10^5 cm/sec, and the velocity in the rectangular bar was 21.29×10^5 cm/sec. Specimen M305-US was a bar originally $6.7 \times .75 \times 2.1$ cm. The velocity along the length of the bar at 1 mc was 21.42×10^5 cm/sec; at 5 mc, it was 21.49×10^5 cm/sec. The sample was then cleaved into two bars, A and B, the thicknesses of which were .29 and .44 cm, respectively. The velocity of a 1 mc longitudinal wave along the length of bar A was 21.28×10^5 cm/sec, and the velocity of the same type of wave in bar B was 21.40×10^5 cm/sec. The difference between the velocities within A and B is suggestive of wave guiding, but material variations along the c-axis may have caused the differences in the velocities.

One other phenomenon which has been observed in the compression-annealed pyrolytic graphite may also be due to wave guiding: it was found impossible to propagate 1 mc longitudinal waves along the c-axis of $1/2$ inch diameter disks without complete distortion of the wave form. No difficulty was encountered in propagating the same longitudinal waves through the same specimens when they were 1-inch disks. Shear waves at 1 mc were easily propagated through the same specimens both before and after machining to $1/2$ inch diameter, and the c_{44} measured were the same in both cases.

7.4. Stress Derivative of c_{33} and c_{44}

The change of c_{33} and c_{44} with c-axis compressive stress was also investigated. Primary interest was in the derivative of the c_{33} with respect to stress and consideration of this measurement will occupy the greater part of this discussion.

In the experiment, the specimen was placed between the ends of the steel cylinders of the apparatus shown in Figure 16, and the assembly was squeezed in a hydraulic press. The change in time of the received signal with force was carefully noted and recorded.

Figure 16
Apparatus for Compressional Stress Derivative Measurements

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The stress derivative of c_{33} , i. e., the fractional change in c_{33} per unit stress σ , is given by $\frac{1}{c_{33}} \frac{dc_{33}}{d\sigma} = \frac{d \ln c_{33}}{d\sigma}$. From the equation $v = \sqrt{E/\rho}$, which gives the velocity v of a wave through a material with modulus E and density ρ , we obtain: $c_{33} = \text{const. } \bar{c} \bar{a}^{-2} t^{-2}$, where $\bar{a}$ and $\bar{c}$ are lattice constants and t is the transit time of a wave pulse.

Taking the logarithm of c_{33} and differentiating with respect to the stress, we obtain

$$\frac{d \ln c_{33}}{d\sigma} = \frac{d \ln \bar{c}}{d\sigma} - \frac{2d \ln \bar{a}}{d\sigma} - \frac{2d \ln t}{d\sigma}.$$

For this stress system and hexagonal symmetry:

$$\frac{d \ln \bar{c}}{d\sigma} = \frac{d\bar{c}}{\bar{c}} \frac{1}{d\sigma} = -s_{33} \text{ and } \frac{d \ln \bar{a}}{d\sigma} = \frac{d\bar{a}}{\bar{a}} \frac{1}{d\sigma} = -s_{13}.$$

In addition,
$$\frac{d \ln t}{d\sigma} = \frac{1}{t} \frac{dt}{d\sigma}.$$

Therefore,

$$\frac{1}{c_{33}} \frac{dc_{33}}{d\sigma} = \frac{d \ln c_{33}}{d\sigma} = -s_{33} + 2s_{13} - \frac{2}{t} \frac{dt}{d\sigma}.$$

For the calculation of $d \ln c_{33}/d\sigma$, s_{13} was assumed to be zero and we chose $1/s_{33} = 3.6 \times 10^{11}$ dynes/cm². A least-squares fit of the data was made to find the slope $dt/d\sigma$, and the value of t which was used was the transit time in the limit of zero stress.

Several measurements of transit time as a function of stress were made on three specimens of M309 and on one specimen of M312. The plot of the data for specimen M312-US1 is given in Figure 17. The average $d \ln c_{33}/d\sigma$ for M309 was 9.1×10^{-11} cm²/dyne; the standard deviation was 1.7×10^{-11} cm²/dyne. Expressed in another set of units, $d \ln c_{33}/d\sigma$ averaged 0.63 per cent per 1000 lb/in². Measurements on M312-US1 gave $d \ln c_{33}/d\sigma = 12.6 \times 10^{-11}$ cm²/dyne. In calculating $d \ln c_{33}/d\sigma$, we assumed that $d^2 \ln c_{33}/d\sigma^2 = 0$, a reasonable assumption in view of the precision of the data. Close examination of the data, however, shows that $d \ln c_{33}/d\sigma$ increases slightly with increasing compressive stress.

