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Electrical Properties of Pyrolytic Graphites*

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Contents

I. INTRODUCTION

SMALL, soft flakes of natural graphite are found in various rock formations throughout the world. Relatively little work has been done on these crystals, since they generally are quite impure, highly twinned, and rather difficult to handle. Carefully selected and purified natural single crystals have nevertheless been successfully used to study various properties of the basic graphite structure.[1] This work has shown that graphite exhibits a considerable degree of anisotropy, if measurements are made along parallel and perpendicular directions to the surface of the flakes. For instance, the electrical conductivity in the parallel direction has been reported as hundred or thousand times greater than in the perpendicular direction.

The task of growing good, reasonably-sized graphite single crystals still presents major unsolved problems. In consequence, past measurements on artificial graphites have been virtually restricted to ceramic products usually made by mixing a petroleum-coke flour with a coal-tar pitch binder. The mixture is extruded or molded to desired shape, baked at a temperature of about 1000°C, and then heat treated in the range of 2500° to 3000°C to give a commercial graphite. Standard commercial graphites have a fairly low density (1.6 to 1.7 g/cm^3), but they are hard and strong. Their electrical properties have been much investigated during the past fifty years.[2] It was soon recognized that they exhibit a moderate degree of anisotropy (of the order of 50 to 60%), and that the heat treatment has a major influence on some of the electrical characteristics of graphitic materials.

In recent years it has been established that massive, coherent deposits of carbon can be produced by the pyrolysis of carbonaceous vapors on a suitable substrate at temperatures of the order of 2000°C.[3] These dense metallic-looking deposits are completely impervious to gases, much stronger than normal graphites, and highly anisotropic with regard to thermal and electrical conductivities. Actually, it has been known for sometime that structures produced by the breakdown of hydrocarbons, structures such as evaporated films or pyrolytic coatings, exhibit unusual properties because the deposited graphite layers[4] tend to orient themselves parallel with the substrate's surface. A general investigation of the properties of pyrolytic carbon coatings prepared from hydrocarbon gases in a furnace at less than 1300°C was carried out by Grisdale *et al.*[5] The coatings consisted of small packets of randomly stacked graphite layers, which were parallel to the surface of the substrate to a certain extent. The process for making pyrolytic carbon deposits, called pyrolytic graphites (PG) by the trade, has since been developed to the point where it is possible to prepare specimens consisting solely of that material, and to reproduce shapes of various dimensions up to a thickness of half an inch. These specimens have a polycrystalline structure, but x-ray analysis reveals varying degrees of preferred

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* A preliminary report on this work was presented at the Detroit meeting of the American Physical Society, March 21–24, 1960. [C. A. Klein, Bull. Am. Phys. Soc. **5**, 187 (1960).]

[1] For a discussion, see D. E. Soule, Phys. Rev. **112**, 698 (1958).

[2] For references, see E. E. Loebner, Phys. Rev. **102**, 46 (1956).

[3] A. R. G. Brown and W. Watt, *Industrial Carbon and Graphite* (Society of Chemical Industry, London, 1958), p. 86.

[4] Plane sheets of carbon atoms in hexagonal arrays.

[5] R. O. Grisdale, A. C. Pfister, and W. van Roosbroeck, Bell Systems Tech. J. **30**, 271 (1951).

orientation. Since each crystallite has anisotropic features reflecting the basic graphite structure, the preferred orientation more or less transfers the intrinsic crystal anisotropy to the bulk properties. The anisotropy of the electrical resistivity of pyrolytic graphites, in correlation with quantitative evaluations of the degree of preferred orientation, has been one of the main points of emphasis in the present investigation.

A significant property of PG, which was already systematically investigated in 1953, is the density.[6] It was found that the density of deposited carbons is strongly dependent upon the temperature of deposition, rising from 1.2 g/cm^3 at 1700°C to 2.23 g/cm^3 at 2100°C. The density increases with the deposition temperature owing to the enhanced degree of preferred orientation and approaches the theoretical density of graphite, 2.26 g/cm^3, if there are no vacant sites. In view of these large variations, it was thought probable that other physical properties would show extensive changes with deposition temperature. This is indeed so with the thermal and electrical conductivities, as was first shown by Brown *et al.*[7]

The present investigation has been undertaken in order to extend the limited range of previous electrical measurements on deposited carbons towards lower and higher ambient temperatures. Much attention has been given to the galvanomagnetic properties, since they have not yet been reported for these materials. Moreover, low-field magnetoresistivity data have been used to determine the average carrier concentrations and mobilities in some of our specimens. In summary, this paper represents a semi-empirical attempt to give an over-all picture of the electronic properties of deposited carbons produced by high-temperature pyrolysis. In addition to the previously mentioned emphasis on correlations between physical anisotropy and structural alignment, our aims have been to cover the more important aspects of transport in pyrolytic graphite, to appraise the dominating factors of the electrical conduction mechanism, and to account quantitatively for some of the observations.

The PG specimens that are being considered in this work were selected to cover a wide range of properties. They actually differ by orders of magnitude in electrical conductivity. In order to demonstrate the interdependency of electrical properties and structural factors, our measurements and the concurrent x-ray analysis were made on test probes taken from the same deposit. These deposits are described in Sec. II. They were prepared by decomposition of a methane-hydrogen mixture against a synthetic graphite substrate, at temperatures ranging from 1700° to 2500°C and using induction- or resistance-heated furnaces. Chemical analysis of the deposits shows that they consist of carbon with minor traces of hydrogen and other impurities (less than 0.25%). In this connection it should be pointed out that pyrolytic graphite provides a means of studying the nature of artificial graphites in which the nongraphitic pitch binder of the usual products is essentially absent. This is of consequence because some of the present interpretations of the synthetic graphite behavior rest on the presence of small, nongraphitic regions.[8,9]

In this paper, data and results are presented after some experimental considerations (Sec. III) under the major headings of room-temperature resistivities (Sec. IV), temperature dependence of the resistivities (Sec. V), and galvanomagnetic effects (Sec. VI). For purposes of clarity the discussion has been divided into two parts: First, an attempt is made to analyze the data in terms of carrier concentrations and mobilities (Sec. VII). This attempt is followed by considerations regarding the conduction mechanism in graphitic systems (Sec. VIII). Since many of the features of these systems can be directly deduced from the crystal structure itself, it is felt appropriate to begin with a summary of the indications revealed by an x-ray diffraction analysis of the selected specimens.

II. STRUCTURAL CHARACTERISTICS[10]

A discussion of the PG structure is most conveniently introduced by considering the graphite crystal lattice of Fig. 1. The lattice is made up of carbon atoms arranged according to a two-dimensional hexagonal pattern. The layers of carbon atoms, or basal planes, are

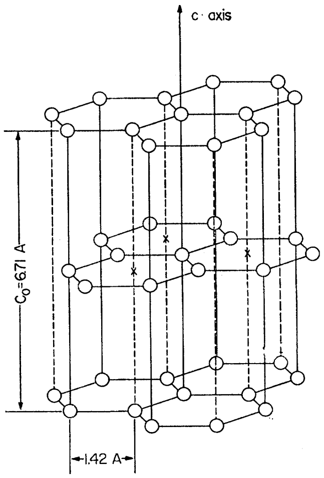

FIG. 1. Crystal structure of ideal graphite. The full vertical lines connect atom sites that are located directly above and below the sites in adjacent layers, whereas sites connected by broken lines are above and below empty carbon hexagon centers.

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[6] A. R. G. Brown, A. R. Hall, and W. Watt, Nature **172**, 1145 (1953). See also R. J. Diefendorf, J. chim. phys. **57**, 815 (1960).

[7] A. R. G. Brown, W. Watt, R. W. Powell, and R. P. Tye, Brit. J. Appl. Phys. **7**, 73 (1956).

[8] A. W. Smith, Phys. Rev. **95**, 1095 (1954).

[9] J. E. Hove, Phys. Rev. **98**, 1563 (1955).

[10] Data and results that are mentioned in this section were obtained by O. J. Guentert, S. Cvikevich, and C. T. Prewitt. They were first reported at the Detroit meeting of the American Physical Society, March 21–24, 1960. [O. J. Guentert and C. T. Prewitt, Bull. Am. Phys. Soc. **5**, 187 (1960).] A paper on x-ray diffraction studies of pyrolytic graphite is in preparation.

TABLE I. Summary of the preparation history and x-ray diffraction study of the pyrolytic graphite specimens considered in this paper. Doubtful data are in parentheses.

	History				*Layer order*			
Specimen	furnace[a]	deposition temperature[b] (°C)	heat treated[c]	Preferred orientation $n_{\max}/n_{\min}$	interlayer spacing (A)	index of graphitization γ	(hkl) reflections	Crystallite size L_a (A)
I-62	Induction	1700	no	5	3.42_5	0	none	≈ 50
I-62*	Induction	1700	yes	5	3.40_5	0.29	none	
I-63	Induction	1900	no	10	3.40_0	0.36	none	≈ 100
I-63*	Induction	1900	yes	13	3.39_0	0.50	none	
R-40	Resistance	2100	no	≈ 2500	3.42_0	0.07	none	285
I-64	Induction	2300	no	(175)	3.38_5	0.57	some	(300)
I-65	Induction	2400	no	≈ 2000	3.35_5	1	all	(600)
R-7	Resistance	2500	no	≈ 3000	3.41_5	0.14	none	325
R-7*	Resistance	2500	yes	≈ 4000	3.37_0	0.79	many	

[a] Shown in Fig. 17 of the Pyrographite brochure distributed by Raytheon Company, Waltham, Massachusetts.
[b] Determined using a Leeds and Northrup optical pyrometer, and maintained constant within ±100°C.
[c] For 3 hr at 2500°C in a high-purity argon atmosphere.

stacked in accordance with an *abab* scheme. Each atom has four valence electrons; three σ electrons which establish tight covalent bonds with the nearest neighbors in the plane, and a loosely bound π electron. This state of affairs results in a lattice that is characterized by the close proximity (1.42 A) of the atoms in a layer as compared to the spacing (3.35 A) between the layers. The anisotropy of graphite is a direct consequence of this structural feature. Another typical feature concerns the stacking scheme. The *abab* scheme produces two types of lattice sites with distinctly different environments, as shown in Fig. 1. One-half of the atoms of a layer are located above and below the carbon hexagon centers in the adjacent layers, whereas the other half has neighbors directly above and below.[11]

Solid carbons, with the exception of diamond, are made up of crystallites consisting of flat, parallel, and equidistant layers of hexagonally arrayed atoms. Besides this common feature, graphitic materials exhibit a great variety of structural configurations: (*a*) The most highly organized structures are those with crystallites of considerable size, well-aligned with respect to each other, and consisting of well-ordered carbon layers. All the *c* axes point in the same direction, and within each crystallite the structure is essentially that of the three-dimensional lattice of "true" graphite. (*b*) The most disorganized structures are found in the so-called "amorphous" carbons. Their crystallites are small (average layer diameter of the order of 25 A), randomly oriented with respect to each other, and turbostratic in the layer arrangement. In other words, they are made up of randomly aligned small stacks of parallel, but randomly rotated graphitic planes. (*c*) In addition to these two extreme configurations, we are confronted with a whole range of intermediate or "transitional" structures. For instance, it has been established that, in essence, the transformation of an amorphous carbon into polycrystalline graphite proceeds through growth and azimuthal readjustment of the graphitic layers.[12] In soft carbons such as petroleum-coke base materials, the crystallite growth and ordering process, a process which is often referred to as graphitization, commences with heat treatment at 1700°C and is practically completed at 2500°C.

