ANL-5524
Physics

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ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

THE STRUCTURE AND PROPERTIES OF ARTIFICIAL AND NATURAL GRAPHITE

by

T. J. Neubert, J. Royal, and A. R. Van Dyken

February, 1956

Operated by The University of Chicago
under
Contract W-31-109-eng-38

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THE STRUCTURE AND PROPERTIES OF ARTIFICIAL AND NATURAL GRAPHITE* **

T. J. Neubert,[†] J. Royal,[††] and A. R. Van Dyken
Argonne National Laboratory, Chemistry Division, Lemont, Illinois

1. INTRODUCTION

It was pointed out in 1942 that graphite was expected to exhibit changes in its physical properties when bombarded with fast neutrons.(1) Such neutron-induced changes do take place and have been the subject of extensive investigation.(2) The purpose of this paper is to record the various physical and chemical properties which characterize the initial unbombarded graphite. No claim is made that the present review is critical or exhaustive. What data have been listed are principally those which have a peculiar interest relative to the problem being investigated.

2. THE GENERAL NATURE OF GRAPHITE

Graphite crystals have rhombohedral symmetry. The structure consists of plane layers of carbon atoms arranged in a hexagonal, honeycomb pattern with adjacent atoms 1.42 A apart. The center of each hexagon in each sheet has, both directly above it and directly below it, a carbon atom of an adjacent sheet. Each of the layers is a giant molecule, separated from adjacent layers by 3.36 A. This distance is so large that there can be no covalent bonding between the layers; superimposed layers are held together only by weak van der Waal's forces.(3)

Graphite sometimes occurs naturally in the form of six-sided, tabular crystals. Natural graphite has a greasy feel, a metallic luster, and a dark steel-gray color. Relatively it is a good conductor of heat and electricity. Thin laminae of graphite are flexible and inelastic.(4)

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* Based upon work done at the Metallurgical Laboratory, University of Chicago (now Argonne National Laboratory) during the period 1943 - 1945 and published as U.S. Atomic Energy Commission Report No. ANL-4022 (Aug. 7, 1947).

** This article was originally intended for publication as paper 3.2 of Vol. 10-B, Radiation Chemistry, of the National Nuclear Energy Series (Plutonium Project Record) under the editorship of Milton Burton.

[†] Present address: Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois

[††] Present address: American Medical Association Laboratories, Chicago, Illinois.

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Graphite is widely distributed in nature, being found especially in many metamorphic rocks. The most famous sources of natural graphite are Madagascar, Siberia, and the Island of Ceylon. Good graphite crystals are, however, very rare and difficult to obtain. Most of the naturally occurring crystals are badly deformed or strongly twinned. The best crystals seem to be obtained when a graphite-bearing rock matrix is dissolved. The graphite occurring in the limestone at Ticonderoga, N. Y., and that at Franklin, N. J., have been particularly recommended.(5) Graphite crystals form during cooling of molten materials in which carbon is dissolved, e.g., metals and silicates. They also form in the solid state by crystallization from solid systems supersaturated in carbon. This latter phenomenon is most familiar in the case of the "graphitization" of steel. Graphite crystals produced artificially are, however, usually even less perfect than those which occur naturally.

Natural graphite is, in general, not very pure. It is used in industry largely in the fabrication of crucibles for high temperature processing. Since there are many industrial applications of graphite for which natural graphite is not suitable, a commercial process for the production of artificial graphite was developed which consists of forming "amorphous" carbon with a binder and firing the formed objects at high temperatures. This converts the carbon to a material with properties similar to natural graphite. Artificial graphite has the advantage that it is purer and stronger than natural graphite.

3. THE MANUFACTURE OF ARTIFICIAL GRAPHITE

Since the National Carbon Company was the principal supplier of the graphite used by the Manhattan District (precursor of the U.S. Atomic Energy Commission), the description of the production of artificial graphite will be based primarily upon what is known of the manufacturing processes within that organization. The relevant information was obtained from Drs. V. C. Hamister and H. G. MacPherson, either in lectures to the Metallurgical Laboratory(6) or in private discussions. A certain amount of information was obtained from the chemical engineering literature.(7,8,9)

The raw materials for artificial graphite are petroleum coke and coal-tar pitch. The petroleum coke is first calcined at temperatures of about 1300°C in order to drive off volatile hydrocarbons and further carbonize the coke. This step, as well as certain others to be described later, is necessary since it is desirable that the finished product have as high a density as possible. During the calcining operation there is a decrease in weight of about 25 - 30 per cent. The calcined coke is next powdered so that about 60 per cent will pass a 200-mesh sieve.(8) The calcined petroleum coke "flour" used by the National Carbon Company has a particle size distribution of <u>ca</u> 2-300 microns.(10) This particle size distribution is intended to give the finished product a minimum of voids.

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The calcined, classified petroleum coke is then mixed with coal-tar pitch in heated mixers and the resultant magma extruded through steam heated dies and cut into bars (e.g., 4 in. x 4 in. x 50 in.). About thirty-two parts of pitch are used for one hundred parts of coke flour. The green bars (density, ca 1.7 g cm^{-3}) are next baked in gas-fired ovens to a minimum temperature of 750°C. During this treatment the pieces are packed in a mixture of sand and crushed carbon in order to maintain their shape. About one week is required to heat up the furnace and its charge, the maximum temperature is maintained for approximately 2 - 3 days. After the heating the furnace is cooled slowly in order to prevent oxidation as air is drawn into the mass. The entire process requires 35 - 48 days. During the gas baking about 40 per cent of the pitch is volatilized and the bars shrink about 1 per cent. The resulting gas-baked carbon is a hard, black substance with a sharp surface and a metallic ring. The density at this stage of production is ca 1.55 g cm^{-3}. In order to improve the density of the final product the graphite is reimpregnated with an additional 15 parts of coal-tar pitch per 100 parts of gas-baked carbon by a heat-vacuum-pressure operation. The bars (density at this stage, ca 1.77 g cm^{-3}) are then graphitized in an electric furnace.

The graphitizing furnace is built on a floor of concrete beams. The charge of reimpregnated raw bars is packed perpendicular to the long axis of the furnace in vertical piles separated by crushed metallurgical coke. At either end of the furnace are graphite electrodes with water-cooled copper leads. The whole assembly is then surrounded by an additional layer of metallurgical coke and insulated with a blanket of coke, sand, and sawdust. Finally, a restraining wall of concrete blocks is built around the furnace.

The graphitizing furnace requires about 60 hours to heat up and three weeks to cool down. Power consumption is approximately 1.6 - 3.0 kw hr per pound. Temperatures are observed with an optical pyrometer which gives good results up to ca 2500°C. At this point the radiation turns green and the apparent temperature drops. This change is attributed to radiation from calcium, which is thought to enter the process principally through the sawdust in the insulating blanket.(6) It is estimated that ultimate temperatures reached during graphitization are 2500 - 2700°C. About 60 per cent of the pitch added in the reimpregnation is lost during graphitization. Table I shows an approximate material balance for the pitch used in the fabrication of artificial graphite and lists the densities at the different stages of production.(10)

The resultant artificial graphite is a soft, gray-black material with a smooth "greasy" surface (when machined). Its density is 1.65 g cm^{-3}, and its ash content less than 0.2 per cent. During the graphitization process a large fraction of the impurities, present in the original materials to the extent of about 1 per cent, distill away, since the temperatures involved are higher than the boiling points of most of the impurity compounds. Of the finished graphite about 20 per cent is estimated to come from the coal-tar pitch; the remaining 80 per cent is from the original coke (see Table I).

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TABLE I

Densities and Approximate Material Balance for Coal-Tar Pitch at Various Stages in the Production of Artificial Graphite.(10)

Amounts of Pitch Involved in Various Operations	Parts of Pitch Per 100 Parts of Coke "Flour"	Approximate Density, g cm^{-3}
1. Used to form original extruded unfired bars	32	1.7
2. Lost in gas baking (0.40 x 32)	13	1.55
3. Added in reimpregnation (0.15 x 119)	18	1.77
4. Lost during graphitization (0.60 x 18)	11	1.65
Total residual "pitch" in finished graphite	26	1.65

4. THE GENERAL NATURE OF ARTIFICIAL GRAPHITE

It is thought that the carbon in artificial graphite is more than 99 per cent graphitized,(10) but that the crystal size is much smaller than that in natural graphite. X-ray diffraction studies of petroleum coke and coal-tar-pitch mixtures as a function of firing temperature indicate that even the "amorphous" ungraphitized material shows some structure.(10) As the firing temperature is increased, the X-ray pattern becomes sharper and sharper, approaching that of natural graphite. This observation is construed to mean that essentially all of the carbon has been graphitized. Thus the function of the graphitizing process is to distill away excess tars and impurities and to perfect the crystalline arrangement, which X-ray diffraction investigations show is already observable in gas-baked ungraphitized carbon.

There are theories of the graphitization process based upon catalysis by impurity compounds, e.g., silicon carbide. That such effects can be made to occur is certain, but it is not certain what role catalytic processes have in modern graphite production techniques. In any event, according to the best information available,(10) the graphite crystals which occur in the ultimate bars of artificial graphite are present in the original cokes and do not grow during the graphitization process by more than (if as much as) a factor of two.

The suggestion that graphite crystals do not grow significantly during the graphitization process is supported by the observations(10) that carbon powders do not sinter even at temperatures of 2500°C and pressures of 4000 lb in.^{2}, and that it is impossible to "graphitize" lampblack. Thus the small natural graphite-type crystallites present in artificial graphite must come from crystallites which were already partially formed in the coking of the petroleum residues from which it was made.

The explanation for the inability to graphitize lampblack is that lampblack, since it is formed in a gas phase carbonization, contains only very minute graphite nuclei. In forming petroleum coke, on the other hand, the carbonization occurs in the liquid phase and it would seem that in this case relatively large, although imperfect, crystals are produced. These crystal nuclei could have their origin in labile organic compounds which become divested of their hydrogen during the coking process, thus building up a continuous pattern of benzene-like rings, only the outer ones of which retain their hydrogen. Accordingly, it is reasonable to expect some dependence of primitive crystallite size on the chemical constitution of the petrolum and the type of apparatus used in the preparation of the coke.

Since the crystallites are present at the time of extrusion, the extrusion process can cause a certain amount of preferential orientation of the crystallites, depending upon their size and shape. There is a definite tendency for graphite crystallites to be aligned with their planes parallel to the axis of extrusion. On this account, many of the physical properties depend upon the manner in which the test specimens are cut from the original graphite bar. In the work on neutron-induced changes in physical properties of artificial graphite, samples were cut with their own axis both parallel to and perpendicular to the axis of extrusion, because it was hoped that such samples would be an aid in the determination of the mechanism of neutron-induced changes. Apart from this reason, however, it was hoped that values for the various physical properties of parallel-cut and perpendicular-cut graphite specimens would be useful in estimating the relative amount of preferential orientation and the crystallite size and shape.

5. CHEMICAL PURITY OF GRAPHITES FOR THERMAL PILES

Two desirable properties of artificial graphite are high chemical purity and high density. Artificial graphite is much purer than natural graphite. Since a part of the ash of artificial graphite seems to be located within the structure of the constituent crystallites, relatively inaccessible

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to acids, alkalis, and gaseous leaching agents, it was thought in 1942 that sufficient purification could not be attained exclusively by chemical processes.(10,11) The solution adopted, therefore, was to produce a graphite from satisfactorily pure raw materials.

Three types of artificial graphite were commercially available when graphite piles were first under construction. Two of these were products of the National Carbon Company, designated AGX (Acheson graphite, extra dense) and AGR (Acheson graphite, regular). AGX was the standard reimpregnated graphite produced by the National Carbon Company. AGR was the product which resulted if the extruded bars were gas-baked and then graphitized without reimpregnation with pitch. The third type of artificial graphite was manufactured by the Speer Carbon Company. Like AGR, Speer graphite is non-reimpregnated.