The main experimental difficulty is a lack of precision. In a typical test, the acoustic wave travels for about $11\mu\text{sec.}$ in the steel and for $1.7\mu\text{sec.}$ in the specimen, making a total of about $13\mu\text{sec.}$ from the time the pulser and scope are triggered until the signal arrives at the crystal receiver. The change in transit time is approximately $.005\mu\text{sec.}$ per 1000 lb/in^2 , and the delay dial used to gage the time changes is valued at $.02\mu\text{sec./div.}$, where the divisions are $1/16$ inch apart. Therefore, in order to obtain good data, the dial reading must be estimated to the nearest $1/160$ inch by eye. A technique was later developed, utilizing the delayed trigger of the pulser, in which the scope was not triggered until just before the wave arrived at the crystal. In this way, the delay dial can be magnified to read $.001\mu\text{sec./div.}$ The data in Figure 17 were obtained in this way.

Figure 17
Transit Time vs. Compressive Force

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A 5 mc frequency was used in this experiment because it was the highest value practical in view of the attenuation. The peaks of the 5 mc wave are .1 μ sec. wide, and the whole effect for the maximum of stress extremes is less than one-half of that value.

An attempt was also made to find the stress derivative of c_{44} , but attenuation of the 5 mc waves forced the use of 1 mc waves, further reducing the precision by a factor of five. In addition, coupling of the shear wave proved difficult. No definite values of the stress derivative of c_{44} were found, but it was determined qualitatively that the derivative is very close to zero or slightly negative.

7.5. Ultrasonic Test Results

Table XII contains a summary of the results of the ultrasonic measurements made in the period covered by this Report. The densities given were measured hydrostatically, and the $\theta_{\frac{1}{2}}$ (crystallite orientation distribution half-width at half height) which are given are averages of measurements made by the optical reflectivity technique. In two cases (M304 and P211-3), two values are given for c_{11} and c_{66} (and, incidentally, for c_{12} and c_{12}/c_{11}). The second set was measured by a wave propagated at right angles to the wave propagated for the first set. The different values of c_{33} and c_{44} for any one specimen were measured at different positions on the face of the disk. An asterisk after a c_{33} or c_{44} value indicates that the measurement was made after the material next to the ram faces was cleaved away.

On specimen M311, a 3-inch diameter disk, measurements of c_{33} were made with the transducer placed in three arbitrarily chosen positions (A, B, C) both before and after the outer layers had been cleaved away. Layers of 1.1 and 2.1 mm thickness were then cleaved from the substrate and top, respectively, leaving surfaces whose crystallite distribution half-width was .38°. Measurements of c_{33} were again made, and the following changes were observed in the stiffness c_{33} at each position:

<u>Position of Transducer</u>	<u>Before</u>	(10^{11} dynes/cm ²)	<u>After</u>
A	3. 32		3. 58
B	3. 15		3. 44
C	3. 25		3. 36