Among transitional graphite structures, deposited carbons distinguish themselves by an unusual degree of preferred orientation. X-ray diffraction studies reveal that if the deposition temperature T_d increases, the crystallites have an increasingly strong tendency to align their basal planes with the face of deposition. In some cases the x-ray pattern exhibits well-developed (*hkl*) reflections indicative of three-dimensional order. Specimens prepared under normal conditions,[13] however, display a conspicuous lack of rotational order; the layer stacking takes place in a random fashion. Both the number and the size of the layers in an average crystallite become greater at higher deposition temperatures. Preliminary results indicate that the crystallites grow in diameter from about 50 A at the lowest deposition temperatures up to hundreds of angstroms at $T_d = 2500°\text{C}$, and they may assemble packets of more than one hundred planes.

Quantitative indications on the history and structure of the PG specimens considered in this paper are listed in Table I. It is outside of our scope to discuss these data in detail.[10] Let us simply mention that:

1. *The preferred orientation* is best described in terms of an orientation density. If $N(\vartheta,\varphi)$ is the number per unit volume of those crystallites whose *c* axis points into the solid angle $\Delta\Omega$ at ϑ degrees from the normal of the sample, the orientation density can be defined as

$$n(\vartheta,\varphi) = N(\vartheta,\varphi)/\Delta\Omega. \qquad (1)$$

If $n(\vartheta,\varphi)$ does not remain constant, the sample is said to possess preferred orientation and to a degree which

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[11] Energy-band calculations suggest that the stacking scheme affects the degree of overlap of the two π bands. References can be found in D. E. Soule and J. W. McClure, J. Phys. Chem. Solids 8, 29 (1959).

[12] R. E. Franklin, Acta Cryst. 4, 253 (1951).

[13] In a resistance-heated furnace with no subsequent heat treatment.

it is convenient to characterize by the ratio $n_{\max}/n_{\min}$. The intensity variations of $(00l)$ reflections, namely the variations as a function of the sample's orientation with respect to the incident x-ray beam, indicate that in deposited carbons $n(\vartheta,\varphi)$ is nearly independent of φ but depends strongly on ϑ. More specifically, it has been found that the degree of preferred orientation $(n_{\max}/n_{\min})$ rises from about 5 in a low-temperature deposit such as I-62 to almost 4000 in heat-treated products deposited at 2500°C.

2. *The layer order* cannot be easily appraised on a quantitative basis. The transition from a disordered to an ordered configuration reveals itself through a gradual build-up of the (hkl) reflections, in particular of the strong (101) line. Simultaneously, the position of the (002) line is shifting towards higher angles, which implies that the ordering process is associated with a reduction of the interlayer spacing $c_0/2$. Since $c_0/2$ decreases from a maximum value of 3.425 A in the initial stage of graphitization to a minimum of 3.355 A for fully ordered carbons, it has been suggested that use be made of the ratio

$$\gamma=\frac{(c_0/2)_{\max}-c_0/2}{(c_0/2)_{\max}-(c_0/2)_{\min}} \tag{2}$$

as an index of the degree of azimuthal order in a transitional graphite structure.[14] If we do this, an inspection of Table I shows that: (a) The induction-grown specimens cover the whole range of degrees of graphitization from $\gamma=0$ when $T_d\approx1700°\mathrm{C}$ to $\gamma=1$ when $T_d\approx2400°\mathrm{C}$. ($b$) As deposited the resistance-grown specimens exhibit very little order, in spite of the excellent crystallite alignment.[15] (c) Heat treatment (3 hr at 2500°C) has marked effects on materials deposited at temperatures above 2100°C in the resistance-heated furnace.

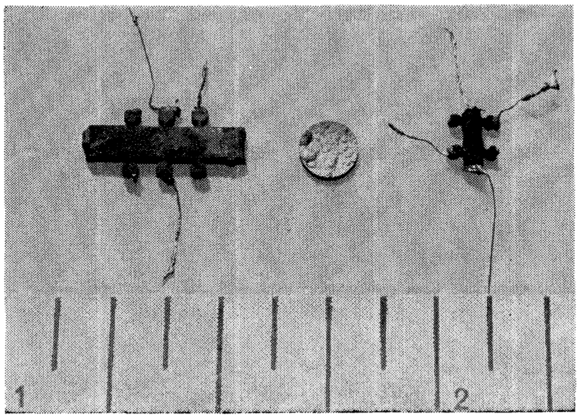

FIG. 2. Pyrolytic-graphite samples shaped for electrical and galvanomagnetic measurements. Note the high metallic reflectivity of the disc, cut from a 2400°C deposit, which is characteristic of the basal planes. The straight edge is graduated in inches.

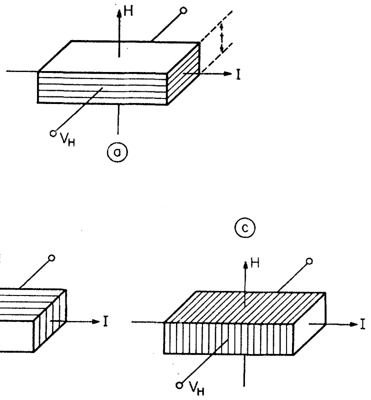

FIG. 3. Three basic arrangements for galvanomagnetic experimentation on pyrolytic graphite.

3. *The crystallite size* is an important factor to take into account, if we are concerned with electrical properties. Since most of the transport phenomena in graphitic systems are conditioned by basal plane mechanisms, we may confine our interest to the dimensions of the layers and their growth with increasing deposition temperatures. The average layer diameters L_a of Table I were deduced from the asymmetric broadening of two-dimensional (hk) reflections with the help of Warren's formula,[16] namely

$$L_a=1.84\lambda/(B\cos\theta), \tag{3}$$

where B is the half-width in radians of the reflection under consideration, θ its Bragg angle, and λ the wavelength of the incident x-ray beam. It is well known that Eq. (3) becomes unreliable in the case of partially or fully ordered materials; the L_a values of I-64 and I-65, as given in Table I, should therefore only be considered as indicative of a trend.

III. EXPERIMENTAL CONSIDERATIONS

Pyrolytic graphite deposits of a few millimeter thickness can be easily machined by means of ultrasonic techniques. This makes it feasible to cut samples with appropriate shapes and to investigate most of the material's properties. Some of the samples that we have used in order to measure electrical resistivities and galvanomagnetic parameters in PG are shown in Fig. 2.

It is common practice to perform galvanomagnetic experimentation with the sample and the current both perpendicular to the magnetic field. Since pyrolytic graphite possesses preferred orientation (a c direction), we must consider the three experimental arrangements schematized in Fig. 3: (a) The magnetic field $\mathbf{H}$ is

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[14] V. I. Kasatochkin and A. T. Kaverov, Doklady Akad. Nauk S.S.S.R. **117**, 837 (1958).

[15] The lack of order in these specimens, as deposited, may be attributed to the high rate of injection and the "external" heat-generation arrangement of the furnace. At high temperatures, deposited carbon atoms link up to form plane layers. In the resistance-heated furnace these layers quickly cool down to a temperature that does not permit rotational ordering. At temperatures below 2000°C, the mobility of deposited carbon atoms is much impaired, and we anticipate smaller crystallites with random order, no matter how the heat is distributed.

[16] B. E. Warren, Phys. Rev. **59**, 693 (1941).

pointing in the c direction; (b) The Hall voltage V_H is measured in the c direction; (c) The current **I** is flowing in the c direction. Pearson-Suhl type bridges[17] corresponding to cut (a) and cut (c) are shown on the left- and right-hand side of Fig. 2, respectively. The Hall effect as well as the magnetoresistivity data discussed in Sec. VI were all obtained in the geometry (a).[18] This choice was dictated by the two following considerations: First, owing to the morphology of the deposits suitable samples can be easily prepared. Second, in the arrangement (a) with most of the crystallites' c axes parallel to **H**, the motion of the carriers is confined to the basal planes, and we are in effect dealing with an isotropic two-dimensional situation. This is indeed attractive, if we are concerned with isothermal transport processes.

Conventional dc methods were used to measure the Hall voltage and the voltage drop induced by magnetoresistive effects. How current-carrying leads and potential-probe wires were soldered to the copper-plated tips of a bridge can be seen in Fig. 2. Such a procedure provides ohmic contacts and homogeneous current distributions, as was checked by noting that a reversal of the magnetic field did not significantly alter the magnetoresistance reading. Hall-voltage measurements as a function of current at a given magnetic field strength were used to eliminate samples with an appreciable zero error. Undesirable thermomagnetic phenomena, with the exception of the Ettinghausen effect, were compensated by taking the average of four measurements utilizing both directions of the electric and magnetic fields. Since our samples were maintained isothermal by direct immersion in the coolant, and since heat transport in graphite proceeds mainly through the lattice,[19] there are actually no reasons to fear perturbations by the Ettinghausen effect. At this point let us recall that, with the arrangement of Fig. 3(a), the Hall coefficient is obtained in cubic centimeters per coulomb according to

$$R_H = 10^8 V_H t/(IH), \tag{4}$$

if V_H is measured in volts, I in amperes, H in gauss, and the sample's thickness in centimeters. Assuming that the magnetic field intensity was determined with an accuracy of 3% throughout the considered range (1 to 25 kgauss), the use of bridge-shaped samples in combination with a constant current technique should make it reasonable to believe that the error in R_H could be kept to less than 6%, in general.