The graphites described in the preceding paragraph were not of extraordinary purity. For this reason the National Carbon Company undertook to prepare special graphite, taking care in its fabrication to prevent the entry of extraneous impurities. In this way better grades of graphite became available. Chemical analyses(12) of batches received in November, 1942, [e.g., AGOT-W (T-15)] indicated: ash ~ 1000 ppm; boron ~ 0.6 ppm; V_2O_5 ~ 250 ppm; TiO_2 ~ 0.40 ppm; Fe_2O_3 ~ 60 ppm; and CaO ~ 370 ppm.

An investigation of means for producing graphite of greater purity was undertaken. Boyd, Curtis, Johnson, et al.,(12) in conjunction with the National Carbon Company, carried out careful chemical analysis of ten raw petroleum cokes and eighteen samples of various pitches. They found significant variations in chemical purity among the different cokes, principally in the V_2O_5 content. All the cokes showed a boron content between 0.2 and 0.4 ppm. In the pitches, on the other hand, there were large differences in the amounts of impurities. The boron content varied between 0.4 and 2 ppm. (Thus, according to the analytical procedures used, the principal source of boron in the finished artificial graphite seemed to be the coal-tar pitch.)

As a result of the long series of chemical analyses a program was outlined(12) in which three trial heats would be undertaken in order to test the analytical results on a plant scale. The three cokes selected were Kendall, Gulf-Cleves, and Whiting. The Kendall and Gulf-Cleves cokes were the purest of all those analyzed, in regard to freedom from both boron and vanadium. The Whiting coke was among the least pure of those analyzed, especially with regard to vanadium, but was selected because it was typical of the coke in standard use in the National Carbon Company. The pitch used was designated Barrett No. 30. It contained ~1 ppm boron. Average analyses of the starting materials and the final products of these three experimental heats are given in Table II. It must be pointed out that the petroleum cokes used in the period 1942 - 1944 are named here only as a means of clarifying the system of designation of experimental samples. The specific

TABLE II

Averaged Chemical Analysis (in ppm) of Starting Materials and Products in Experimental Heats No. 1583 (Kendall), No. 1591 (Gulf-Cleaves), and No. 1600 (Whiting).(12)

Material	Ash	B	V_2O_5	TiO_2	Fe_2O_3	CaO
Barrett No. 30 pitch	1130	0.99	9	52	486	98
Kendall coke	2115	0.26	44	42	822	150
Kendall graphite	373	0.48	14	21	25	212
Cleves coke	2080	0.14	48	32	501	220
Cleves graphite	481	0.56	48	34	15	247
Whiting coke	4960	0.26	460	30	590	858
Whiting graphite	840	0.66	254	20	17	369

cokes mentioned are not all available now, and after the elapse of eleven years those that are available under the same names are somewhat different in their characteristics as a result of changes in oil refinery processing and in the sources of the crude petroleum used.

The data of Table II indicate that, except for boron, impurities introduced into the graphite during fabrication are lost to a great extent in the firing operations. The boron apparently accumulates. Kendall graphite turned out to be purest from a standpoint of chemical analysis. It also had a density (1.75 g cm^{-3}) which was considerably in excess of the usual density of twice-fired, reimpregnated artificial graphite (1.60 - 1.66 g cm^{-3}). In addition to the impurities listed in Table II, analyses have been made on a typical bar of Kendall graphite from the experimental heat to determine the amounts of sulphur and hydrogen. The results, which should be treated only as estimates, are H - ca 320 ppm and S - ca 175 ppm.

Some experiments have been done to determine the amounts and character of the gases evolved from the graphite on heating. Rubinson(13) has reported that graphite sticks, heated at 525°C (32 hr) give 0.04 cc gas (STP)/g; graphite sticks heated at 850°C (15 hr) give 0.11 cc gas (STP)/g. Graphite dust heated at 525°C (20 hr) and at 850°C (8 hr) gives 0.16 and 0.20 cc gas (STP)/g, respectively. The amounts and compositions of gases evolved in various other experiments by Rubinson(13) in the Metallurgical Laboratory and in experiments at higher temperatures by Lebeau and Picon(14) in 1924 are listed in Tables III and IV, respectively.

TABLE III

Amount and Composition (Fraction by Volume) of Gases Evolved by Four Samples of Artificial Graphite Dust (250 g) Upon Heating in Vacuo.(13)

Temperature (°C)	550	550[a]	550	550[a,b]
Time of Heating (hr)	3.5	6.5	22	2.0
H_2O	?	0	?	0
CO_2	0.514	0.403	0.197	0.137
CO	0.279	0.198	0.155	0.169
$(CH_2)_n$	0.173	0.149	0.022	0.137
N_2	0.021	0.202	0.502	0.022
H_2	-	-	-	0.524
O_2	0.014	0.047	0.125	0.011
Total cc (STP) Evolved	14	12	16	15

[a] Dried for 9 days at 110°C.

[b] Contained 4 chunks of uranium (*ca* 640 g) embedded in the graphite dust.

TABLE IV

Amount and Composition (Fraction by Volume) of Gases Evolved From a Sample of Artificial Graphite (Solid Tube, 6 g) Upon Heating in Vacuo.(14)

Temperature (°C)	700	1000	1500	2000
Time of Heating (hr)	1.0	2.5	3.5	3.5
H_2O	0	0	0	0
CO_2	0.150	0.035	tr	tr
CO	0.400	0.225	0.407	0.440
$(CH_2)_n$	0.300	0.194	0.038	0.026
H_2	0.150	0.546	0.554	0.531
Total cc (STP) Evolved	0.13	5.65	12.4	13.3

6. TYPES OF GRAPHITE STUDIED

Graphites manufactured by the National Carbon Company with special care in the selection and handling of raw materials are designated by the code letters AGOT and AGNT. AGOT graphite is from the central part of the graphitizing furnace, AGNT graphite from the edges. The distinction was made because at one time it was thought that central graphite was necessarily more pure than outside graphite. In the production of the graphite, however, it was customary to manufacture the bars slightly oversize and then to cut away the outer surface. Analytical data indicated that with this procedure AGOT and AGNT had equivalent purity.(12) AGOT graphites have been made from several different cokes and pitches. These and the other various kinds of graphites used in fast neutron-bombardment studies by the Metallurgical Laboratory are described in separate paragraphs below.

(a) AGOT-W. This graphite was made in experimental heat No. 1600 from Whiting Refinery coke and Barrett No. 30 pitch. The "W" in the code name stands for Whiting Refinery coke. In the course of the research, two different bars from the same experimental heat were used. These two bars were similar in properties, but in those cases where differences are significant or interesting the two bars have been identified by the designations AGOT-W (I) and AGOT-W (II).

(b) AGOT-W (T-15). This is the designation of one of the first batches (T-15) of AGOT graphite received in Chicago. It was made from Whiting Refinery coke and coal-tar pitch. Many of the initial measurements of neutron-induced changes were made with samples taken from a typical bar of AGOT-W (T-15).

AGOT-W type graphite (e.g., batch T-15 and similar batches) was used in early exponential and sigma pile experiments, in the construction of the first chain reacting pile (CP-1, later rebuilt as CP-2), and in the first pile at Oak Ridge Laboratories.

(c) AGOT-C. The raw materials of AGOT-C are Gulf-Cleves petroleum coke and Barrett No. 30 coal-tar pitch. The only samples available in Chicago have come from bars taken from experimental heat No. 1591. In cases where it is important in the sections which follow, Roman numerals designate the accession number (in the research laboratory) of the particular bar employed.

(d) AGOT-K. This graphite is made from Kendall Refinery coke and coal-tar pitch. It was produced by the National Carbon Company (heat No. 1583). In this first experimental heat Barrett No. 30 coal-tar pitch was used and the resulting product was the purest and densest of the graphites manufactured by the National Carbon

Company. In the work on neutron-induced changes in graphite, four bars of heat No. 1583 were used. Here again Roman numerals designate the accession number of a particular bar.

(e) AGOT-KC. Because of the initial success in the production of Kendall type graphite an effort toward improvement was made by substituting Chicago Barrett No. 7HO pitch, which seemed to be a purer pitch than Barrett No. 30. The graphite thus produced was designated AGOT-KC. In commercial production however, it turned out that artificial graphite made with Kendall coke and 7HO pitch was not as dense as that made in the experimental heat No. 1583. The density for AGOT-KC was 1.68 g cm^{-3}, to be compared with 1.71 g cm^{-3} for AGOT-K.

Variations between AGOT-K, AGOT-C, and AGOT-W seem to arise from differences in original cokes. The Gulf-Cleves and Whiting cokes are by-products from gasoline refineries which use mid-continent and Texas crudes, while Kendall comes from Pennsylvania crudes. The stills and coking furnaces used to process the two types of petroleum crude oils are not the same. The result is that the crystallization centers present in Kendall coke are probably much larger than those in Whiting or Gulf-Cleves coke. Furthermore, the National Carbon Company(5) has found that density is dependent upon the sulphur content of the coke. They attribute the higher density of AGOT-K not to crystal size alone (since larger crystallites are expected to align themselves more compactly in the extrusion process), but also to the fact that Pennsylvania crude oils have a lower sulphur content than do other petroleums.

In addition to the preceding reactor graphites a certain amount of work has been done on a series of specially prepared experimental graphites. These graphites were supplied by the National Carbon Company to indicate the changes which occur during graphitization and to aid in the study of the mechanism of the Wigner effect. Pieces were cut from Whiting gas-baked stock, originally extruded in the form of long bars. The pieces were then reimpregnated with pitch in the laboratories of the National Carbon Company and subsequently heated at various temperatures to produce specimens with different degrees of graphitization. These specially prepared graphites are identified as follows:

(f) Sp 2100. This material was heated to 2100°C. The resulting product is characteristic of carbon in which the graphitization process has barely begun.

(g) Sp 2400. This material was partially graphitized by heating to 2400°C.

(h) Sp 3000. This material was graphitized at 3000°C. It should be typical of completely graphitized AGOT type graphite, but

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tables in the latter portions of this report show real differences, which are possibly attributable to the fact that laboratory conditions do not really reproduce full-scale plant conditions. Logically, its properties should be similar to those of the AGOT-W graphites.

In order to have available materials with widely different crystallite size for use in studies of neutron-induced changes, two additional pseudographites were obtained from the National Carbon Company.

(i) pbL. This carbon was made from lampblack bonded with coal-tar pitch and fired at 3000°C. It represents a "graphite" with an especially small crystallite size. Because of the minute particle size of lampblack, pbL exhibits no preferential orientation upon extrusion; and so the properties described in later sections exhibit no variations dependent on how the sample was cut from the stock piece.

(j) pbNG. This material was made by bonding natural graphite flour with coal-tar pitch and firing at 3000°C. The precise method of preparation of this sample is not known to the authors, but it is believed that the material was not extruded. Nevertheless, almost any method of preparation should give preferential orientation of the crystallites. However, no systematic investigation of variations of the particular properties of pbNG in different directions has been made.

Some work was done with natural graphite (NG) samples. Most of the properties reported are taken from the physical literature, but some were measured in these laboratories. The samples used were cut from a piece of Ceylon Graphite (ash, 0.12 per cent) given to us by Dr. V. C. Hamister of the National Carbon Company.

7. X-RAY DIFFRACTION STUDIES

Graphite has a layer lattice structure, as shown in Fig. 1. Carbon atoms are arranged in planes, the atoms within a plane forming a network of hexagons. In ideal graphite crystals, planes of carbon atoms are parallel to one another. The usual form of graphite (see Fig. 1, type 1) has alternate planes displaced in such a way that carbon atoms in the second plane are above centers of hexagons in the first plane. The third layer repeats the first. The lattice periods(15,16,17) for natural graphite are $a_1 = 2.456$ A, $a_3 = 6.697$ A. Period a_1 represents the separation of carbon atoms on alternate corners of hexagons, period a_3 twice the distance between planes. The smallest inter-atomic distance in the plane is $a_1/\sqrt{3} = 1.418$ A.