TABLE XII
SUMMARY OF ELASTIC STIFFNESS CONSTANTS FOR
COMPRESSION-ANNEALED PYROLYTIC GRAPHITE

Sample	ρ (g/cc)	$\theta^{1/2}$	C_{44}	C_{33}	C_{66}	C_{12}	C_{11}	C_{12}/C_{11}
M108-25			0.0271					
M108-27			0.0222	3.22				
M108-28			0.0272	3.06				
P202-1	2.2567	0.62°	0.0208		44.2	18.0	106.4	0.169
P207-1			0.0193	3.23				
P207-3			0.0236					
P207-4			0.0230	3.29				
P211-3		0.79°			46.6 46.7	14.0 11.3	107.2 104.7	0.130 0.108
			0.0296 0.0314					
P213-2	2.2567	1.8°			36.2	15.7	88.1	0.178
M304	2.2603	0.15°			44.3 43.7	18.0 16.6	106.6 104.0	0.169 0.160
			0.0244 0.0241 0.0243 0.0277	3.37 3.32 3.01 3.38 3.45				
			0.0248 0.0242 0.0246					
M305	2.2608	0.46°					104.3	
M307		0.21°			43.5	17.7	104.7	0.169
M308	2.2609	0.19°			43.7	18.5	105.9	0.175
M309		0.54°	0.0313	3.10	42.1	21.2	105.4	0.201
M311		0.38°			44.2	17.6	106.0	0.166
			0.0316 0.0336 0.0322 0.0369	3.32 3.26 3.26 3.15 3.25 3.44* 3.36* 3.57*				
					Stiffnesses are in 10^{11} dynes/cm ² .			
M312		0.19°	0.0288* 0.0286* 0.0292*	3.40* 3.45* 3.45*				

* Measured after cleaving.

These data indicate that the material is not perfectly uniform and that misoriented material in the outer layers may be causing the measured c_{33} to be 3 to 10 per cent lower than that obtained for well-ordered material in the central portion of the disk. Figures 1 and 2 help to corroborate this result.

A possible error may be introduced in the determination of both c_{33} and c_{44} by an incorrect determination of the thickness of the specimen when the specimen is tapered or wedge shaped.* The difference in thickness of a tapered specimen can introduce as much as five per cent error in the elastic constant. The problem will be alleviated in future specimens by machining the specimen faces parallel before testing. This operation was previously thought impossible, but it has been found that it can be accomplished in a lap ring on very fine but sharp flint paper. The final polish can be applied by a disposable wiper wetted with acetone.

8. ANALYSIS OF RESULTS

G. B. Spence and E. J. Seldin

Introduction

The elastic constants of compression-annealed pyrolytic graphite have been measured by static, sonic resonance, and ultrasonic time-of-transit tests. Since the material possesses hexagonal symmetry, there are a total of five elastic constants. In terms of the compliances s_{ij} , these are s_{11} , s_{12} , s_{13} , s_{33} and s_{44} , each of which is determined directly in one of the static tests. Alternatively, there are a set of five stiffnesses c_{ij} (c_{11} , c_{12} , c_{13} , c_{33} , c_{44}) which are directly related to the five s_{ij} . The sonic tests yield some of the s_{ij} and the ultrasonic tests yield some of the c_{ij} .

The Young's modulus $1/s_{11}$ is obtained in a static tensile test in which the applied stress is parallel to the a-axis; measurement of the transverse strains along the a-axis and along the c-axis yield s_{12} and s_{13} , respectively. The Young's modulus $1/s_{33}$ is obtained in a static compression test in which

* Wedge shaped samples also introduce the problem that the acoustic wave is not propagated normal to the basal plane. This condition perturbs the measurement several per cent in the case of c_{44} and less than one per cent for c_{33} .

the applied stress is along the c-axis; although the transverse strain is proportional to s_{13} , the Poisson ratio $-s_{13}/s_{33}$ is so low (of the order of .01) that s_{13} cannot, in practice, be determined accurately in a compression test. The shear modulus $1/s_{44}$ is obtained in a static torsion test in which the axis of rotation is parallel to the c-axis.

A bar, with its long dimension along the a-axis, can be made to resonate in either a longitudinal or flexural mode. The longitudinal mode of vibration of this resonant bar yields the elastic constant $1/s_{11}$, whereas the flexural modes of vibration yield, through Timoshenko's equation, $1/s_{11}$ and the shear modulus $1/s_{44}$. A compound torsion oscillator (CTO), consisting of a short cylindrical graphite specimen with its axis parallel to the c-axis and two cylindrical metal end pieces, was used to determine the shear modulus $1/s_{44}$. Unfortunately, this compound oscillator could not be excited in a longitudinal resonance to give the modulus $1/s_{33}$. However, a compound longitudinal oscillator (CLO) was used in which the axis of the graphite specimen was parallel to the a-axis; the longitudinal resonance yielded the modulus $1/s_{11}$, but the values which were obtained were consistently lower than those obtained from the resonant bar and static tests.