Simultaneously with the galvanomagnetic experimentation, as well as independently of it, we have made electrical resistivity measurements over wide temperature ranges along and across the various PG deposits listed in Table I. Whenever possible, we have used standard potentiometric techniques (with constant currents of up to 0.5 amp). Parasitic thermal effects were minimized by taking all the readings with normal and reversed current. Attempts to collect reliable high-temperature data were only partly successful, since they usually ended with contact failures at about 1000°C.[20] With specimens too thin to permit the cutting of a bridge in the (c) geometry, the c-direction resistivity measurements were made by clamping disk-shaped samples (Fig. 2) between copper plates, and probing the sample itself through tungsten probes operated by micromanipulators. The four-probe method eliminates contact-resistance difficulties (this was checked by potentiometric measurements on "thick" specimens), but is limited to room-temperature work. It should also be mentioned here that these little disks (0.110 in. in diameter, 0.038 in. in thickness) were found very convenient for c-direction resistivity measurements at microwave frequencies, if one uses a slab-line procedure.[21] How the microwave data compare with the dc results will be discussed in the next section.

IV. ROOM TEMPERATURE RESISTIVITIES

In graphite, band structure and scattering mechanisms give rise to electrical characteristics which, in many ways, are intermediate between those of semiconductors and metals. Furthermore, energy surfaces and relaxation times show large anisotropies: In single-crystal flakes the resistivity along the c axis is some two or three orders of magnitude larger than along the basal planes. For these two reasons we expect the room-temperature resistivities of graphitic materials to be very sensitive to factors such as impurity content, degree of preferred orientation, and crystalline perfection. A glance at Fig. 4 will convince us that this is indeed the case.

The electrical conductivities of annealed and purified single-crystal graphite flakes of North American origin have been carefully investigated at the Argonne National Laboratory.[22,23] Measurements of the a-axis resistivity, ρ_a,[24] were quite reproducible and in good agreement with the results of earlier work, namely 40 μohm-cm, in contrast to the 800 or 1000 μohm-cm of extruded synthetic graphites.[25] The c-axis measurements were much less reproducible, but it appeared that crys-

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[17] G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1951).

[18] Preliminary experiments in the geometries (b) and (c) were inconclusive insofar as the Hall effect is concerned. They show, however, that there is no measurable magnetoresistivity in the c direction of well-oriented specimens.

[19] R. W. Powell and F. H. Schofield, Proc. Phys. Soc. (London) **51**, 153 (1939).

[20] Current electrodes and potential leads were pressed against the copper-plated tips by springs.

[21] These measurements were performed by M. H. Sirvetz and J. H. Saunders. They are described in Memo M-527, Research Division, Raytheon Company (unpublished).

[22] W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).

[23] W. Primak, Phys. Rev. **103**, 544 (1956).

[24] Also basal plane resistivity, because the flow direction along carbon-hexagon networks does not influence the conductivity.

[25] In this connection we should like to mention that some highly-oriented graphite crystal *compounds* have basal plane resistivities that are almost one order of magnitude lower than those of pure single crystals. [A. R. Ubbelohde, L. C. F. Blackman, and I. F. Mathews, Nature **183**, 454 (1959).]

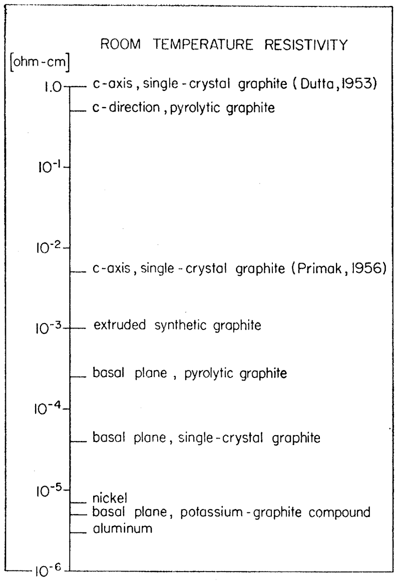

FIG. 4. Room-temperature resistivities measured on various graphitic structures. Highly-oriented potassium-graphite compounds exhibit basal plane conductivities that compare with the conductivity of nickel or aluminum (see reference 25).

tals without serious morphological defects had a maximum resistivity of about 5 mohm-cm. It must be said, however, that working with Ceylanese graphite crystals, Krishnan and Ganguli,[26] and more recently Dutta,[27] have measured c-axis resistivities ρ_c which are at least two orders of magnitude higher (see Fig. 4). We shall discuss how pyrolytic graphite behaves in this respect after a brief presentation of the basal plane results.

A. Basal Plane

The electrical resistivity of pyrolytic carbons, as measured at room temperature and along the deposit, exhibits a remarkable dependence on the temperature of deposition. Figure 5 shows that in this regard data taken on the specimens listed in Table I agree very well with results of Brown and Watt[3] for materials deposited from propane at $1600° \leq T_d \leq 2100°$C. The ±100°C uncertainty in the deposition temperature of our specimens is indicated by horizontal bars, whereas the vertical extent of each point does roughly correspond to the spread in the ρ_a values measured for different samples prepared from the same deposit. In view of the good reproducibility of these measurements, the variations must be attributed to inhomogeneities in the deposits, inhomogeneities which are presumably caused by temperature gradients especially during heat treatment. On the same figure we have also plotted the relative resistance (R/R_0) of a heat-treated soft carbon rod, as determined by Loebner[2] at an ambient temperature of 305°K, against the heat treatment temperature (T_{ht}). Here, R_0 represents the initial resistance of the carbon rod, that is, the resistance before heat treatment.

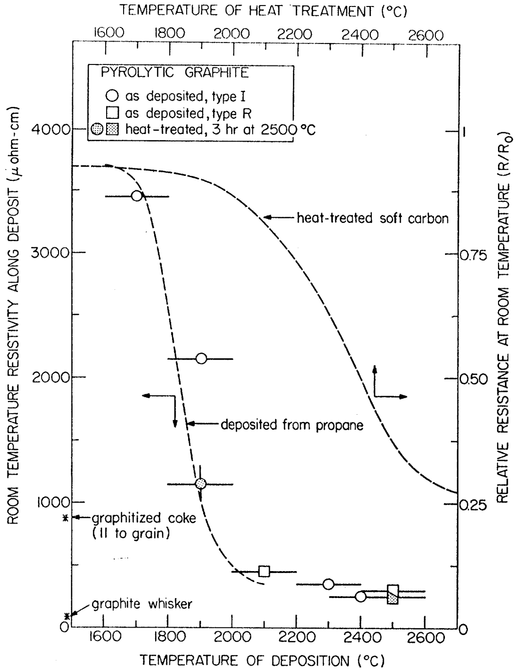

FIG. 5. Basal plane resistivity vs deposition temperature. The PG data are confronted with results reported for graphite filaments (reference 31), for synthetic graphites (as measured in the direction of extrusion), and for the resistivity variations of a soft carbon as a function of the heat-treatment temperature (reference cited in footnote 2). Note that the curve labeled "deposited from propane" is due to Brown and Watt (reference 3).

The two curves of Fig. 5 have essentially the same shape. They both seem to exhibit a low-temperature plateau which extends to a knee occurring at $T_{ht} \approx 1900$°C in commercial carbons, but occurring already at $T_d \approx 1700$°C in deposited materials. The significance of this shift will be made clear in Sec. VII. High deposition temperature PG has an appreciably lower resistivity than the commercial stocks, mainly because of the much enhanced degree of preferred orientation and the lack of macroporosity in a high-density deposit.[28] On the other hand, even at the highest deposition temperatures (2500°C) our specimens do not compare, in terms of basal plane resistivities, with natural graphite[22] or some of the whisker-like structures examined by various authors.[29–31] For instance, by maintaining a cellulose xanthogenate fiber at 2500°C in a hydrocarbon atmosphere and subsequently heating the

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[26] K. S. Krishnan and N. Ganguli, Nature **144**, 667 (1939).

[27] A. K. Dutta, Phys. Rev. **90**, 187 (1953).

[28] It is well known that the porosity of synthetic carbons and graphites affects their resistivity. Mrozowski has shown how to take this into account in order to arrive at "true" figures. [S. Mrozowski, Phys. Rev. **85**, 609 (1952); **86**, 1056 (1952).] With our specimens corrections of this nature can be ignored owing to the high densities of deposited carbons.

[29] M. Pirani and W. Fehse, Z. Electrochem. **29**, 168 (1929).

[30] J. C. Bowman, J. A. Krumhansl, and J. T. Meers, *Industrial Carbon and Graphite* (Society of Chemical Industry, London, 1958), p. 52.

[31] R. Bacon, J. Appl. Phys. **31**, 283 (1960).

deposited material up to 3000°C, Pirani and Fehse produced graphite filaments for which they quoted room-temperature resistivities as low as 47 μohm-cm.[29] The exact value depended on the heat treatment, the resistivity falling and the temperature coefficient becoming more metallic as T_{ht} was raised. Systematic investigations of the effects of a heat treatment on the electrical properties of PG have not yet been undertaken. On the basis of Fig. 5 it appears that after a prolonged exposure at 2500°C, the low-temperature specimens exhibit basal plane resistivities typical of fully graphitized coke-base material, whereas little seems to be gained in the case of high-temperature deposits.