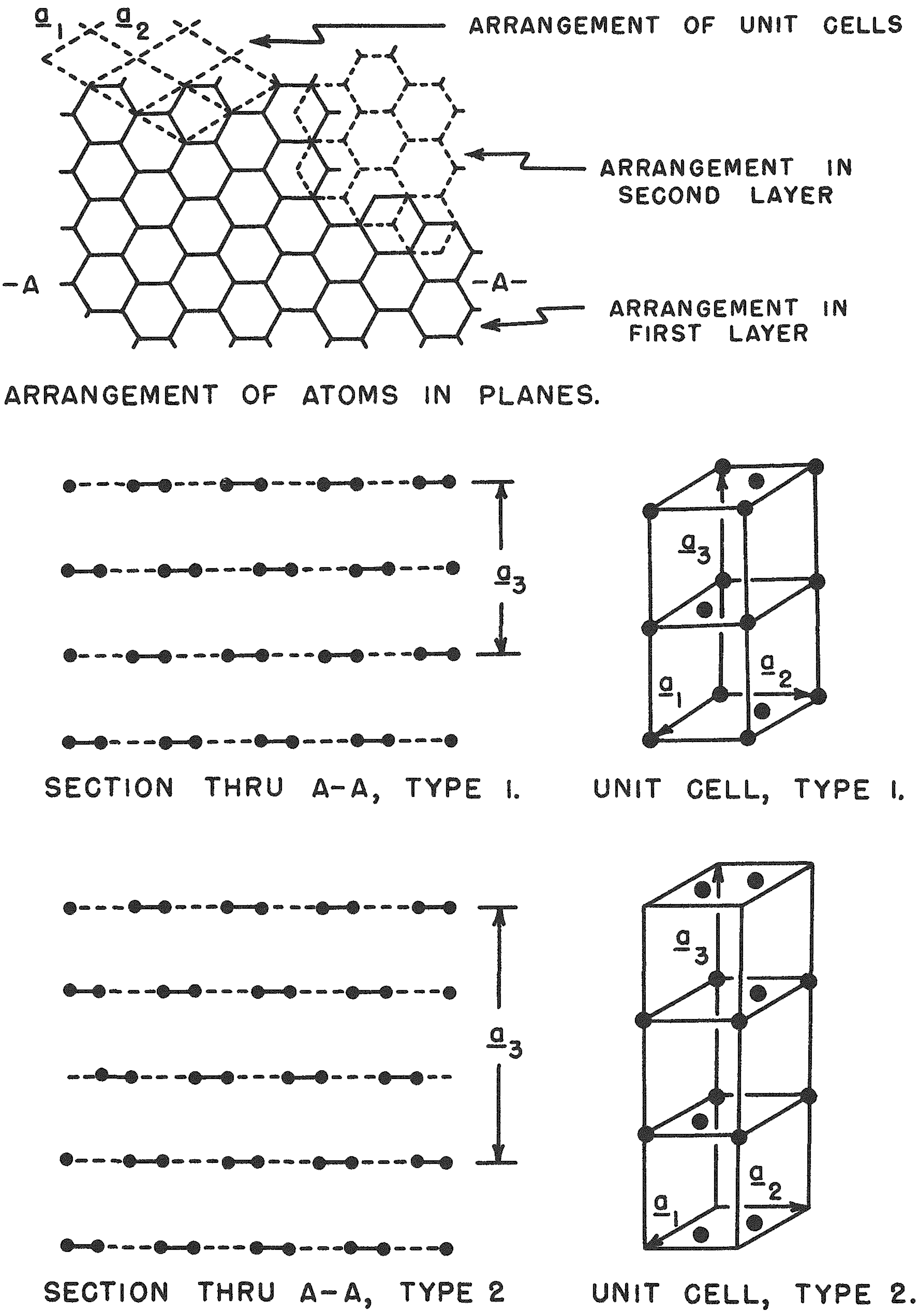

Fig. 1. Arrangement of Carbon Atoms in Graphite

Natural graphite exists in a second modification, proposed by Lipson and Stokes(18) to account for the occurrence of extra lines in X-ray diffraction photographs (see Fig. 1, type 2). The structure consists of hexagonal layers and carbon atoms identical to the normal structure, but arranged in such a way that the third layer is displaced in reference to the second in just the same way as is the second in reference to the first. Thus, every fourth layer repeats the first layer. The a_3 period is therefore 6.697 x 3/2 A. Samples of natural graphite sometimes exhibit as much as 12 per cent of this second modification.

The lattice spacings of the graphites described in Section 6 were measured by Zachariasen, Mooney, Koehler, Plettinger, et al.(15,16,17) and are summarized in Table V. Within experimental error the a_1 and a_3 lattice periods of pbNG are the same as those of natural graphite. The a_1 lattice periods for natural graphite and AGOT-type graphites are also the same within experimental error, but the a_3 periods of the artificial graphites are significantly larger than that of natural graphite, indicating a certain amount of stacking disorder(19) in the artificial graphites.

TABLE V

Lattice Spacings of Artificial and Natural Graphite(15,16,17)

Type	a_1 period (Å)	a_3 period (Å)
AGX	2.457 ± 0.002	6.713 ± 0.007
AGR	2.457 ± 0.002	6.711 ± 0.005
Speer	2.454 ± 0.002	6.715 ± 0.005
AGOT-K (I)	2.455 ± 0.002	6.709 ± 0.005
AGOT-C (I)	2.457 ± 0.002	6.711 ± 0.005
AGOT-W (I)	2.457 ± 0.002	6.712 ± 0.005
AGOT-W (T-15)	2.458 ± 0.002	6.708 ± 0.005
Sp 2100	2.450 ± 0.003	6.820 ± 0.01
Sp 2400	2.450 ± 0.003	6.784 ± 0.005
Sp 3000	2.456 ± 0.004	6.717 ± 0.005
pbL	2.450 ± 0.005	6.770 ± 0.01
pbNG	2.4564 ± 0.0006	6.697 ± 0.0017
NG	2.4564 ± 0.0006	6.697 ± 0.0017

The series Sp 2100, Sp 2400, and Sp 3000 shows the changes in lattice spacing which occur during the graphitizing process concomitant with a decrease in stacking disorder.(17) The X-ray pattern for Sp 2100 has a very few lines. These are broad and exhibit a character which would be expected for layers two-dimensionally well ordered but randomly located with respect to each other. The pattern observed for Sp 2400 is similar to that observed for Sp 2100 except that there is evidence of better stacking order. The pattern for Sp 3000 is comparable to those of the AGOT-type graphites. The pattern of pbL is somewhat similar to that of Sp 2400. Apparently pbL is very nearly two-dimensional, but is more ordered than the random layer lattices reported for unfired lampblack.(16)

The "crystals" in both natural and artificial graphite are reported(16,17,19) to be agglomerates of small units, of a number of layers of atoms (like decks of cards), over which there is good order. Thus, the crystalline agglomerate in graphite can be described as a stack of several "decks" of well-ordered planes. This is illustrated in Fig. 2, where A_1 described the diameter of the stack, A_3 the total height of the stack, and D_3 the distance over which good order obtains (i.e., the thickness of a "deck").

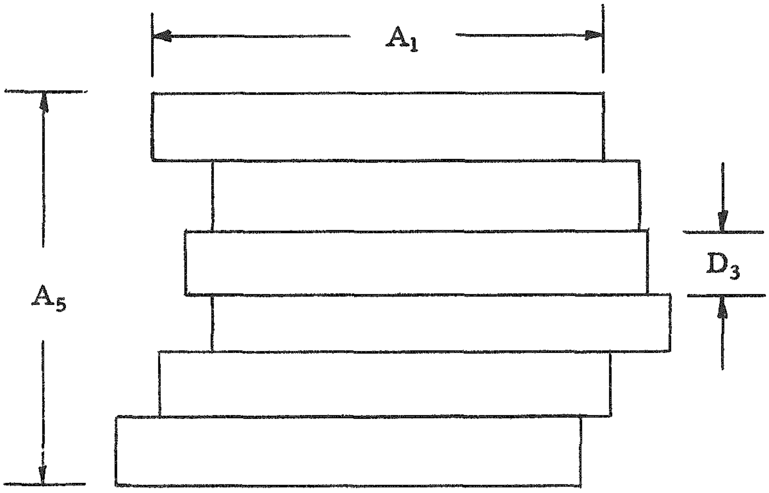

Fig. 2. Arrangement of graphite in stacked "decks."

The height of the ordered stacks in natural graphite was found to be greater than 1000 A; the stacking height for pbNG also was greater than 1000 A.(16,17) In the AGOT-type graphites Zachariasen reports that A_1 is always much greater than A_3; the approximate value of A_3 is 150 A; the value of A_1 is $>$ 1000 A. Table VI summarizes some of the values of A_1, A_3, and D_3 reported by W. S. Koehler(16) and by Zachariasen.(17)

C. S. Barrett and J. S. Koehler (then at Carnegie Institute of Technology) made use of X-ray diffraction photographs to investigate the extent of preferred orientation of crystallites in extruded artificial graphite.(20) A method was devised for obtaining semi-quantitative values for the ratio

TABLE VI

A_1, A_3, and D_3 Dimensions Estimated by W. S. Koehler(16) and Zachariasen(17)

(see Fig. 2)

Type	A_1 (A)	A_3 (A)	D_3 (A)
NG	∝[a]	∞	>1000
pbNG	∞	∞	>1000
AGOT-K	>1000[b]	165	46
AGOT-C	>1000	200	40
AGOT-W	>1000	100	55
Sp 3000	>1000	175	28
Sp 2400	235	100	[20][c]
Sp 2100	157	100	[14]
pbL	137	32	[20]

[a] The designation ∞ indicates dimensions too large to permit measurement.

[b] The designation >1000 indicates dimensions too large to measure, but yet not so large as those designated ∞ .

[c] Values in square brackets are uncertain.

$N_{||}/N_{\perp}$, where $N_{||}$ represents the number of graphite crystals per cm^3 having their basal plane parallel to the extrusion direction, and $N_{\perp}$ is the number of crystals per cm^3 with their basal plane perpendicular to the extrusion direction. Measurements of AGOT-W artificial graphite indicate values for the ratio $N_{||}/N_{\perp}$ of 2 to 3. For AGOT-K graphite the ratio $N_{||}/N_{\perp}$ is 5 to 6. Thus, the indications are that AGOT-K graphite exhibits much more preferred orientation than the AGOT-W graphite.

8. DENSITY DETERMINATIONS

Graphite which is made from petroleum coke and coal-tar pitch and graphitized immediately after the gas-baking operation has a bulk density of ca 1.5 g cm^{-3}. In order to make the density higher, gas-baked carbon bars are reimpregnated with coal-tar pitch and then graphitized (see Section 3). This increases the density to ca 1.6 - 1.7 g cm^{-3}, depending upon the coke which is used and other production variables.

Table VII lists average values for the bulk density of the various graphites which came to the attention of the Metallurgical Laboratory. Good specimens of natural graphite usually exhibit densities of ca 2.25 g cm^{-3}. Ideal densities, calculated from the lattice constants of natural and AGOT-type graphites, are 2.27 - 2.28 g cm^{-3}.