Measurements of the transit times of pulses in the ultrasonic frequency range also yielded values for the elastic constants. Depending on whether the wave was longitudinal or transverse, a pulse along the c-axis yielded either c_{33} or $c_{44} = 1/s_{44}$. In a similar manner, a pulse along the a-axis yielded either c_{11} or $c_{66} = (c_{11} - c_{12})/2$.

In this section, we summarize the results by giving the average experimental values of all of the elastic constants which were measured and the limits of experimental error. We then invoke the symmetry relationships between the elastic constants in an analysis of the experimental results. The purpose of the analysis is to define the probable limits of accuracy in the data and to deduce a self-consistent set of elastic constants for graphite.

8.1. Between-Plane Shear

The values for the shear modulus $1/s_{44}$ of compression-annealed pyrolytic graphite fell in the range 0.018 to 0.035×10^{11} dynes/cm². Excellent agreement was obtained between the values of $1/s_{44}$ measured in sonic, ultrasonic, and static tests on the same specimen; this agreement is evidence that the experimental techniques give true and accurate measurements of the shear modulus. However, given the spread in values from specimen to specimen, the limiting value of $1/s_{44}$ as crystalline perfection is approached is still not known.

8.2. All Other Moduli

The experimental values of the elastic constants are summarized in Table XIII, which gives an average value and spread of values for each of the constants which were measured. Characteristically, the sonic and ultrasonic measurements are determined to a higher degree of accuracy than the static measurements. There is also much less variation in the sonic and ultrasonic values of the elastic constants from one material to another. Therefore, the values of c_{11} , c_{12} , and c_{33} in Table XIII impose strong limitations on the values of the compliances which are obtained in the static tests.

TABLE XIII
EXPERIMENTAL VALUES OF ELASTIC CONSTANTS
FOR COMPRESSION-ANNEALED PYROLYTIC GRAPHITE
(c_{ij} in 10^{11} dynes/cm², s_{ij} in 10^{-11} cm²/dynes)

c_{11}	=	105.6 ± 1.6	$1/s_{11}$	=	88 ± 11
c_{12}	=	16 ± 5	s_{12}	=	$-.0018 \pm .0006$
c_{13}	=	-----	s_{13}	=	$-.0033 \pm .0008$
c_{33}	=	$3.35 \pm .30$	$1/s_{33}$	=	$3.7 \pm .5$
c_{66}	=	44 ± 3	$s_{13}^2/s_{11}s_{33}$	=	$.0035 \pm .002$
c_{12}/c_{11}	=	$.16 \pm .04$	$c_{44} = 1/s_{44}$	=	$.025 \pm .010$
$K_3 = s_{33} + 2s_{13} = .28 \pm .01$ (Reference 8)					

The hexagonal symmetry of the graphite causes the following relationships⁽⁹⁾ to exist between the compliances s_{ij} and the stiffnesses c_{ij} :

$$c_{11} + c_{12} = s_{33}/X, \quad c_{11} - c_{12} = 1/(s_{11} - s_{12}),$$

$$c_{13} = -s_{13}/X, \quad c_{33} = (s_{11} + s_{12})/X, \quad \text{and} \quad c_{44} = 1/s_{44},$$

$$\text{where } X = s_{33}(s_{11} + s_{12}) - 2s_{13}^2.$$

From these relationships, the following equations have been derived:

$$1/s_{11}c_{11} = (1-p) [1 - (c_{12}/c_{11})^2],$$

$$1/s_{33}c_{33} = (1 - c_{12}/c_{11}) / [(1+p)/(1-p) - c_{12}/c_{11}], \quad \text{and}$$

$$s_{12}/s_{11} = p - (1-p) c_{12}/c_{11}$$

$$\text{where } p = s_{13}^2/s_{11}s_{33}.$$

The equations above are plotted in Figure 18 as three nomograms in which the ordinate is the left side of the equation and the abscissa is c_{12}/c_{11} . The curves in each nomogram correspond to fixed values of the parameter p , which is a small dimensionless number. Since the value of c_{12}/c_{11} from experiment is $0.16 \pm .04$, the abscissas were made to extend only to 0.2. Although curves are drawn for several values of p , the data indicate that p is approximately 0.0035; thus, it is effectively equal to zero on the nomograms.