B. *c* Direction

The room-temperature resistivity of deposited carbons, if measured across the thickness, increases with T_d from a few milliohm-centimeters to almost an ohm-centimeter (see Fig. 6). The variation parallels the resistivity decrease along the layer planes, though the dependence does not seem to be as orderly. Each "point" of Fig. 6 represents the average of data taken on four probes (disk- and bridge-shaped samples) cut out of a given deposit. In general, the spread in ρ_c values did not exceed the uncertainty of the measurement. At low deposition temperatures ($T_d \approx 1600°C$), our values[32] approach the figures quoted by Grisdale *et al.*[5] for pyrolytic carbon films deposited at less than 1300°C. At higher deposition temperatures the data are consistent with results of Brown and Watt for materials deposited from benzene.[3] They are also consistent with the indications of Ubbelohde *et al.*,[33] who report that the *c*-direction resistivity of their samples, prepared by cracking methane at an unspecified temperature, is about 0.5 ohm-cm.

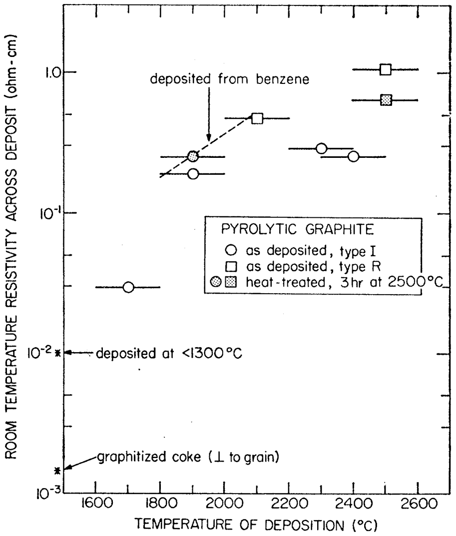

FIG. 6. *c*-Direction resistivity vs deposition temperature. The data taken on our PG specimens are confronted with results reported for synthetic graphites (as measured perpendicularly to the direction of extrusion), for low-temperature carbon deposits (reference 5), and for specimens prepared by Brown and Watt from benzene (reference 3).

Resistivity measurements across the thickness of heat-treated PG deserve special attention. In the case of specimen I-63 the *c*-direction resistivity rose after heat treatment, in contrast to the behavior of specimen R-7. In both cases the x-ray evidence points toward an improvement in preferred orientation, but whereas I-63 remained turbostratic, R-7 graphitized to some extent (see Table I). It appears that an improvement of the degree of preferred orientation is actually translated by an increase in the ρ_c value of randomly ordered structures, but more than compensated by the layer ordering and concurrent lattice-spacing reduction in the case of specimen R-7*. From an exceptionally high value of 1.1 ohm-cm as deposited, ρ_c decreases to 0.65 ohm-cm after a three-hour exposure at 2500°C.[34] The rather well-graphitized specimens prepared in the induction-heated furnace have a ρ_c of about 0.25 ohm-cm. To what extent this range of values around 0.5 ohm-cm is indicative of the intrinsic *c*-axis resistivity of single-crystal graphite, remains open to discussion, since it exceeds by two full orders of magnitude the presently accepted figure of Primak.[23] (See also Fig. 4.) Two comments are felt to be appropriate:

1. *Ubbelohde's measurements* were made on selected graphite deposits with basal plane resistivities as low as 47.5 μohm-cm and positive temperature coefficients, hence excellent specimens with essentially single-crystal characteristics in terms of ρ_a. Since this is obviously not the case with our samples, the close agreement between Ubbelohde's and our ρ_c values is indeed surprising. It might, therefore, be questioned whether PG deposits "permit definite inferences about the behavior of single crystals, and in particular about the anisotropy of the electronic properties along the *a* and *c* axis of graphite."[33]

2. *A nonuniform current flow* induced by microcracks might possibly account for the "anomalous" *c*-direction resistivity of PG, and one might wonder if microwave measurements would support such an interpretation. This is not so. More specifically, it has been found[21] that for a specimen similar to R-40 with a dc resistivity of 0.51 ohm-cm across the deposit, ρ_c at 3.8 kMc/s should be only slightly smaller than 0.57 ohm-cm. Even at higher frequencies there is no evidence of any significant capacitive shorting,[35] in other words, the *c*-direction resistivity of pyrolytic graphite remains essentially constant over the whole frequency spectrum.

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[32] In this respect our data differ from those of Brown and Watt (reference 3), who report a much higher *c*-direction resistivity (0.27 ohm-cm) for 1600°C deposits.

[33] See the reference cited in footnote 25.

[34] Note that as a result of radiation-induced disorder, the *c*-axis conductivity of single-crystal graphite decreases by a factor of about 2 or 3. [W. Primak and L. H. Fuchs, Phys. Rev. **103**, 541 (1956).]

[35] S. R. Steele (private communication).

C. Anisotropy vs Deposition Temperature

Resistivity measurements along and across PG layer planes reveal the enormous electrical anisotropy of deposited carbons. At room temperature, materials prepared at 2500°C in our resistance-heated furnace have ρ_c/ρ_a ratios of the order of 3×10^3 or more. A significant anisotropy was certainly to be expected considering the structure of these materials, but perhaps not on that scale.[36] Right now, it does not seem profitable to further comment on this, beyond saying that ρ_c/ρ_a experiences a sharp drop with T_d in correspondence with the degree of preferred orientation, as can be seen in Fig. 7. Quantitative correlations between *electrical anisotropy* and *degree of preferred orientation* require not only a knowledge of $n_{\max}/n_{\min}$ but also the detailed shape of the (002) intensity distribution function. Such correlations will be attempted in a forthcoming publication.[37]

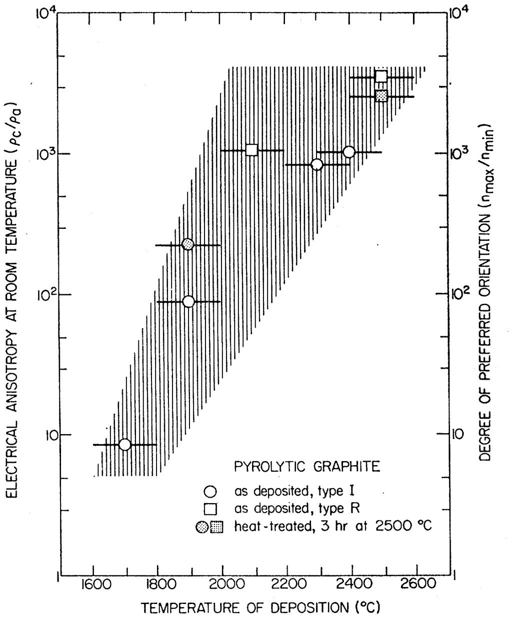

Fig. 7. Electrical anisotropy vs deposition temperature. The shaded area covers roughly the range of degrees of preferred orientation indicated by x-ray diffraction studies.

V. RESISTIVITY TEMPERATURE DEPENDENCE

Room-temperature resistivities of carbons and graphites are easy to measure and are often used to monitor the "quality" of these materials. In the framework of an investigation of electrical transport properties, we expect that even more valuable information will be gained from the temperature dependence. Apparently, the resistivity temperature dependence tends to be insensitive to macroscopic factors such as porosity or preferred orientation and is mainly conditioned by the crystalline perfection of the material.[38] (The low-temperature behavior of PG provides a striking illustration of this state of affairs, as we shall see in discussing the data of Fig. 9) This is most conveniently shown by first considering Fig. 8, which exhibits low-temperature resistivity characteristics for several representative graphitic species, and, by the same token, conveys a general impression about the temperature dependence as a crystal perfection test in these materials.

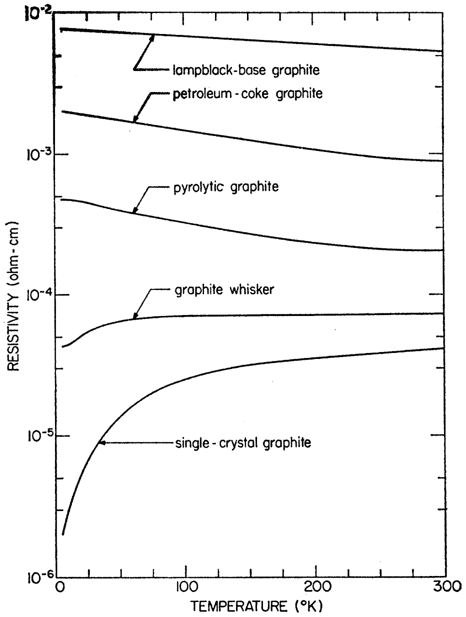

Fig. 8. Basal plane resistivity of various graphitic structures as a function of the ambient temperature. References to the original data are given in Sec. V.

The basal plane resistivity of single-crystal graphite has been measured as a function of temperature by Kinchin,[39] by Primak and Fuchs,[22] and more recently by Soule.[1] They all report positive temperature coefficients with typical $\rho_a(273°\mathrm{K})/\rho_a(4.2°\mathrm{K})$ values of 15. Below room temperature the common synthetic materials have negative temperature coefficients; polycrystalline graphite with crystallites of the order of a few tenths of a micron[40] or less, exhibits a monotonic increase in resistivity as the temperature is lowered to the liquid helium range (see Fig. 8). The relatively high conductivity of pyrolytic graphites and graphite whiskers is a direct consequence of the crystallites' alignment, as we have seen in the previous section. Along their axis, graphite whiskers[41] and carbon filaments[30] behave much like single crystals. On the basis of

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[36] According to Primak and Fuchs, perfect single crystals of graphite have a ρ_c/ρ_a ratio of 140. In damaged structures the anisotropy seems to decrease, since it is only of the order of twenty in heavily bombarded samples (reference cited in footnote 34).

[37] O. J. Guentert and C. A. Klein (to be published).

[38] I. B. Mason, *Industrial Carbon and Graphite* (Society of Chemical Industry, London, 1958), p. 60.

[39] G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, 9 (1953).

[40] Average crystallite size of a petroleum-coke base stock commercially graphitized at more than 2800°C.

[41] See reference 31. Note that Fig. 1 has been incorrectly drawn.

specific heat and thermal conductivity measurements it is estimated that these structures are made up of crystallites whose average L_a exceeds one micron. With crystallites of that size, electron-phonon scattering becomes the determining factor insofar as electrical resistivities are concerned and this leads to positive temperature coefficients. In the case of massive PG deposits the slope reverses sign presumably because of the much smaller crystallites (see Sec. VIII B).