TABLE VII

Densities (g cm^{-3}) for Various Artificial Graphites and Natural Graphite

Type	Helium Density	Bulk Density
AGX	-	1.64
AGR	-	1.54
Speer	-	1.58
AGOT-K (I)	2.17	1.71
AGOT-C (I)	2.10	1.61
AGOT-W (I)	2.12	1.60
AGOT-W (T-15)	2.10	1.62
Sp 2100	2.01	1.49
Sp 2400	1.96	1.48
Sp 3000	2.00	1.50
pbL	1.93	1.45
pbNG	2.11	1.77
NG	(2.25)[a]	(2.25)[a]

[a] Not measured in this instance, included only as a reference point.

The difference between the X-ray density and the bulk density may be used to estimate the volume of voids. In the AGOT-type graphites voids amount to 25 - 30 per cent. Attempts to determine the true density of artificial graphite were made by Novick(21) using a technique of helium displacement, which essentially amounted to a measurement of the volume of helium necessary to fill the void spaces in graphite. Values for the various graphites range from 1.93 to 2.17 g cm^{-3} and are listed in Table VII. The reliability of these measurements is estimated to be ca 2 per cent. The lack of agreement between the "ideal" densities (calculated from lattice spacings) and those measured by helium displacement suggests that not all the void spaces are accessible to helium.(21)

9. SURFACE AREA AND POROSITY

In the course of pore volume measurements, Novick(21) observed that there was a detectable uptake of helium throughout a period of at least forty-eight hours. A carefully degassed sample of AGOT-W (T-15) graphite was immersed in helium at constant pressure and the apparent volume change of the helium determined as a function of time at 37.0 ± 0.005°C. Pressures were held constant to 0.1 mm Hg. Table VIII illustrates the results obtained on the sample at three different pressures.

TABLE VIII

Variation with Time of Apparent Pore Volume of AGOT-W (T-15) Graphite for Various Helium Pressures, t = 37°C(21)

Sample weight, M = 5.064 g; Initial volume,[a] $V_0 = 2.410$ cm^3;
Apparent pore volume per cc, $(V_p/V_0) = 1 - (D_a/D_i)$;
Ideal density, $D_i = \sim 2.25$ g cm^3;
Apparent density, $D_a = M/(V_0 - \Delta V)$

Time (hr)	0	1	2	4	8	24	48
p (mm Hg)	Volume change ΔV, in cm^3						
251	0	0.010	0.015	0.021	0.035	0.048	0.060
339	0	0.010	0.015	0.018	0.025	0.043	0.055
478	0	0.010	0.013	0.018	0.025	0.037	0.055

[a] V_0 is the initial volume as measured by the difference between volume of the measuring apparatus and volume of gas initially introduced.

Penneman(22) has determined the rate of diffusion of helium along the extrusion direction of a sample of AGOT-type graphite. From the data reported by Penneman, it is possible to calculate(23) a value of ca 10 $cm^2 min^{-1}$ for the diffusion coefficient of helium in graphite at one atmosphere total pressure and 30°C.

The surface area of AGOT-W graphite has been measured by Novick,(21) using the nitrogen adsorption at liquid nitrogen temperature. S-shaped isotherms were obtained which gave a surface area of 0.480 ± 0.008 $m^2 gm^{-1}$ when calculated by the method of Brunauer, Emmett, and Teller.(24)

10. ELASTIC MODULUS AND ENERGY DECREMENT

In the graphite research it has been customary to determine the elastic modulus of samples by the quartz piezo-electric oscillator technique. A dynamic measurement of this sort was essential because measurements of high precision were required and because it was important that samples be measured and remeasured. In static testing the samples are necessarily destroyed or else strained so badly that remeasurements are meaningless.

A certain amount of static data for AGOT-W graphite (parallel-cut) are, however, available from compression tests made for the Metallurgical Laboratory by C. J. Overbeck and E. W. Skinner(25) of Northwestern University. The form of the stress-strain curve obtained was such that no straight-line section was evident. The specimens exhibited plastic flow over the entire stress range. Elastic moduli calculated from the slope of the stress-strain curve near its origin indicated values of $7 - 11 \times 10^{10}$ dynes cm^{-2}. There was considerable variation among the three specimens used, even though they were cut from the same region of a single piece of graphite. One sample, which was over-loaded, broke along a plane at an angle of ca 30° to the sample axis (i.e., to the direction of stress) indicating the plastic nature of graphite when investigated by static techniques. Some sort of an elastic hysteresis effect was suggested by differences between strains observed with load increasing and with load decreasing.

Static measurements emphasize the necessity of determining elastic moduli by some dynamic method which involves small strain amplitudes. The techniques employed are described elsewhere.(26) Table IX lists the longitudinal elastic moduli (i.e., Young's modulus) for the various graphites which have been used. Most of the values are averages of ten or more samples (indicated by numbers in parentheses); mean absolute deviations are given to show the bar-to-bar variation among graphites of the same type. The sample-to-sample variation within a bar is not large (also see Table XII).

TABLE IX

Longitudinal Elastic Moduli of AGOT Graphites, Especially Graphitized Materials, and Pseudo Graphites.

Type of Graphite		E, Elastic Modulus, Units of 10^{10} dynes cm^{-2}	Type of Graphite		E, Elastic Modulus, Units of 10^{10} dynes cm^{-2}
AGOT-K (I)	(||)[b]	12.86 ± 0.46 (20)[a]	AGOT-W (I)	(||)	9.78 ± 0.31 (48)
	(⊥)	5.0 (1)		(⊥)	6.4 (1)
AGOT-K (II)	(||)	13.66 ± 0.40 (55)	AGOT-W (II)	(||)	9.96 ± 0.25 (126)
	(⊥)	5.68 ± 0.24 (18)		(⊥)	6.63 ± 0.30 (18)
AGOT-K (III)	(||)	14.43 ± 0.28 (5)	Sp 3000	(||)	7.05 ± 0.14 (12)
	(⊥)	5.82 ± 0.10 (4)		(⊥)	5.45 ± 0.20 (12)
AGOT-KC	(||)	12.0 ± 0.3 (5)	Sp 2400	(||)	6.60 ± 0.18 (10)
				(⊥)	5.47 ± 0.26 (12)
AGOT-C (I)	(||)	9.86 ± 0.25 (30)	Sp 2100	(||)	6.41 ± 0.14 (11)
	(⊥)	5.7 (1)		(⊥)	4.91 ± 0.19 (11)
AGOT-C (II)	(||)	10.63 ± 0.29 (43)	pbL		5.83 ± 0.08 (11)
	(⊥)	6.44 ± 0.18 (17)			
AGOT-W (T-15)	(||)	10.75 ± 0.31 (20)	pbNG		15.62 ± 0.99 (7)

[a] Figures in parentheses indicate the number of samples included in the average.

[b] The designations (||) and (⊥) indicate orientation of sample axes relative to the axes of extrusion of the stock bar.

It will be noticed that the elastic modulus in the direction of the axis of extrusion is approximately twice that in the direction perpendicular to the axis of extrusion. Since crystallites in the AGOT-type graphite tend to be aligned with their basal planes parallel to the axis of extrusion, this observation suggests that the elastic modulus of natural graphite in the direction of the planes should be high. It would be desirable to have information on this point from direct measurements on large natural graphite crystals. Precise measurements of this sort, however, have not yet been accomplished, both because suitable samples have not been obtained and because of experimental difficulties in the observation of the resonance point of a composite quartz-natural graphite oscillator. Crude measurements, however, have indicated that the elastic modulus of natural graphite parallel to the planes is indeed high, $80 - 100 \times 10^{10}$ dynes cm^{-2}. In this connection there are statements in the mineralogical literature that graphite is relatively hard in the direction parallel to the basal plane.(27) The well-known softness of natural graphite and the weak interplanar bonding further suggest that the elastic modulus in the direction perpendicular to the planes is very low.

J. S. Koehler has determined the modulus of rigidity of AGOT-K (IV) graphite.(28, 29) The moduli reported are $3.26 \pm 0.12 \times 10^{10}$ dynes cm^{-2} in the direction parallel to the axis of extrusion and $2.19 \pm 0.08 \times 10^{10}$ dynes cm^{-2} in the direction perpendicular to the axis of extrusion. Each of these values is the average of measurements on four samples.

Koehler(28) has also determined the energy decrement(30) in graphite. The decrement, Δ, as reported by Koehler, is dimensionless, and is defined by the expression,

$$\Delta = W^d/2W^v \quad ,$$

where W^d is the energy dissipated per cycle by an elastic wave in the sample, and W^v is the average total vibration energy per cycle. The decrement for AGOT-K graphite, in longitudinal vibration, is of the order of magnitude 16×10^{-3} for both parallel-cut and perpendicular-cut specimens. Decrement measurements are apparently very difficult and values obtained are widely divergent. For explicit details of the variations in decrement which depend upon the orientation of sample axes relative to the axis of extrusion of the stock bar, the mode of vibration, the technique of machining the specimens and upon the sample history, Koehler's reports(28, 29) must be consulted.

Measurements have been made by J. S. Koehler on one sample of AGOT-K (||-cut) graphite to determine whether the elastic modulus and the decrement depend on strain amplitude.(29) He found that both properties depend on strain amplitude. It was further found that, within the range of strain amplitudes investigated, values of the two properties did not depend markedly on the previous strains to which the samples had been subjected. The results are illustrated in Fig. 3.

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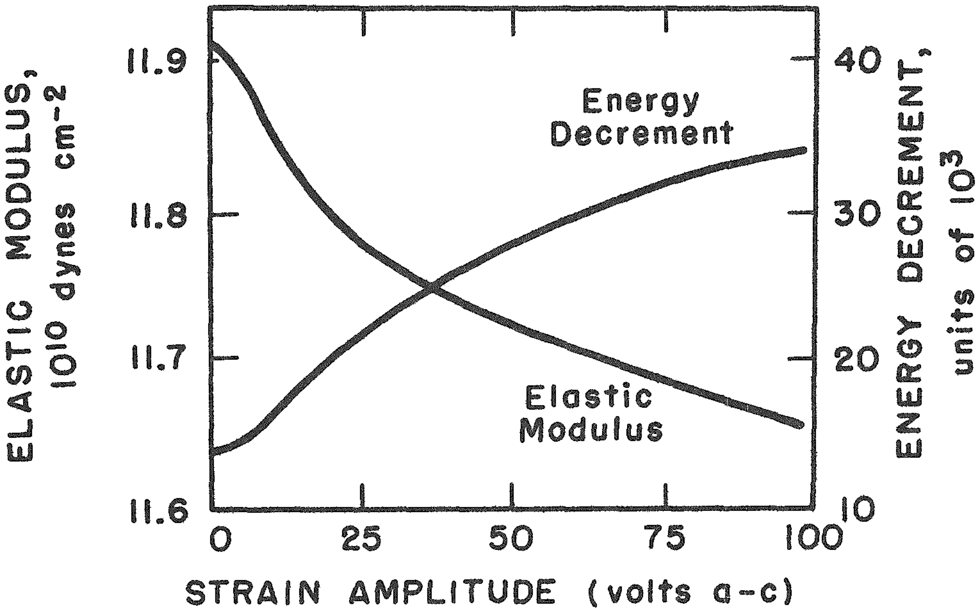

Fig. 3. Dependence of longitudinal elastic modulus and energy decrement of graphite on strain amplitude, J. S. Koehler.(29)

There is one further interesting property of graphite which it seems pertinent to mention at this time. In measurements of the thermal expansion coefficient of AGOT-type graphite (see Section 14) it was observed that a slight "bump" in the slope of the expansion curve occurred at ca 65°C. For this reason the elastic modulus in that region was studied and also found to show a bump at ca 65°C. The experiment, however, was very crude and only one sample was measured. Whether the phenomenon observed is a property of graphite or of the particular sample studied or of the composite quartz-graphite oscillator, was not further investigated.

11. COMPRESSIBILITY

The compressibility of a specimen of natural graphite in the region 1 - 20000 kg cm^{-2} has been reported by Basset.(31) Mean compressibilities at 18°C, calculated according to the expression $\mu = (V-V')/V(P-P')$, are listed in Table X.