Figure 18
Relations Between Elastic Constants for
Material with Hexagonal Symmetry

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When the above values for c_{12}/c_{11} and p are used, the first plot in Figure 18 indicates that $1/s_{11}$ should be about 3 per cent lower than c_{11} . If we assume that the ultrasonic measurement of c_{11} given in Table XIII is correct, the true value of $1/s_{11}$ is slightly greater than any value we have measured. Apparently, the static measurement is more sensitive to material imperfections than the sonic and ultrasonic measurements; thus, imperfections in the material will substantially lower the effective $1/s_{11}$.

The second plot in Figure 18 indicates that, although $1/s_{33}$ is always equal to or less than c_{33} , the low value of p should cause the two to be almost identical for graphite. If we assume that the value of c_{33} in Table XIII is correct, the average value of $1/s_{33}$ in Table XIII must be slightly high.

The third plot in Figure 18 indicates that the ratio $-s_{12}/s_{11}$ must be equal to or greater than c_{12}/c_{11} . The value of s_{12}/s_{11} as determined from the average values of s_{12} and s_{11} in Table XIII is about -0.20, which is outside of the allowable values indicated by Figure 18. We conclude from this reasoning that $1/s_{11}$ must be greater than the average value in Table XIII and/or s_{12} must be numerically smaller than the average value in Table XIII. The third nomogram indicates that, for $c_{12}/c_{11} = .17$, the value of $-s_{12}/s_{11}$ should be between .16 and .17, which is within the range of measured values.

Unfortunately, no direct measurement could be made of c_{13} , and the equations and nomograms which provide the checks on the other elastic constants are very insensitive to the absolute value of s_{13} . We rely, therefore, entirely on the static tensile test for the measurement of s_{13} . There is one other piece of evidence, however, which may be considered. The c-axis compressibility K_3 , as measured by Kabalkina and Vereshchagin,⁽¹⁰⁾ on Ceylon graphite and spectroscopically pure polycrystalline graphite, depends on s_{33} and s_{13} and is given in Table XIII. The best that can be said about s_{13} from this analysis is that the measured values are reasonable.

In conclusion, the symmetry relationships which must be satisfied by a self-consistent set of elastic constants cause us, through this analysis, to believe that the true elastic constants are, in some cases, different from the average values which are listed in Table XIII. We place greatest faith in the sonic and ultrasonic measurements of c_{11} , c_{12} , and c_{33} , and we use the value

of s_{13} from the static tensile test as the only available measurement of this constant. Therefore, we present in Table XIV a self-consistent set of elastic constants, with probable errors, which represents our best estimate of the true elastic constants of compression-annealed graphite. By setting a relatively high value for $1/s_{11}$, we are, in effect, saying that in a static tensile test, one can only approach the true Young's modulus. The value of s_{12} in Table XIV is consistent with experiment, and the values of $1/s_{44}$ represent the observed values for which there is no crosscheck with other elastic constants. The greatest uncertainty is in the value of c_{13} .

TABLE XIV
ESTIMATE OF ELASTIC CONSTANTS FOR GRAPHITE
(c_{ij} in 10^{11} dynes/cm², s_{ij} in 10^{-11} cm²/dynes)

$c_{11} = 106 \pm 2$	$1/s_{11} = 101.5 \pm 3$
$c_{12} = 18 \pm 2$	$s_{12} = -.0015 \pm .0004$
$c_{13} = 2.72 (x 2^{\pm 1})$	$s_{13} = -.0063 (x 2^{\pm 1})$
$c_{33} = 3.6 \pm .1$	$1/s_{33} = 3.48 \pm .2$
$c_{12}/c_{11} = .17 \pm .01$	
$c_{44} = 1/s_{44} = .018 \text{ to } .035$	

9. IRRADIATION PROGRAM

The irradiation program proposed in Quarterly Progress Report No. 3 was discussed with personnel of the Oak Ridge National Laboratory. As a result of these discussions, Oak Ridge National Laboratory made a cost study of the irradiation program. The most optimistic cost analysis placed the irradiation program beyond the financial scope of the present program. It was then decided that, when the pre-irradiation testing was completed, a revised (and reduced) irradiation program would be considered.

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