The exact shape of the basal plane resistivity temperature dependence of some of the specimens listed in Table I is detailed in Fig. 9 (low temperatures) and Fig. 10 (high temperatures). Precisely how the temperature dependence arises in polycrystalline carbons and graphites is not yet well understood. A theoretical discussion or our data might therefore best be undertaken by first investigating more basic elements such as carrier concentrations and mobilities and therefore will be deferred to Sec. VIII.

A. Low Temperatures

It is well known that the electrical conductivity of carbons and graphites has a temperature dependence that is quite sensitive to such parameters as the position of the Fermi level or the mean free path of the carriers. In the case of pyrolytic graphite, we thus anticipate significant variations in the temperature dependence with the state of crystalline perfection, that is with deposition temperature and heat treatment. This is borne out in Fig. 9. where we have plotted the relative resistance (R/R_0) of PG specimens at low temperatures in confrontation with fully and partially graphitized common synthetic products. Here, R_0 is the resistance of each sample at 300°K.

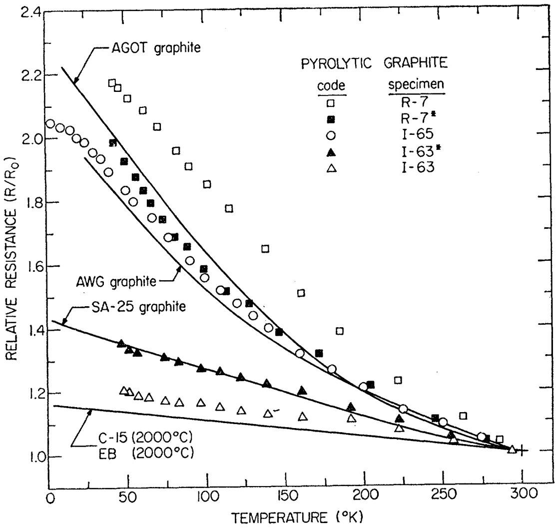

FIG. 9. Temperature dependence below 300°K of the basal plane resistivity of representative PG specimens. The curves labeled AGOT, AWG, and SA-25 graphite were derived from measurements reported in reference 42. After heat treatment at 2000°C, coke-base (C-15) and lampblack-base (EB) stocks exhibit identical temperature-dependence characteristics (reference 30).

In polycrystalline graphite, the resistivity variations with temperature result primarily from carrier-density variations. We shall substantiate this statement later on (Sec. VIII A). Changes in the *magnitude* of the temperature dependence, which is obviously associated with the degree of graphitization (see Fig. 9), are believed to be caused by a shift of the Fermi level away from the valence-band edge. Supporting evidence has been provided by the effects of a neutron bombardment on synthetic graphites,[42] and also by Hennig's studies of brominated materials.[43] However, we notice that:

1. Specimen R-7 does not fit into the temperature-dependence pattern supplied by standard synthetic graphites. This is not completely unexpected considering the unique structural characteristics of the deposit, namely excellent preferred orientation in combination with a conspicuous lack of three-dimensional order. Yet, after heat treatment and concurrent graphitization the temperature dependence is much like that of good commercial petroleum-coke base stocks, for instance the type AGOT-KC or the type AWG.[44]

2. Specimen I-65, a well-oriented and well-ordered pyrolytic deposit, behaves strictly in accordance with fully-graphitized synthetic materials, in spite of their much lower conductivities. Incidentally, this agreement justifies the usual assumption that the electrical conductivity of synthetic graphites must be determined by basal plane processes and that the temperature dependence of the basal plane conductivity is a matter of crystallite size and layer order, rather than preferred orientation. We also note that in the liquid-helium temperature range the resistance of specimen I-65 remains virtually constant, as reported by Reynolds *et al.* for a common polycrystalline graphite.[45]

3. Specimen I-63 as deposited ($T_d \approx 1900°C$), exhibits low-temperature characteristics reminiscent of carbons that have been heat treated[30] somewhat above 2000°C. This is in line with the 200°C shift already noted in Sec. IV A. Significantly, after heat treatment at 2500°C, this and similar specimens behave strictly like a molded pitch-bonded lampblack baked at 2800°C (type SA-25).[46] In accordance with the x-ray indications of Table I, we conclude that our low-temperature PG deposits do not graphitize in the proper sense of the word, though they possess relatively high conductivities after heat treatment. Why these deposits have carbon-black features is

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[42] A. W. Smith and N. S. Rasor, Phys. Rev. **104**, 885 (1956).

[43] G. R. Hennig, J. Chem. Phys. **19**, 922 (1951); **20**, 1438, 1443 (1952).

[44] Type AGOT-KC is an extruded coke graphite with a density of 1.65 g/cm^3, an estimated particle size of 50 μ, and a crystallite size of 0.3 μ or greater. Type AWG is a molded coke graphite with a density of 1.75 g/cm^3, a particle size of 25 μ, and a crystallite size of 0.2 μ or greater.

[45] J. M. Reynolds, H. W. Hemstreet, and T. E. Leinhardt, Phys. Rev. **91**, 1152 (1953).

[46] Type SA-25 has a density of 1.55 g/cm^3, a particle size of the order of 0.3 μ, and a crystallite size of about 0.05 μ.

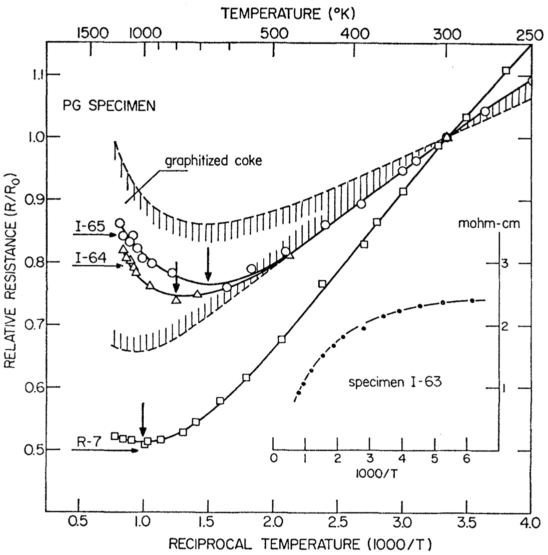

FIG. 10. Temperature dependence above 300°K of the basal plane resistivity of as-deposited PG specimens. The resistivity minima are marked by heavy arrows and occur at similar temperatures as in well-graphitized synthetic materials (reference 39).

strictly speaking beyond the scope of this paper, but will be touched upon in the conclusion.

B. High Temperatures

Under this subheading we shall report on an attempt made to measure the basal plane resistivity of PG at temperatures well above 300°K. Figure 10 shows some of our data plotted in terms of relative resistances, R/R_0, against the reciprocal ambient temperature, or rather $1000/T$ in $(°\mathrm{K})^{-1}$. For reasons mentioned in Sec. III, most of the data taken on heat-treated samples were not well reproducible; they have been left out of Fig. 10.

It has been known that the resistivity temperature coefficient of polycrystalline graphite changes sign and becomes positive under the influence of enhanced thermal lattice scattering at high temperatures.[47] The hachures of Fig. 10 give an idea of the type of variations reported for coke-base stocks[39] graphitized at temperatures between 2300° and 2600°C. The PG specimens I-65 and I-64 exhibit similar variations; they both go through a resistivity minimum at about 650° and 800°K, respectively. It is gratifying to note that, on a partially ordered deposit, Brown *et al.*[7] have measured resistances which amounted to 87% of the room-temperature value at 100°C and to 79% at 200°C. These two figures agree quite well with the data that we have collected on similar deposits (I-64). This is not so with the resistance-grown specimen R-7, whose steep negative slope prolongates an odd low-temperature behavior. A resistivity minimum, nevertheless, occurs at around 1000°K and is plainly visible in Fig. 10. In contrast to these high-temperature deposits, the resistivity of I-63 decreases monotonically with increasing temperature without showing any evidence of a "bottom" below 1500°K. Since we know already that I-63 behaves in many respects like a carbon black, the failure to observe a minimum actually substantiates Shepard and Dexter's results for lampblack-base stocks.[48]

Anticipating the discussion in Sec. VIII, we should like to emphasize that the main incentive hehind these high-temperature measurements lies in the fact that the minimum's position on the temperature scale permits, in principle, an independent appraisal of the average basal plane diameter of graphite crystallites.[38] A shift of the resistivity bottom toward higher temperatures, for example, implies smaller crystallites. This is indeed what can be inferred from examining Fig. 10 in the light of the L_a column of Table I.

C. Anisotropy vs Ambient Temperature

In addition to basal plane work, we have also carried out some resistivity temperature dependence experiments in the c direction. More work of this nature is still in progress.[49] Figure 11 shows data taken on a standard PG deposit, namely on a specimen deposited from methane heated at 2100°C in a resistance-type furnace. We note the following "c axis" features: (a) a finite resistance at the lowest temperatures; (b) a constant or slightly falling resistance up to about 100°K; (c) a more steeply falling resistance finally turning into a $\log(1/T)$ dependence above room temperature. The basal plane resistivity, on the contrary, goes through a broad minimum followed by the usual linear rise above 1000°K. Owing to these contrasting characteristics, the electrical anisotropy (ρ_c/ρ_a) drops

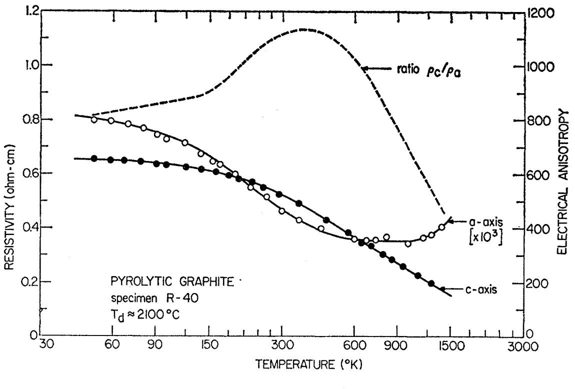

FIG. 11. Basal-plane resistivity, c-direction resistivity, and electrical anisotropy of specimen R-40 as a function of the ambient temperature. The basal plane resistivity has been multiplied by a thousand in order to allow a confrontation.

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[47] See, for instance, the reference cited in footnote 28.