TABLE X

Mean Coefficient of Compressibility of Graphite at 18°C, Basset(31)

Pressure Range, kg cm^{-2}	Compressibility, Units of $10^6/cm^2/kg^{-1}$
1 - 5000	4.41
5000 - 10000	3.27
10000 - 15000	2.50
15000 - 20000	1.90

12. ELECTRICAL RESISTIVITY

Table XI lists the resistivities (corrected to 25°C) of various graphites, measured by passing a constant direct current through the sample and determining the potential drop across two probes in contact with the sample. Values given are usually averages of several samples; mean absolute deviations are included, and figures in parentheses indicate the numbers of samples counted in the averages. The apparatus and techniques employed are described elsewhere.(32)

It will be noticed that, as in the case of the elastic modulus, there are considerable bar-to-bar variations. The variations within a given bar are not very large and occur principally between samples cut from the outer skin of the bar and those from the inside of the bar. Average values of the electrical resistivity, elastic modulus, and density for nine sets of six-parallel-cut samples, taken from along the center line and along the surface of bars AGOT-K (I), AGOT-C (I), and AGOT-W (I), are shown in Table XII.

In general, at the surface of the bar the density is higher, the resistivity lower, and the elastic modulus higher. One hypothesis to explain these observations is better orientation of crystallites near the extrusion surfaces. In the usual work relating to neutron-induced changes in graphite the outer portions of the bar were not used. Furthermore, since all changes were computed as fractional effects, small variations in initial properties were considered not significant. Bar-to-bar and sample-to-sample variation within a bar necessitated measurement of the initial properties.

The resistivity of a sample of natural graphite has been determined by Ganguli and Krishnan(33) who report a specific resistance of 10^{-4} ohm cm in the direction parallel to the basal plane and 2 - 3 ohm cm in the direction along the c-axis (i.e., the a_3 axis) perpendicular to the basal plane.

TABLE XI

Electrical Resistivity of AGOT (pile) Graphites, Specially Graphitized Materials, and Pseudo Graphites Measured at 25°C

Type of Graphite		ρ, Electrical Resistivity 10^{-4} ohm cm	Type of Graphite		ρ, Electrical Resistivity 10^{-4} ohm cm
AGOT-K (I)	(∥)[b]	6.45 ± 0.32 (20)[a]	AGOT-W (I)	(∥)	8.45 ± 0.25 (48)
	(⊥)	12.4 (1)		(⊥)	11.5 (1)
AGOT-K (II)	(∥)	5.79 ± 0.35 (55)	AGOT-W (II)	(∥)	8.41 ± 0.25 (126)
	(⊥)	10.49 ± 0.36 (18)		(⊥)	11.81 ± 0.55 (18)
AGOT-K (III)	(∥)	4.90 ± 0.10 (5)	Sp 3000	(∥)	9.41 ± 0.13 (12)
	(⊥)	10.71 ± 0.10 (4)		(⊥)	11.44 ± 0.79 (11)
AGOT-KC	(∥)	7.0 ± 0.5 (5)	Sp 2400	(∥)	21.8 ± 1.7 (10)
				(⊥)	21.7 ± 1.9 (12)
AGOT-C (I)	(∥)	7.44 ± 0.10 (6)	Sp 2100	(∥)	37.7 ± 0.7 (11)
	(⊥)	11.4 (1)		(⊥)	44.9 ± 2.8 (11)
AGOT-C (II)	(∥)	7.65 ± 0.15 (43)	pbL		65.3 ± 1.2 (12)
	(⊥)	11.93 ± 0.42 (17)			
AGOT-W (T-15)	(∥)	7.80 ± 0.23 (21)	pbN		9.71 ± 0.46 (8)

[a] Figures in parentheses indicate the number of samples included in the average.

[b] The designations (∥) and (⊥) indicate the orientation of sample axes relative to the extrusion axis of the stock bar.

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TABLE XII

Variations in Physical Properties of Artificial Graphites in the Surface and at the Center of Bars (Parallel-cut Samples)

Designation		D, Density, Units of g cm^{-3}	R, Electrical Resistivity, Units of 10^{-4} ohm cm	E, Elastic Modulus, Units of 10^{10} dynes cm^{-2}
AGOT-K (I)	center	1.699 ± 0.006	6.425 ± 0.068	12.51 ± 0.20
	surface	1.739 ± 0.009	5.992 ± 0.218	14.26 ± 0.40
	all	1.719 ± 0.020	6.174 ± 0.318	13.39 ± 0.94
AGOT-C (I)	center	1.599 ± 0.007	7.435 ± 0.107	9.72 ± 0.24
	surface	1.633 ± 0.007	6.868 ± 0.075	10.73 ± 0.12
	all	1.616 ± 0.017	7.152 ± 0.305	10.22 ± 0.55
AGOT-W (I)	center	1.593 ± 0.003	8.393 ± 0.053	9.95 ± 0.48
	surface	1.610 ± 0.014	8.064 ± 0.095	10.25 ± 0.18
	all	1.601 ± 0.016	8.229 ± 0.197	10.10 ± 0.32

The corresponding anisotropy of resistivity is 2 - 3 x 10^4. In a later colloquium, (34) however, Krishnan mentioned that by means of more careful measurements he had been able to observe resistivities in the direction of the planes as low as 0.4 x 10^{-4} ohm cm and an anisotropy factor 2 x 10^5.

Bulk specimens of artificial graphite behave as semi-conductors. In the region of room temperature they have temperature coefficients of resistivity varying between - 0.001 and - 0.002 per °C, depending upon the type of graphite and the way in which the sample was cut from the original stock. As the temperature is raised the resistivity decreases with a decreasing temperature coefficient until, at ca 450°C, the temperature coefficent is zero and the electrical resistivity is ca 82 per cent of its room temperature value. As the temperature is raised above 450°C the temperature coefficient becomes positive and the electrical resistivity increases. Tables XIII, XV, XVI, and XVII list some typical values of resistivities at various temperatures taken from curves in the literature.

The resistivities of carbon filaments, prepared by thermal decomposition of CCl_4 on carbonized artificial silk fibers, have been investigated by Nishiyama(36) as a function of temperature for filaments with different heat-treatment histories. It was found that fibers, when first prepared, had high resistivities and negative temperature coefficients which became positive at temperatures above 1000°C. Fibers which were annealed for 30 to 60 minutes at 2500°C showed lower resistivities and a lower temperature

TABLE XIII

Temperature Dependence of Electrical Resistivity of Kendall-Type Artificial Graphite Between 12° K and 300° K, Goetz and Holzer (1942)(35)

Temperature (° K)	Electrical Resistivity (Units of 10^{-4} ohm cm)	
	⊥-Cut	‖-Cut
12	30.8	15.3
25	30.2	15.0
50	28.3	13.9
75	25.1	12.5
100	22.8	11.5
125	21.3	10.6
150	19.8	10.0
175	18.8	9.5
200	17.8	9.1
225	17.0	8.8
250	16.4	8.6
275	15.9	8.4
300	15.5	8.2

TABLE XIV

Electrical Resistivity of Natural Graphite (in the Direction Perpendicular to the a_3 Axis, Along the Basal Plane) for Temperatures Between -179°C and +179°C, Roberts(37)

Temperature (°C)	Relative Resistivity ρ/ρ_0
-179	0.75
- 75	0.95
0	1.00
+ 18	1.01
+ 97	1.10
+179	1.20
$\rho_0 = 0.5 \times 10^{-4}$ ohm cm	

TABLE XV

Temperature Dependence of the Electrical Resistivity and Thermal Conductivity of a Sample of Artificial Graphite, Powell(39) (1937)

Temperature (°C)	ρ [a]	κ [a]
0	8.21	0.402
100	7.31	0.357
200	6.92	0.312
300	6.68	0.268
400	6.60	0.240
500	6.59	0.217
600	6.65	0.197
700	6.78	0.178
800	6.92	0.160

[a] The electrical resistivity, ρ, is given in units of 10^4 ohm cm; the thermal conductivity, κ, in cal cm^{-1} sec^{-1} deg^{-1}.

TABLE XVI

Temperature Dependence of Electrical Resistivity and Thermal Conductivity of Carbon and Artificial Graphite, Collier, Stiles, and Taylor(40) (1939)

Temperature (°C)	Carbon		Graphite I[a,b]		Graphite II[a,b]	
	ρ	κ	ρ	κ	ρ	κ
0	66.3	0.0038	10.5	0.280	8.2	0.402
250	-	-	8.4	0.218	6.8	0.29
500	-	-	7.8	0.160	6.6	0.21
700	47.4	0.0055	8.0	0.128	6.8	0.178
1000	44.4	0.0070	8.6	0.088	7.2	0.128
1200	42.6	0.0080	-	-	7.6	0.100
1500	39.5	0.010	-	-	8.2	0.064
2000	28.4	0.025	-	-	9.6	0.036
2500	-	-	-	-	10.9	0.029

[a] ρ is given in units of 10^4 ohm cm; κ in cal cm^{-1} sec^{-1} deg^{-1}.

[b] The values of ρ and κ for these samples suggest that I is a perpendicular-cut specimen, and that II is a parallel-cut specimen.

TABLE XVII

Temperature Dependence of Electrical Resistivity and Thermal Conductivity of Artificial Graphite and Carbon; Buerschaper (1944)(41)

Temperature (°C)	Graphite		Carbon
	$\parallel$-Cut	$\perp$-Cut	
Electrical Resistivity (10^4 ohm cm)			
-191	11.36	23.8	54.0
- 85	7.69	17.2	47.2
0	6.49	13.5	45.4
100	5.75	12.8	43.8
Thermal Conductivity (cal cm^{-1} sec^{-1} deg^{-1})			
-191	0.595	0.424	0.0033
- 85	0.485	0.330	0.0096
0	0.425	0.275	0.0148
100	0.348	0.225	0.0206

coefficient which became zero at ca 800°C. Fibers which were annealed at 3000°C for 30 minutes showed still lower resistivities and smaller negative temperature coefficients of resistivity which became positive at approximately 300°C. The most completely annealed filament studied (3000°C - 60 minutes) had a slight negative temperature coefficient of resistivity in the region 50 - 100°C and positive coefficient for higher temperatures.

The changes described are typical of the phenomena which accompany the graphitization of artificial graphite. They further suggest that the temperature coefficient of natural graphite should be positive. Values for the temperature coefficient of resistivity of natural graphite given in the literature vary, being sometimes positive and sometimes negative. Positive temperature coefficients have been reported by Roberts,(37) who measured the resistance of several samples of Ceylon graphite at various temperatures between - 179°C and + 179°C.(38) The samples were cut so that the measured resistivity was that along the basal planes, perpendicular to the a_3 crystal axis. Table XIV (p. 25) lists values taken from curves which he gives.

13. THERMAL CONDUCTIVITY

Data for the thermal conductivity of various artificial graphites at room temperature are listed in Table XVIII. They were determined by observation of the temperature drop along a specimen of known length and cross section while a steady known flow of heat was maintained. It will be observed that artificial graphite has an extraordinarily high thermal conductivity. In the direction parallel to the axis of extrusion AGOT-K compares with aluminum, and in the direction perpendicular to the axis of extrusion, with brass. It appears that the predominant mechanism for thermal conduction in artificial graphite is by lattice vibrations, since the electronic part (from the Wiedemann-Franz rule) should be comparable with the electrical conductivity, which, as is seen from Table XI, is quite low. For example, the electrical conductivity of aluminum is <u>ca</u> 3×10^5 ohms^{-1} cm^{-1}, while that of parallel-cut artificial graphite is <u>ca</u> 1.5×10^3 ohms^{-1} cm^{-1}.

Satisfactory data for the thermal conductivity of natural graphite have been very difficult to find in the literature. The International Critical Tables(42) list the value 0.85 cal cm^{-1} sec^{-1} deg^{-1} in the direction of the basal plane. The thermal anisotropy is given as 4.0. Thus, the conductivity in the direction perpendicular to the planes should be <u>ca</u> 0.2 cal cm^{-1} sec^{-1} deg^{-1}.

The temperature dependence of the thermal conductivity of graphite and "amorphous carbon" bars reported by Powell,(39) by Collier, Stiles, and Taylor,(40) and by Buerschaper,(41) is recorded in Tables XV, XVI, and XVII.

TABLE XVIII

Thermal Conductivity of AGOT (pile) Graphite, and Specially Graphitized Materials, at 25°C

Type of Graphite		κ, Thermal Conductivity ($\text{cal cm}^{-1}\text{sec}^{-1}\text{deg}^{-1}$)		Type of Graphite		κ, Thermal Conductivity ($\text{cal cm}^{-1}\text{sec}^{-1}\text{deg}^{-1}$)	
AGOT-K(I)	(‖)[b]	0.546	(1)[a]	AGOT-W(I)	(‖)	0.397	(1)
AGOT-K(II)	(‖)	0.560 ± 0.002	(3)	AGOT-W(II)	(‖) (⊥)	0.398 ± 0.013 0.303 ± 0.002	(2) (2)
AGOT-K(III)	(⊥)	0.291 ± 0.002	(3)	Sp 3000	(‖)	0.344	(1)
AGOT-KC	(‖) (⊥)	0.45 (?)[c] 0.28 (?)[c]	(?) (?)	Sp 2400	(‖)	0.187	(1)
AGOT-C(II)	(‖)	0.428 ± 0.001	(2)				
AGOT-C(III)	(‖) (⊥)	0.455 ± 0.003 0.320 ± 0.004	(3) (2)	Sp 2100	(‖)	0.073	(1)

[a] Figures in parentheses indicate numbers of samples.

[b] The designations (‖) and (⊥) indicate the orientation of sample axes relative to the extrusion axis of the stock bar.

[c] Reported in H.E.W. Interim Report (September 26, 1944 - March 15, 1945, document No. 3-2305, W. E. Jordan).

14. THERMAL EXPANSION

Measurements of the thermal expansion coefficients (α_1 in the a_1 direction, α_3 in the a_3 direction) of graphite by X-ray diffraction techniques have been reported by Nelson and Riley.(43) They found that the a_1 dimension shows a slight contraction in the temperature region up to 400°C and a small expansion in the region above 400°C, and that the thermal expansion coefficient in the a_3 direction, α_3, is large, with an average value of about 28×10^{-6} deg^{-1}. Table XIX lists the significant data.

TABLE XIX

Thermal Expansion Coefficients of Crystalline Graphite According to Nelson and Riley(43)

$\alpha_1 = \frac{1}{a_1} \frac{\partial(a_1)}{\partial T}$	$\alpha_3 = \frac{1}{a_3} \frac{\partial(a_3)}{\partial T}$
$\alpha = 2/3\,(\alpha_1) + 1/3\,(\alpha_3)$	
T(°C)	α_1(deg^{-1})
0 - 150	-1.5×10^{-6}
~ 400	0
600 - 800	$+0.9 \times 10^{-6}$
$\alpha_3 = 27.00 \times 10^{-6} + 3.05 \times 10^{-9}\,T(°C)$	

Other data for the thermal expansion of the various graphites, supplied (in conversation) by V. C. Hamister, are given in Table XX.

It will be noticed that the thermal expansion coefficient for perpendicular-cut specimens is approximately twice that for parallel-cut specimens supporting the notion of preferential orientation of crystals in the extrusion process in the case of AGOT graphites.

Yuster measured the linear thermal expansion of the AGOT graphites produced in the three experimental heats described in Section 6. Differential linear thermal expansion coefficients are listed in Table XXI; mean linear thermal expansion coefficients between 25°C and T°C are shown in Fig. 4.

TABLE XX

Approximate Mean Values for the Thermal Expansion Coefficients of Various Graphites and Carbon Over the Temperature Interval 25 - 100°C(9)

Material	Thermal Expansion Coefficient (10^{-6} deg^{-1})	
	Parallel	Perpendicular
NG Specimen	0.2	7.5
AGOT-K	1.3	3.6
AGOT-C	1.6	3.4
pbL	4.5	

TABLE XXI

Differential Linear Thermal Expansion Coefficients of AGOT Graphite for Various Temperatures

Temperature (°C)	(1/L)(dL/dT) (in units of 10^{-6} deg^{-1})					
	AGOT-K (I)		AGOT-C (I)		AGOT-W (I)	
	∥	⊥	∥	⊥	∥	⊥
50	0.97	3.18	1.29	2.66	1.64	2.95
150	1.36	4.04	1.68	3.29	2.01	3.43
250	1.62	4.48	2.04	3.95	2.36	3.86
350	1.90	4.48	2.36	4.21	2.67	4.20
450	2.007	4.48	2.57	4.21	2.91	4.36
550	2.29	4.48	2.82	4.21	3.10	4.38

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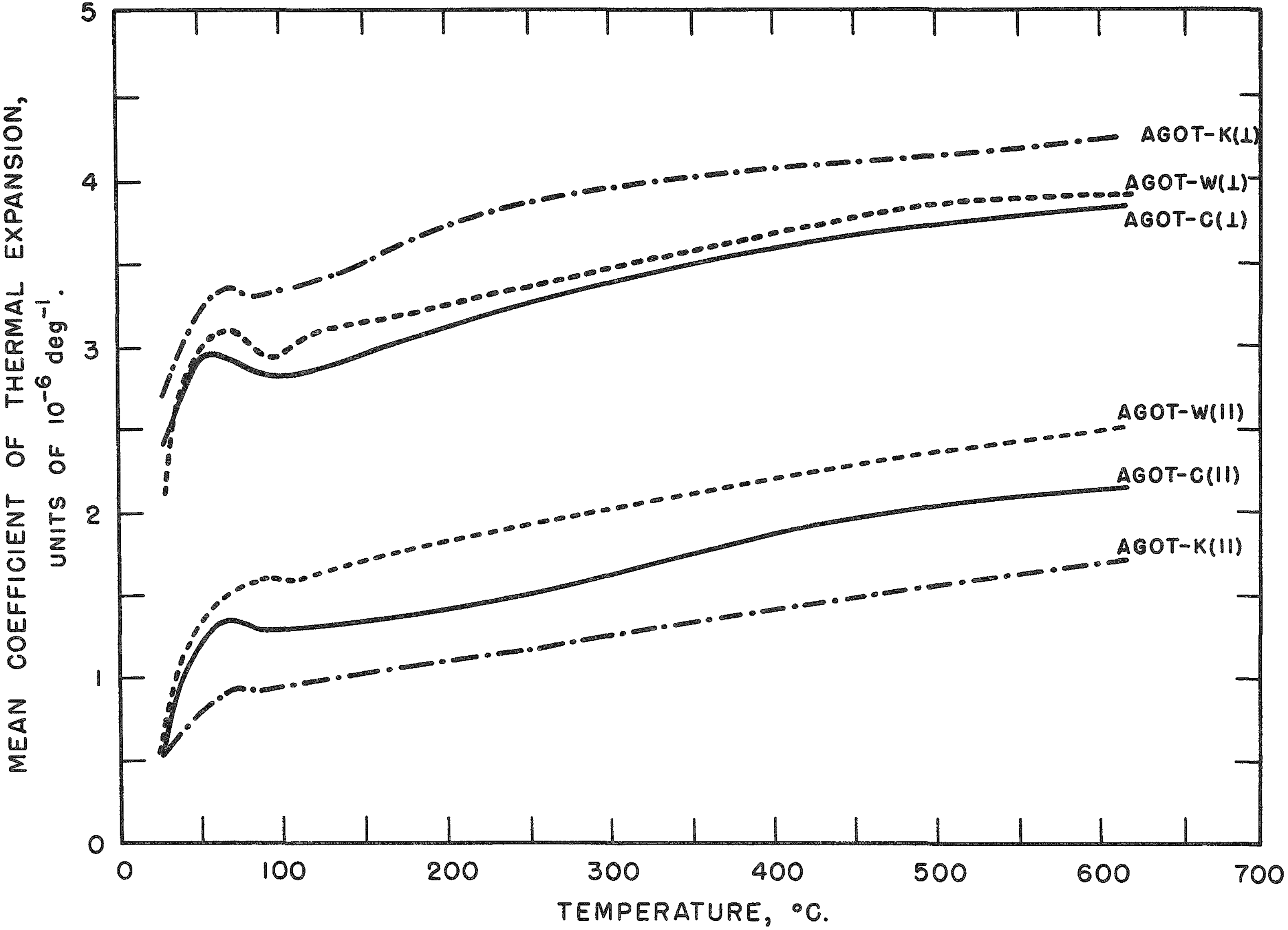

Fig. 4. Mean Coefficients of Linear Thermal Expansion for Various Graphites for the Temperature Range 25 to T°C.

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15. MECHANICAL PROPERTIES

Determinations of the mechanical strength of graphite have been made by Gensamer and Koehler(44) of Carnegie Institute of Technology and by Van Dyken(45) and Burns.(46) Gensamer obtained the modulus of rupture in tension, S, by determination of the force (at the center) necessary to break a sample supported at the ends. Calculations were made according to the formula, $S = 1/2\,(Mc/I)$, where M is the bending moment necessary to break the specimen, c is the thickness, and I is the moment of inertia of the cross section. He also determined the modulus of rupture in compression, S', using the relationship, $S' = F/A$, where F is the force required to break the specimen, and A is the cross sectional area. Gensamer's data are summarized in Table XXII.

TABLE XXII

Breaking Strength of Artificial Graphite, Gensamer and Koehler(44)

Type of Graphite	Tension (S)	Compression (S')
AGX ⊥-Cut	1600 - 2000 psi avg. 1870 psi (1.29×10^8 dynes cm^{-2})	4420 - 5300 psi avg. 4950 psi (3.41×10^8 dynes cm^{-2})
AGOT-K (IV) ‖-Cut	2450 - 3320 psi avg. 2920 psi (2.01×10^8 dynes cm^{-2})	3460 - 5120 psi avg. 4400 psi (3.03×10^8 dynes cm^{-2})
AGOT-K (IV) ⊥-Cut	1270 - 2030 psi avg. 1620 psi (1.12×10^8 dynes cm^{-2})	3550 - 5070 psi avg. 4220 psi (2.91×10^8 dynes cm^{-2})

Data for the cross-breaking strengths of AGOT graphites measured in the Metallurgical Laboratory(45,46) are given in Table XXIII. The samples were cylinders, ca 0.156" in diameter. In a measurement the specimen was supported between two supports (3 cm apart) and the load at the center was increased to the breaking point. The cross-breaking strength was then calculated by the formula, $S_0 = (gWL)/(\pi r^3)$, where gW is the breaking load in dynes, L is the distance between the points of suspension (3 cm), and γ is the radius of the specimen in cm. Data for the average elastic modulus of the samples broken are included to indicate the extent of the correlation between cross-breaking strength and elastic modulus.

TABLE XXIII

Comparison of Cross-Breaking Strength and Elastic Modulus of AGOT Graphites(45,46)

Material	S_b, 10^8 dynes cm^{-2}	E, 10^{10} dynes cm^{-2}
AGOT-K (I) ||-Cut	8.4 ± 0.6	12.9
AGOT-K (II) ||-Cut	8.4 ± 1.2	13.8
AGOT-K (II) ⊥-Cut	6.2 ± 0.6	5.6
AGOT-W (II) ||-Cut	7.9 ± 0.8	10.6

The changes in physical properties of artificial graphite under mechanical mistreatment were investigated in one series of experiments. Elastic modulus and electrical resistivity were measured on four AGOT-W samples. After the initial measurements each sample was placed on a heavy flat iron plate and pounded with a hammer. The procedure was to hit the sample four or five times along its length and then to repeat the process at four or five places around the circumference. The hammer blows were intended to be heavy enough to break crystallites apart, but not to be heavy enough to smash the sample. The process has been described as "bashing." After each bashing treatment the elastic modulus and electrical resistivity were remeasured. Usually a sample could be bashed three or four times before it broke.