[48] See Fig. 8 in L. Currie, V. Hamister, and A. McPherson, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, August, 1955* (Columbia University Press, New York, 1956), Vol. 8, p. 451.

[49] C. A. Klein and W. D. Straub (to be published).

from a maximum value of 1150 slightly above room temperature to less than 400 at 1500°K, and this trend seems to be maintained at even higher temperatures.

Resistivity vs temperature characteristics of graphitic materials have been published by many authors,[50] but a full account similar to the one presented in Fig. 11 has never been given before. Obviously, any theory that claims to describe the experimental situation in carbons and graphites ought to explain the main features of a "transitional" product such as specimen R-40. Some of the features, especially the temperature dependence of the c-direction resistivity at low temperatures, resemble those of neutron-irradiated natural graphite.[51] In consequence, it seems reasonable to attribute the magnitude of the c-direction resistivity of pyrolytic graphites to the presence of a large number of scattering centers, stacking faults for instance,[52] which alter the flow conditions perpendicularly to the basal planes. In this connection it should be pointed out that Ubbelohde's PG samples also had a negative temperature coefficient in the c-axis direction.[33] To what extent this is compatible with the alleged absence of serious crystal defects remains debatable (see Sec. IV B).

VI. GALVANOMAGNETIC EFFECTS

The galvanomagnetic properties of graphitized materials have been investiaged since the beginning of this century.[53] In recent years, extensive studies were made by Kinchin,[39] who measured the Hall coefficient of well-graphitized specimens at various temperatures, and by Mrozowski and his associates, who have investigated the effects of a heat treatment on the Hall coefficient and the magnetoresistance of soft carbons[54] as well as carbon blacks.[55] Insofar as graphite single crystals are concerned, the magnetic field dependence of galvanomagnetic effects revealed a great deal of information on basal plane processes.[56] Most interesting are the strong Hall-coëfficient (R_H) variations, including changes in sign, that have been observed in all these experiments. They must be attributed to the close balance of electron-hole concentrations and mobilities; these circumstances give rise to a small R_H which is very sensitive to the Fermi level behavior. Magnetoresistance measurements revealed extremely high mobilities in the basal planes of graphite single crystals. In polycrystalline material they revealed a remarkable dependence on history and geometry. Because of the crystallites' anisotropy, the transport properties of polycrystalline graphite must depend upon the crystallites' alignment. Hence, we have some reason to believe that an investigation of galvanomagnetic effects in PG specimens with widely differing degrees of preferred orientation will prove worthwhile.

All our measurements were made with the magnetic field parallel to the c direction, as explained in Sec. III. At room temperature, the Hall voltage varies linearly with field strength, within experimental uncertainty.[57] The Hall coefficients of Fig. 12 were therefore taken as an average of readings made at various intensities ranging from 1 to 25 kgauss. Concurrently, we performed magnetoresistance measurements on all our samples (Fig. 13). These measurements were quite reproducible, even in the case of low-temperature deposits where the magnetoresistance is very small and in some cases negative. Since there is little information available as to the temperature dependence of the Hall and magnetoresistivity effects in carbons and graphites, their study via PG should help to shed light on the nature of electronic processes in graphitic materials. Some of the data obtained with a transverse magnetic field of 2500 gauss are shown in Figs. 14 and 15. The results of a more detailed investigation will be presented in a later publication.

A. Hall Coefficient

The room-temperature Hall coefficients of the 9 PG specimens listed in Table I are plotted in Fig. 12 as a function of the deposition temperature. They were evaluated according to Eq. (4) with Hall voltages taken as mentioned before. Circles and squares give an idea of the reproducibility of results obtained with several bridges cut out of the same deposit. In one case (specimen R-7), there was a considerable scatter from sample to sample owing to nonuniformities in the structure of the original deposit.

Pyrolytic carbons prepared at less than 2100°C appear to always exhibit positive Hall coefficients regardless of the heat treatment, if T_{ht} does not exceed 2500°C. At higher deposition temperatures, on the contrary, we have both positive and negative Hall coefficients. However, if we consider the graphitization indices γ (see Fig. 12), it becomes clear that the Hall response of "disordered" material ($\gamma \leqslant 0.5$) remains systematically positive, whereas "graphitized" specimens ($\gamma > 0.5$) turn out to be n type with a small Hall coefficient typical of natural graphite[58] ($R_H \approx -0.05$ cm^3/coul). We also note the p- to n-type transformation which accompanies the heat treatment of R-7. The transformation must be related to the concurrent graphitization process characterized by a γ-index increase from 0.14 to 0.79 and the emergence of (hkl) reflections. We know already

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[50] Among others, Powell and Schofield (reference 19), Kinchin (reference 39), W. W. Tyler and A. C. Wilson [Phys. Rev. **89**, 870 (1953)].

[51] See Fig. 3 of the reference cited in footnote 34.

[52] G. R. Hennig (private communication).

[53] For references to the early work, see S. Mrozowski and A. Chaberski, Phys. Rev. **104**, 74 (1956).

[54] See the reference cited in footnote 53.

[55] S. Mrozowski, A. Chamberski, E. E. Loebner, and H. T. Pinnick, *Proceedings of the Third Conference on Carbon, Buffalo, New York, June 1957* (Pergamon Press, New York, 1959), p. 211.

[56] See the reference cited in footnote 1.

[57] In agreement with observations of Mrozowski and Chaberski on heat-treated carbons, for $H \leqslant 10.5$ kgauss. At higher field strengths, however, there are indications of a slight Hall-coefficient increase, but we did not detect any systematic trend.

[58] n-type pyrolytic graphite always exhibits (hkl) reflections; this has never been the case with p-type material.

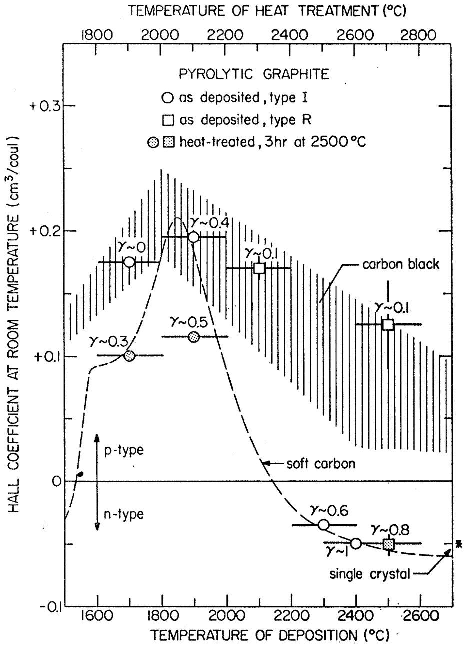

FIG. 12. Hall coefficient vs deposition temperature in the geometry of Fig. 3(a). The index γ characterizes the degree of graphitization according to Eq. (2). The dashed curve reproduces the heat-treatment temperature dependence of the Hall coefficient of a soft carbon (reference cited in footnote 53); the shaded zone reflects data reported for various carbon blacks (reference 60).

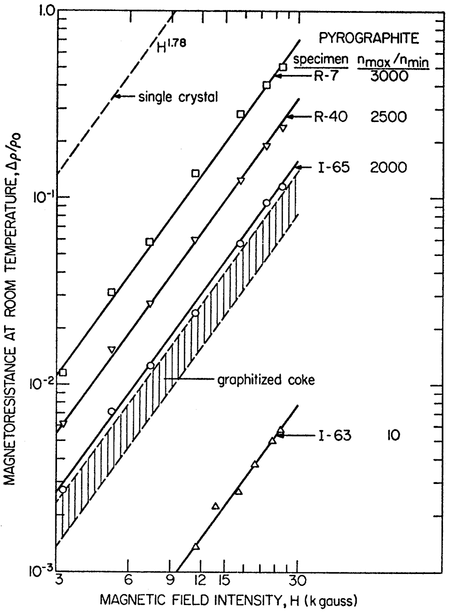

FIG. 13. Basal plane magnetoresistance of as-deposited PG specimens at high magnetic field strengths. The field dependence follows the $H^{1.78}$ law of single crystals (reference cited in footnote 1), the magnitude of $\Delta\rho/\rho_0$ is seen to be quite sensitive to the degree of preferred orientation $n_{\max}/n_{\min}$.

that low-temperature deposits such as I-62 or I-63 do not graphitize as easily. A trend toward the n side has nevertheless been observed after heat treatment at 2500°C, in accordance with the slight interlayer-spacing reduction.

If we attach significance to the absolute values of our Hall coefficients, it appears that the largest of the measured values ($R_H = 0.20$ cm³/coul for I-63) is almost identical to Mrozowski and Chaberski's Hall coefficient maximum at room temperature.[54] The maximum occurs at a heat-treatment temperature $T_{ht} \approx 2100$°C, whereas I-63 was deposited at $T_d \approx 1900$°C. In two previous instances we noticed a similar 200°C shift in the behavior of heat-treated carbons as compared to deposited carbons. This suggests a plotting of Mrozowski and Chaberski's Hall data in confrontation with PG, but in such a way that their *temperature of heat treatment* corresponds to our *temperature of deposition* plus 200°C. We can see in Fig. 12 that the procedure leads to an excellent agreement between heat-treatment dependence of soft carbons and deposition-temperature dependence of induction-grown PG.[59] This is not the case with deposits that were prepared in the resistance-heated furnace, presumably because of the lack of layer order. Supporting evidence is provided by data recently taken on carbon blacks.[55,60] The shaded zone in Fig. 12, for instance, corresponds to the Hall coefficient vs heat-treatment temperature "area" covered by Hauser's measurements on products characterized by turbostratic structures even after heat treatment at 3000°C. Carbon blacks remain always p type and exhibit Hall-coefficient maxima in a heat-treatment temperature range that correxponds to PG deposition temperatures of about 1800°C. A tentative interpretation will be given in the next section. It is already clear that, in a "natural" geometry, the Hall coefficient of a PG specimen reflects the morphological perfection of the deposit strictly in terms of crystallite size and rotational order.

B. Magnetoresistance

At high field strengths ($H > 3$ kgauss), room-temperature measurements of the transverse magnetoresistance, $\Delta\rho/\rho_0$, yielded the data of Fig. 13. They have been plotted against the magnetic field intensity, on a log-log scale, in confrontation with Soule's data for a graphite single crystal (EP-14)[56] and Hauser's indications for graphitized petroleum-coke based stocks.[60] In the high-field region, single-crystal as well as polycrystalline graphite exhibit a magnetoresistance field dependence which obeys the empirical relation

$$\Delta\rho/\rho_0 = kH^{(1.78\pm0.03)}, \tag{5}$$

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[59] If it is true that "the electronic properties of carbons are actually mainly a function of the crystallite size" (reference cited in footnote 53), the correspondence between T_{ht} and $T_d + 200$°C may be understood by comparing the crystallite diameters given on top of Mrozowski and Chaberski's Fig. 2 with the L_a column of Table I. In soft as well as pyrolytic carbons the Hall-coefficient maximum develops with crystallite sizes of about 100 A.

[60] O. Hauser, Z. physik, Chem. **210**, 151 (1959).

where k is a parameter sensitive to the ambient temperature and the crystalline structure.[61] The behavior of pyrolytic graphites appears to be in substantial agreement with Eq. (5), regardless of the deposition temperature. At lower field strengths, however, the field-dependence factor has an exponent that is close to two (Fig. 17). There we have plotted $\Delta\rho/(\rho_0 H^2)$ vs H in order to emphasize the conversion to a quadratic dependence previously noted by Soule in working with single crystals.[56]

In well-oriented PG specimens such as I-65, R-40, or R-7, the room-temperature magnetoresistance becomes quite large and may exceed 50% at 25 kgauss. This is appreciably more than what has been reported for the usual synthetic graphites, but still a whole order of magnitude below single-crystal magnetoresistances. In a sense, Fig. 13 provides a striking illustration of the transitional nature of pyrolytic graphites; this is especially true in the light of the close correlation between $\Delta\rho/\rho_0$ and $n_{\max}/n_{\min}$, the magnetoresistance of as-deposited materials increasing tremendously with the degree of preferred orientation. Of course, it must be kept in mind that we cannot have a one-to-one correspondence between $\Delta\rho/\rho_0$ and $n_{\max}/n_{\min}$. In essence, Fig. 13 demonstrates the great sensitivity of the magnetoresistance to the relative alignment of the crystallites, in other words, demonstrates the influence of "geometrical" factors on the transport mechanism in a graphitic system. If we recall that, with $\mathbf{H}$ perpendicular to the c direction, the magnetoresistance is too small for a study in the range of commonly available field strengths,[18] these observations are consistent with the anisotropy of the zero-field electrical resistivities. As mentioned before, the anisotropy must be attributed to the layer-type structure of graphite. We shall see later (Sec. VII) how the magnetoresistivity associated with current carriers travelling along the layers is actually related to their mobilities in these layers.

On low-temperature deposits, reliable room-temperature magnetoresistance measurements can only be performed in the high-field region. (Specimen I-62, for example, has a $|\Delta\rho/\rho_0|$ of less than 10^{-4} at 7 kgauss.) These measurements are nevertheless of interest, because they reveal *negative magnetoresistances* whose field dependence obeys a quadratic law.[49] This surprising result was actually not quite unexpected, since Mrozowski *et al.* have also reported negative magnetoresistances, namely for carbons heat treated in the temperature range where the Hall coefficient reaches its positive maximum.[54,55] We have a very similar situation in PG, the deposition temperature playing the role of the heat-treatment temperature. Once again we note the close correlation between deposited and heat-treated carbons in that critical temperature range from 1700° to 1900°C on the T_d scale and from 1900° to 2100°C on the T_{ht} scale. Roughly speaking, it seems that insofar as band structure and transport are concerned, the pyrolytic introduction of preferred orientation produces changes equivalent to a 200°C heat-treatment temperature rise.

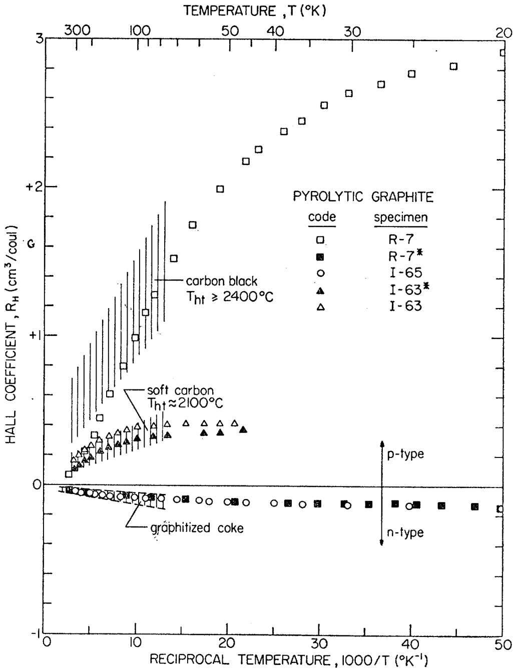

FIG. 14. Temperature dependence of the Hall coefficient of representative PG specimens. The data are confronted with indications reported for graphitized materials (reference 39), for carbons heat-treated at approximately 2100°C (reference cited in footnote 53), and for highly heat-treated carbon blacks (reference 55).

C. Temperature Dependence

Figure 14 shows how the Hall coefficient of various PG specimens[62] behaves as a function of the ambient temperature. This behavior is extremely sensitive to deposition process and heat-treatment variables; much more than the room-temperature Hall coefficient. It follows that the temperature dependence of R_H provides a most responsive means of probing the crystalline perfection (not the preferred orientation!) of carbon deposits. In this context, it should be of interest to compare the indications of Fig. 14 with some of the comments of Sec. V A concerning low-temperature resistivity data, especially since carrier-density variations are presumed to condition the resistivity temperature dependence of polycrystalline graphites.

1. *Specimen R-7*, a p-type semiconductor below room temperature, exhibits a strongly temperature-dependent Hall coefficient vaguely resembling that of a P-33 carbon

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[61] The field dependence has also been investigated, with similar conclusions, by Kinchin (reference 39), by Mrozowski and Chaberski (reference cited in footnote 53), and by J. D. McClelland [Phys. Rev. **100**, 1807 (1955)].

[62] The reader will note that these specimens are the same as those considered in Fig. 9 apropos of low-temperature resistivity studies.

black heat-treated above 2400°C.[55,63] This strong temperature dependence appears to be responsible for the "odd" resistivity characteristics of R-7. We have seen that these characteristics become "normal" after heat treating the deposit for 3 hr at 2500°C. In fact, the Hall coefficient then behaves just about exactly as in highly graphitized stocks (see Fig. 14).

2. *Specimen I-65* behaves as expected of *n*-type polycrystalline graphite, but rather in agreement with Kinchin[39] than with Mrozowski and Chaberski,[54] since graphitized PG specimens show some temperature dependence in the Hall coefficient.

3. *Specimen I-63* and its annealed twin are both confronted, in Fig. 14, with a soft carbon that has been heat treated in the 2000° to 2200°C range.[54,63] We note the strikingly similar characteristics: they substantiate our previous assertions concerning this deposit.

In Fig. 15, the transverse magnetoresistance of R-7 and R-7* measured at 2500 gauss is plotted against the reciprocal temperature. As deposited, this specimen has a positive $\Delta\rho/\rho_0$ above 90°K and a negative $\Delta\rho/\rho_0$ at lower temperatures. After heat treatment $\Delta\rho/\rho_0$ remains positive throughout the temperature range, increasing to about 1% below 50°K. This trend is typical of good polycrystalline graphite, as evidenced by Kinchin's measurements at a similar field strength.[39,64] The transition from a positive to a negative magnetoresistance, which is observed in *p*-type PG, ought to be examined in detail; it seems unlikely, however, that a full explanation can be given at present.

VII. BAND MODEL, CARRIER CONCENTRATION, AND MOBILITY

Energy-band calculations have been quite successful in describing and correlating many of the electrical properties of single-crystal graphite. A straightforward approach is to neglect the weak interlayer interaction and to consider the two-dimensional case of an infinite hexagonal array of carbon atoms. On this basis Wallace concluded that, insofar as transport is concerned, attention need only be given to the loosely bound π electrons and their band system.[65] This system appears to be populated in such a way that the lower π band (or valence band) is nearly filled and the upper π band (or conduction band) nearly empty. The Hall-coefficient behavior, for instance, must be due to the simultaneous presence of free electrons and holes; and cyclotron-resonance experiments suggest that they have approximately equal concentrations.[66] Three-dimensional models substantiate these experimental findings, inasmuch as they indicate that the bands overlap by about about 0.03 ev at the Brillouin-zone corners. By the same token, the calculations show that the amount of overlapping depends on the layer-stacking scheme or degree of layer order.[11] The overlap concept, therefore, does not necessarily apply to turbostratic graphites. We shall see that there are reasons for believing that an energy gap may actually develop between the two π bands of poorly-graphitized carbon crystallites.

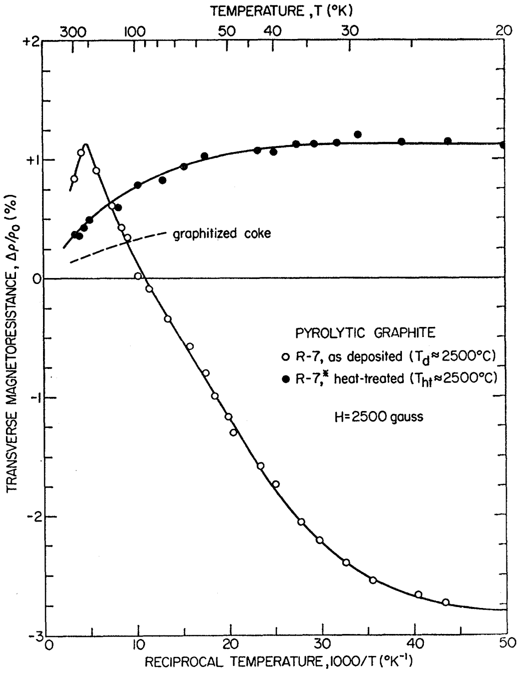

FIG. 15. Temperature dependence of the 2500-gauss magnetoresistance of a resistance-furnace deposit before and after heat treatment. The dashed curve is based on Kinchin's measurements at 2140 gauss on extruded graphite (reference 39).