The results of these experiments are, of course, very qualitative, but the general trends are clear. Bashing invariably decreases the sharpness of the resonance curves in the modulus measurement, decrease the elastic modulus and increases the electrical resistivity. Figures 5 and 6 depict the changes observed plotted against the resonance frequency of the quartz-graphite oscillator used in the measurement of the elastic modulus.

The decrease in the sharpness of the resonance curves, shown in Fig. 5, is an indication of a very large increase in the energy decrement. The trends depicted in Figs. 5 and 6 suggest that should any other deteriorating process in graphite, e.g., air oxidation, reach important proportions, the different physical properties will change in the directions indicated. This had been observed in the case of artificial graphite samples heated at 300°C in a stream of ozonized air for 30 days.(47) As a result of that treatment the electrical resistivity increased <u>ca</u> 4 per cent and the elastic modulus decreased <u>ca</u> 7 per cent.

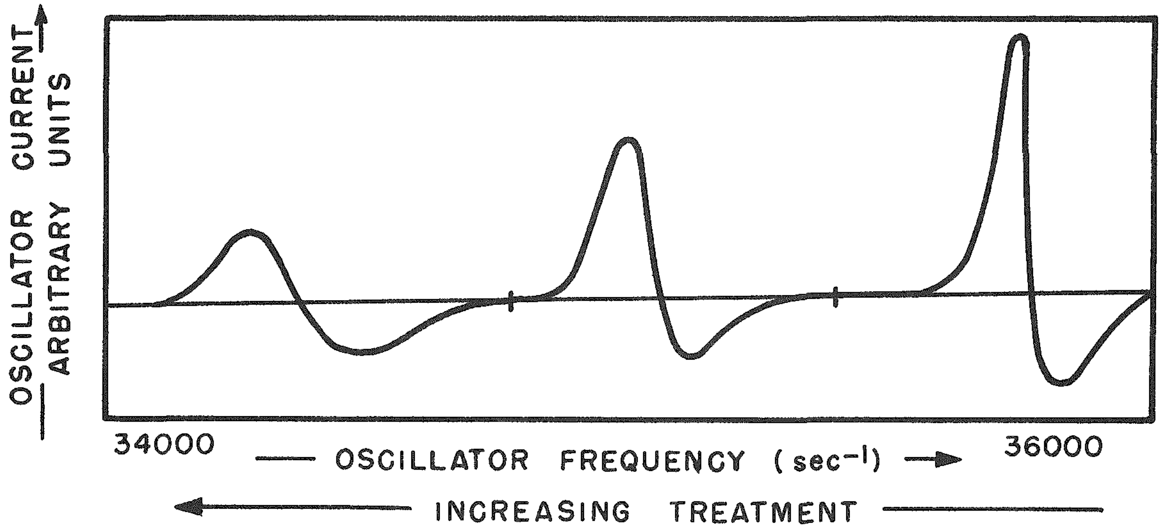

Fig. 5. Decrease in the Sharpness of Resonance Curves (Increase in Energy Decrement) of Artificial Graphite with Mechanical Mistreatment.

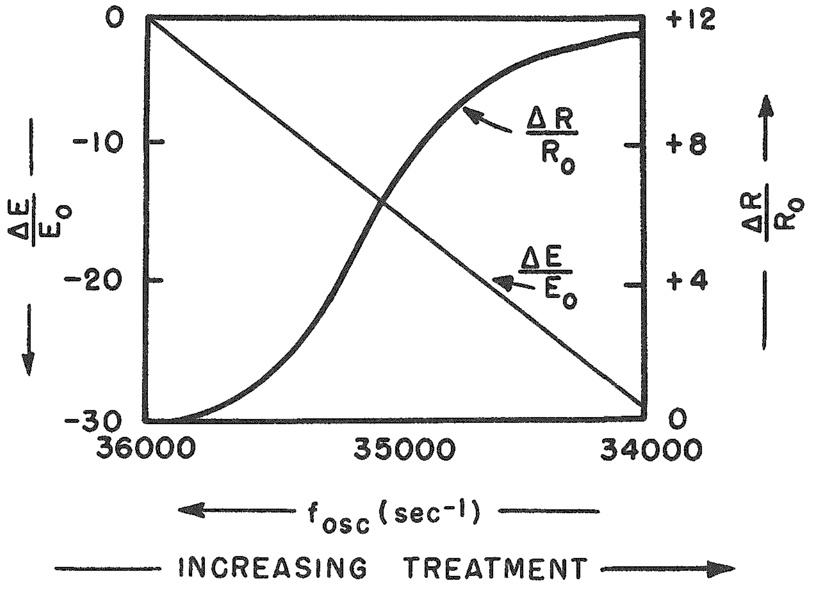

Fig. 6. Changes in Elastic Modulus and Electrical Resistivity of Artificial Graphite with Mechanical Mistreatment.

NOTE: The $\Delta E/E_0$ curve is merely the graphical expression of the relationship between the elastic modulus and the oscillator frequency given by know formulas.(25)

16. SPECIFIC HEAT

Leaf and Novick(48) measured the specific heat of AGOT-K graphite in the temperature range 30 - 500°C. The data they report are in agreement with an equation for the molar heat capacity of graphite given by Kelley.(49)

$$C_p = 2.673 \pm 2.617 \times 10^{-3}T^{-1} - 1.169 \times 10^{5}T^{-2} \quad .$$

Here $\underline{T}$ is the temperature in degrees Kelvin. The equation is reported to represent the specific heat of graphite in the region 275°K to 1373°K to within 2 per cent.

In later work (1946) at the Argonne National Laboratory the older specific heat data reported by Magnus(50) were used. The molar heat capacity is satisfactorily described by the equation

$$C_p = 1.824 + 9.3324 \times 10^{-3}T - 1.0278 \times 10^{-5}T^2$$

$$+ 7.067 \times 10^{-9}T^3 - 2.631 \times 10^{-12}T^4 \quad ,$$

where $\underline{T}$ is the temperature in degrees Centigrade. Values calculated from this equation are listed in Table XXIV.

Estermann and Kirkland(51) (Carnegie Institute of Technology) determined specific heats at low temperature. Table XXV summarized their results for a sample of AGOT-K (II) artificial graphite (Sample 10 V) in the temperature range 25 - 120°K. Table XXVI lists the results for one sample of AGOT-KC graphite (Sample 14) in the temperature interval 15 - 30°K. The estimated error for the data in Table XIX is ca ± 0.002 cal/mol at lower temperatures, and ca 2 per cent at higher temperatures. The estimated error for the data in Table XX is ± 0.003 cal/mol for the lower temperatures and less than 1 per cent for the higher temperatures.

Gurney has recently made a study of the lattice vibrations in graphite(52) considering the atomic arrangement and the size and shape of the crystallites in artificial graphite. He concluded that the (constant volume) specific heat, C_v, at low temperatures should be given by a "two-dimensional" Debye expression of the form

$$C_v = 9.6\ RT^2/\theta^2 \quad .$$

The appropriate Debye temperature he found to be 614°K. The high temperature dependence of C_v is described by an ordinary Debye function (including only those modes of vibration not already counted in the two dimensional expression) with a Debye temperature of 2100°K. The data used for calculation of the Debye temperatures were, for the low temperatures, those of Estermann and Kirkland(51) (see Tables XXV and XXVI) and for the higher temperatures

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TABLE XXIV

Specific Heat of Graphite, According to Magnus(50)

Temp. (°C)	C_p (cal gm^{-1} deg^{-1})	Temp. (°C)	C_p (cal gm^{-1} deg^{-1})
0	0.152	380	0.3516
20	0.1672	400	0.3581
40	0.1818	420	0.3643
60	0.1949	440	0.3703
80	0.2090	460	0.3759
100	0.2218	480	0.3811
120	0.2339	500	0.3863
140	0.2456	520	0.3916
160	0.2568	540	0.3959
180	0.2673	560	0.4007
200	0.2776	580	0.4049
220	0.2874	600	0.4090
240	0.2965	620	0.4128
260	0.3056	640	0.4165
280	0.3142	660	0.4198
300	0.3224	680	0.4230
320	0.3302	700	0.4260
340	0.3376	720	0.4287
360	0.3448	740	0.4313

TABLE XXV

Specific Heat of Kendall-Type Artificial Graphite [AGOT-K (II)] in the Range 25 - 110°K, Estermann and Kirkland(51)

Temp. (°K)	C_p (cal mol^{-1} deg^{-1})	Temp. (°K)	C_p (cal mol^{-1} deg^{-1})
25	0.036	65	0.201
30	0.049	70	0.227
35	0.064	75	0.255
40	0.082	80	0.285
45	0.103	85	0.314
50	0.125	90	0.347
55	0.149	100	0.411
60	0.175	110	0.475

TABLE XXVI

Specific Heat of Kendall-Type Artificial Graphite (AGOT-KC) in the Range 15 - 30°K, Estermann and Kirkland(51)

Temp. (°K)	C_p (cal mol^{-1} deg^{-1})	Temp. (°K)	C_p (cal mol^{-1} deg^{-1})
15	0.0100	23	0.0248
16	0.0116	24	0.0272
17	0.0132	25	0.0300
18	0.0149	26	0.0326
19	0.0169	27	0.0356
20	0.0184	28	0.0390
21	0.0204	29	0.0433
22	0.0224	30	0.0488

those of Magnus(50) (see Table XXIV). Figure 7 (taken from Gurney's report(52)) shows the agreement between the theoretical curves and experimental. Curve (a) represents the contribution of the "two-dimensional" Debye function with θ = 614°K. Curve (b) shows the contribution of the ordinary Debye function with θ = 2100°K. Curve (c) is the sum of curves (a) and (b), i.e., the total specific heat at constant volume for artificial graphite. The points in the figure are experimental values of C_p, which should be very nearly equal to C_v at temperatures below 1000°K.

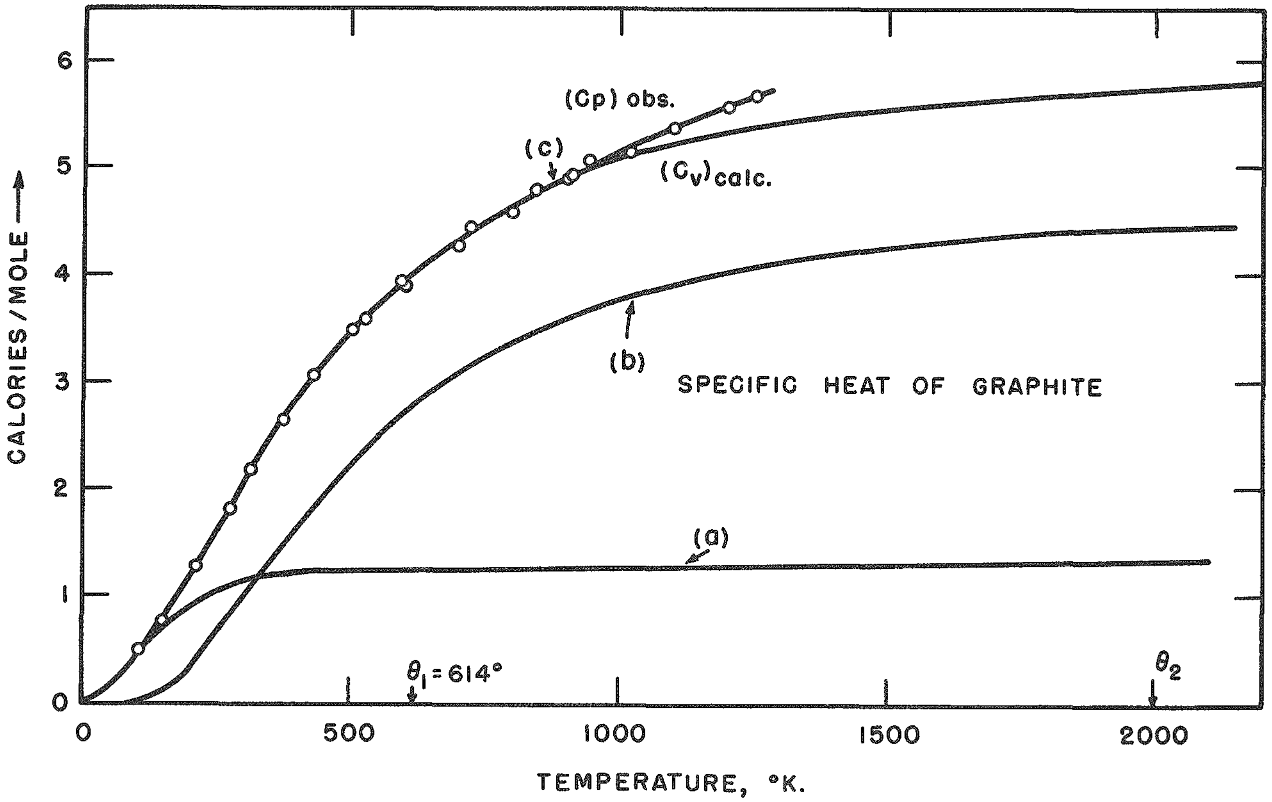

Fig. 7. Molar Heat Capacity of Graphite as a Function of Temperature, Gurney.(50)

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17. HEAT OF COMBUSTION

The heats of combustion of samples of AGOT-K type artificial graphite were determined by Rossini and Prosen of the National Bureau of Standards. The results, together with heats of combustion of various other forms of carbon,(53,54) are listed in Table XXVII. Other information relative to the heats of combustion of carbon and carbon compounds and the experimental techniques have been published by Rossini, *et al.*(55,56,57)

TABLE XXVII

Heats of Combustion of Various Forms of Carbon

Material	cal g^{-1}
AGOT-KC, (one sample, two measurements)[a]	7845.6 ± 1.6
AGOT-K (III), (one measurement)[a]	7842.6 ± 1.6
Graphite[b]	7831.1 ± 0.9
Diamond[b]	7868.8 ± 1.9
Diamond, Black	7873
Carbon, amorphous, acetylene	7885
Carbon, amorphous, sugar	8027
Carbon, amorphous, gas	7985 - 8035

[a] Determined by Rossini, *et al.*, at the National Bureau of Standards, Washington, D.C.

[b] Recent "best values," ΔH° 298.16, Prosen E. J., Jessup, R. P., and Rossini, F. D.(54)

All other data have been taken from Bichowsky, F. R., and Rossini, F. D.(53)

18. CHEMICAL PROPERTIES

Graphite exhibits a number of interesting chemical properties which are principally characteristic of the layer lattice structure. Thus many chemical substances penetrate between the carbon layers, causing swelling of the graphite and in some cases forming stable and relatively definite interlamellar "compounds." Among the substances which interact with graphite are fluorine, bromine, oxygen (e.g., potassium chlorate plus acid), bisulfate ion, antimony trichloride, ferric chloride, potassium and caesium. Many of these reactions have been described by Riley(58) and a few are discussed in the standard textbooks of inorganic chemistry, for example, Emeleus and Anderson.(59)

The reaction of potassium metal with graphite has been studied by Fredenhagen and Cadenbach,(60) by Fredenhagen and Suck,(61) and by Tammann and Sworkyin.(62) The compounds formed are reported to be C_8K and $C_{16}K$, depending upon the amounts of graphite and potassium which are permitted to interact. The former compound (C_8K) is rust-red; the latter compound ($C_{16}K$) is blue. The heat of the reaction has been measured by Fredenhagen and Cadenbach(60) to be 125 cal/g of C_8K formed. X-ray diffraction investigations of the compounds of graphite and potassium and of graphite and caesium have been made by Schleede and Wellmann.(63) The reaction of bromine with graphite has been discussed by Rudorff(64) and by Novick.(65,66)

One further chemical property of graphite is its combustibility. Burning temperatures are usually said to be in the region of 450°C. In one experiment(47) samples heated for 30 days in a slow stream of ozonized air at 300°C lost *ca* 0.7 per cent of their weight. These samples were enclosed in a small electric furnace and were in addition protected by a wrapping of aluminum foil. The figure quoted is thus probably only a lower limit. In oxygen at a temperature of 1200°C a one gram chunk of artificial graphite can be burned nearly completely in about 45 minutes.

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REFERENCES

1. E. P. Wigner, CP-387, (Dec. 15, 1942), p. 4.

2. T. J. Neubert, et al., ANL-5472 (Jan. 1956).

3. L. Pauling, The Nature of the Chemical Bond, second edition, (Cornell University Press, Ithaca, 1944), p. 172.

4. C. Palache, H. Berman, C. Frondel, Dana's System of Mineralogy, seventh edition, Vol. 1, (John Wiley and Sons, Inc., New York,1944), p. 153.

5. C. Palache, Am. Min. 27, 709 (1941).

6. V. C. Hamister, Research Laboratories, National Carbon Company, Cleveland, Ohio, Lecture at Research Associates Meeting, Metallurgical Laboratory, March 19, 1943.

7. C. L. Mantell, Industrial Carbon, second edition, Chapters XII to XVI. (D. VanNostrand Company, Inc., New York, 1946).

8. E. R. Riegel, Industrial Chemistry, (Reinhold Publishing Company, New York, 1936), Chapter 17.

9. National Carbon Company, Inc., National Acheson Carbon and Graphite Products.

10. V. C. Hamister and H. G. MacPherson, Research Laboratories, National Carbon Company, Cleveland, Ohio, private communication.

11. J. A. Lane, editor, Metallurgical Project Handbook, CL-697, Chapters II, E, 1.

12. G. E. Boyd, R. E. Curtis, and W. H. Johnson, CC-976 (December 22, 1943).

13. C. D. Coryell and W. Rubinson, CT-482 (February, 1943).

14. P. Lebeau and M. Picon, Compt. rend., 179, 264 (1924).

15. F. W. H. Zachariasen, CP-961, (September 25, 1943).

16. W. S. Koehler, unpublished thesis, University of Chicago.

17. F. W. H. Zachariasen, private communication.

18. H. Lipson and A. R. Stokes, Proc. Roy. Soc. A181, 101 (1942).

19. F. W. H. Zachariasen, Phys. Rev. 71, 715 (1947).

20. J. S. Koehler and C. S. Barrett, CC-3109, (August 31, 1945).

21. T. J. Neubert, M. G. Bowman, A. Novick, R. C. Hirt, A. R. VanDyken, and E. H. Phillips, CC-918 (September 11, 1943).

22. R. A. Penneman and M. Burton, Metallurgical Laboratory Memo, MUC-MB-283 (September 18, 1944).

23. J. R. Arnold and W. F. Libby, CC-3643 (October 10, 1946).

24. S. Brunarer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc., 60,309 (1938).

25. C. J. Overbeck and E. W. Skinner, private communication.

26. T. J. Neubert, R. C. Hirt, and A. R. VanDyken, Paper II of ANL-5472 (Jan. 1956).

27. H. Schneiderhohn and P. Ramdohr, Lehrbuch der Erzmikroskopie, Volume II, p. 17, (Gebruder Borntraeger, Berlin 1931).

28. J. Handloser, J. Michener, and J. S. Koehler, CC-3162, (September 17, 1945).

29. J. S. Koehler, J. Handloser, J. Michener, C. Williamson, and A. Hammond, CC-2367 (December 11, 1944).

30. T. A. Read, Phys. Rev. 58, 371 (1940).

31. J. Basset, Compt. rend. 213, 829 (1941).

32. T. J. Neubert, M. G. Bowman, A. R. VanDyken, and J. Royal, Paper III of ANL-5472 (Jan. 1956).

33. N. Ganguli and K. S. Krishnan, Nature 144, 667 (1939).

34. K. S. Krishnan, Chemistry Department Colloquium, University of Chicago, 1946.

35. A. Goetz and A. Holser, Trans. Electrochem. Soc. 82, 391 (1942).

36. Z. Nishiyama, Sci. Reports, Tohoko University, I, 21, 171 (1932).

37. D. E. Roberts, Ann. Phys. 40, 453 (1913).

43

38. More recently W. Primak and L. H. Fuchs have reported much more extensive and precise measurements, see Phys. Rev. 95, 22 (1954).

39. R. W. Powell, Proc. Phys. Soc. (London) 49, 419 (1937).

40. L. J. Collier, W. S. Stilus, and W. G. A. Taylor, Proc. Phys. Soc. (London) 51, 149 (1939).

41. R. A. Buerschaper, J. Appl. Phys. 15, 452 (1944).

42. International Critical Tables, first edition, Vol. V, (McGraw-Hill Book Company, Inc., New York, 1939), p. 231.

43. J. B. Nelson and D. P. Riley, Proc. Phys. Soc. (London) 57, 486 (1945).

44. M. Gensamer and J. S. Koehler, CC-2656, (February 16, 1945).

45. A. R. VanDyken and T. J. Neubert, CC-2321, (November 9, 1944).

46. T. J. Neubert, A. Novick, W. R. Burns, and M. Burton, CC-1543, (April 7, 1944).

47. T. J. Neubert, A. Novick, R. T. Schenck, E. Shapiro, and A. R. VanDyken, CC-2758 (March 9, 1945).

48. B. Leaf and A. Novick, CC-3086 (July 3, 1945).

49. K. K. Kelley, Bur. Mines Bull. 371, 78 (1934).

50. A. Magnus, Ann. Phys. 70, 303 (1925).

51. I. Estermann and G. E. Kirkland, CC-3616 (September 5, 1945).

52. R. W. Gurney, CP-3801, Theoretical part, Section 7, p. 37 (April 14, 1947), published in Phys. Rev. 88 465 (1952).

53. F. R. Bichowsky and F. D. Rossini, The Thermochemistry of Chemical Substances, (Reinhold Publishing Company, New York, 1936), p. 229 et seq.

54. E. J. Prosen, R. P. Jessup, and F. D. Rossini, J. Research Nat. Bur. Standards 33, 447 (1944).

55. E. J. Prosen and F. D. Rossini, ibid. 33, 439 (1944).

56. E. J. Prosen and F. D. Rossini, ibid. 27, 289 (1941).

57. E. J. Prosen and F. D. Rossini, ibid. 33, 255 (1944).

58. H. L. Riley, Fuel in Science and Practice, XXIV, 8 (1944) and XXIV, 43 (1944).

59. H. J. Emeleus and J. S. Anderson, Modern Aspects of Inorganic Chemistry, (Routledge and Sons, London, 1938), p. 455.

60. K. Fredenhagen and G. Cadenbach, Z. anorg. u. allg. Chem. 158, 249 (1926).

61. K. Fredenhagen and H. Suck, ibid. 178, 353 (1928).

62. G. Tammann and A. Sworykin, ibid. 168, 218 (1927).

63. A. Schleede and M. Wellmann, Z. phys. Chem. 18B, 1 (1932).

64. W. Rüdorff, Z anorg. u. allg. Chem. 245, 383 (1941).

65. A. Novick, Paper X of ANL-5472 (Jan. 1956).

66. The very interesting work of G. R. Hennig should be consulted for more recent and more extensive information about the chemical properties of graphite.

67. G. Herzberg, Phys. Rev. 70, 762 (1947).