Several years ago, Mrozowski proposed to interpret the electrical transport processes in molecular solids of the carbon-graphite variety by assuming that the current which flows along aromatic planes is made up of "intrinsic" as well as "excess" carriers.[47] By intrinsic we mean the upper energy-band π electrons and the holes that are left behind in the lower π band. Supposedly, there is an energy gap between the two bands, a gap which is large for small aromatic systems, but which gradually decreases as the size of the molecular planes increases. The gap finally disappears, or may even end in a band overlap, when the crystallite size becomes of the order of 1000 A. The excess carriers are holes that come into being as a result of the presence of π-electron trapping states. In Mrozowski's model these states are identified with the σ orbitals of free unengaged carbon valencies on the periphery of condensed benzene rings. If electrons are trapped out of the valence band, the Fermi level will be depressed. This allows a positive hole conduction mechanism even at the lowest tempera-

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[63] Mrozowski's measurements were made as a function of heat treatment, at two ambient temperatures only (300° and 77°K). A comparison with our data may help to reveal common trends but not to correlate the results on a quantitative basis.

[64] The preferred orientation accounts for the enhanced magnitude of the magnetoresistance in pyrolytic graphite (see subsection B).

[65] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[66] J. K. Galt, W. A. Yager, and H. W. Dail, Jr., Phys. Rev. **103**, 1586 (1956).

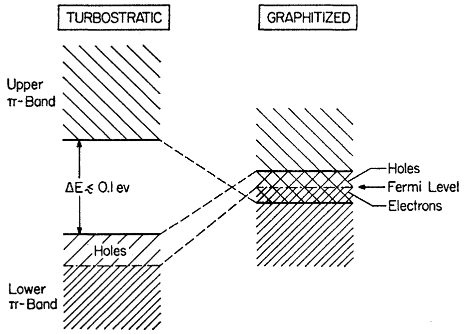

FIG. 16. Schematic energy-band diagram for turbostratic and graphitized carbons.

tures.[67] Since a depression of the Fermi level is also required to explain the variations of the Hall coefficient, we shall attempt to interpret the PG data according to the energy-band model displayed in Fig. 16. The figure exhibits a schematic one-dimensional diagram showing the band gap, the band overlap, and the approximate position of the Fermi level in poorly- and highly-graphitized carbons.

A. *p*-Type Materials

Basal plane conductivities, Hall coefficients, and magnetoresistances, especially the variations as a function of deposition temperature, can be qualitatively understood in a framework delineated by the preceding considerations. More specifically,

1. *The room-temperature resistivities* shown in Fig. 5 exhibit a resistance plateau for $T_d \lesssim 1700$°C (pyrolytic graphite) and $T_{ht} \lesssim 1900$°C (soft carbon). This plateau may well be due to the compensating effects of a decreasing number of excess carriers and of a reduced amount of boundary scattering, both induced by the growth of the crystallites. The subsequent knee, and the sharp decrease in resistance with increasing deposition or heat-treatment temperature, results from the addition of intrinsic carriers, of thermally activated electrons in particular.[68] Following Mrozowski's model, it appears that in the transition region ($1700° \leqslant T_d \leqslant 2100$°C) the energy difference between the bottom of the conduction band and the Fermi level steadily decreases (see Fig. 16), becoming ultimately of the order of kT or less and thus allowing a considerable number of electrons to be lifted into the upper π band. If this is correct, the fact that the transition to a two-carrier conduction proceeds at an accelerated pace on the T_d scale confirms that the vapor-phase deposition process enhances the growth of the crystallites.

2. *The Hall coefficients* shown in Fig. 12 go through a positive maximum in the deposition-temperature range that corresponds to the transition region in terms of resistivities. As the Fermi level gradually rises with increasing deposition temperature, the negative contribution of activated electrons with a higher mobility than the holes will outweigh the positive contribution resulting from a decreasing number of excess holes. The Hall-coefficient maximum has to occur in that particular configuration where a balance is actually reached. At room temperature this seems to be the case in pyrolytic materials deposited at about 1900°C, while the usual carbons must be heat treated above 2000°C. The shift is significant and supports our interpretation of the ρ_a vs T_d behavior. At this point, we may also try to answer why PG specimens, as deposited in the resistance-heated furnace, exhibit *p*-type characteristics even with crystallites of more than 300 A diameter which should normally lead to negative Hall coefficients.[69] It is well established that neutron-irradiated graphite converts from *n*- to *p*-type.[70] Concurrently one observes a progressive disappearance of the (*hkl*) reflections[71]; in other words, the Hall-coefficient conversion is associated with an "order-disorder" type of transformation. Since radiation-induced defects in graphite act as electron traps,[72] and since the heat treatment of a PG specimen such as R-7 induces structural and physical modifications expected from a radiation-damage annealing experiment, it may be assumed that the positive Hall coefficient of resistance-grown material is due to an accumulation of vacancies, which upsets the intrinsic electron-hole balance to the benefit of excess holes. Recalling what has been said in footnote 15, we have reasons to believe that these vacancies are actually "quenched-in" during deposition, and that the "frozen-in" interstitials impair the rotational ordering process.

3. *The negative magnetoresistances* of poorly-graphitized carbons have been tentatively interpreted by assuming that they are, in some way, associated with the positive current carriers.[54] If there are enough electrons in the conduction band (at room temperature this seems to be the case in pyrolytic carbons deposited at $T_d \gtrsim 1800$°C) a positive electron-induced magnetoresistance appears, which overbalances the effects of intrinsic and excess holes. Whatever its true merits are, the picture applies rather well to the observations reported in Fig. 15. As the temperature is lowered and the π electrons are deactivated, we observe a steady reduction and even a change in sign of the magnetoresistance as measured on a *p*-type specimen.

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[67] Crystallite growth tends to decrease the relative number of peripheral traps; a depletion in the concentration of excess carriers results. In consequence, we expect the Fermi level of transitional carbons to gradually rise toward the top of the lower π band throughout the structural range from amorphous carbons to polycrystalline graphites.

[68] See the reference cited in footnote 2.

[69] See Fig. 2 of the reference cited in footnote 53.

[70] G. H. Kinchin, J. Nuclear Energy **1**, 124 (1954).

[71] G. E. Bacon and B. E. Warren, Acta Cryst. **9**, 1029 (1956).

[72] When a carbon atom is knocked out of a well-developed hexagonal array, three valencies become available. Presumably, one or two free electrons can be trapped by the vacancy (see the reference cited in footnote 53). Taking into account the π-electron state of the missing atom, it appears that an average of between two and three excess holes will be generated by each vacant carbon site.

B. *n*-Type Materials

The purpose of subsection A has been to give a broad explanation of some of the electrical features of pyrolytic carbons, in particular of the deposition-temperature dependence. Quantitative treatments cannot be of much significance until the nature of electronic processes in *carbons* is better understood. If we confine our attention to *graphites*, however, an analysis may be undertaken on much safer grounds. At room temperature, for instance, the Hall coefficient of well-graphitized PG specimens reminds us of perfect single crystals; it is slightly negative and in harmony with predictions made from a two-band model. Furthermore, it appears that the magnetic field dependence of R_H, as illustrated in Fig. 17, is in substantial agreement with Soule's observations on crystal *EP*-14 for $H>1$ kgauss.[56,73] The single-crystal data can be fitted using a procedure in which Hall coefficient and magnetoresistance are both expressed in terms of appropriate components of the magnetoconductivity tensor.[74] Assuming that polycrystalline graphites obey the same theoretical pattern, we anticipate a quadratic $\Delta\rho/\rho_0$ vs H dependence in a low-field situation. The room-temperature magnetoresistance behavior of our PG specimens I-65 and R-7* is shown in the lower part of Fig. 17, where the magnetoresistive coefficient A, defined as

$$A=\Delta\rho/(\rho_0H^2),\tag{6}$$

has been plotted against the magnetic field intensity for $H<5$ kgauss. In this range we have indeed a quadratic law, which makes it meaningful to consider a "zero-field" magnetoresistive coefficient A_0 for n-type pyrolytic graphite. It was found that the A_0 of I-65 is approximately equal to the magnetoresistive coefficient of fully graphitized carbon, namely 2.56×10^{-10} gauss^{-2}, as reported by Donoghue and Eatherly.[75] The magnetoresistive coefficient rises with preferred orientation and turns out to be about twice as large in specimen R-7*. This reflects the corresponding increase in relaxation time and *ipso facto* stresses the intimate relationship between magnetoresistance and mobility.

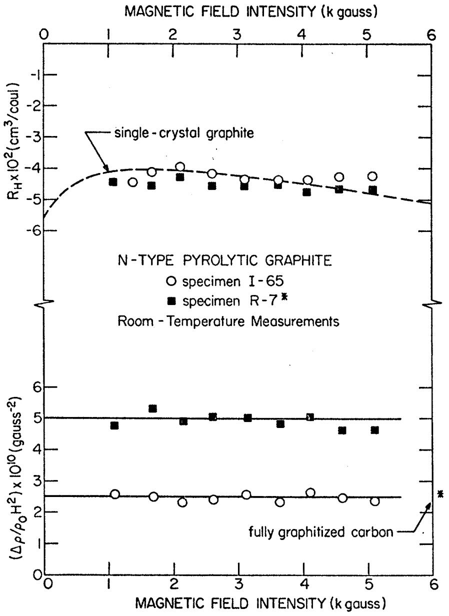

FIG. 17. Hall and magnetoresistive coefficients of two n-type specimens at low field strengths. The Hall coefficients compare favorably with Soule's single-crystal results (reference cited in footnote 1). The magnetoresistive coefficient of a 2400°C induction-furnace deposit is almost exactly as reported in reference 75 for a commercial carbon graphitized at 2750°K.

McClure's[74] analysis of Soule's[56] galvanomagnetic data for single-crystal graphite has made it clear that the ratio of electron and hole densities, n_e/n_h, remains very close to unity throughout the temperature range. If we assume, with Kinchin,[39] that this is also the case with pure polycrystalline graphite, in other words if it is true that in highly graphitized deposits the concentration of excess holes becomes negligible,[76] we may attempt to interpret the data of Fig. 17 using the following expressions for the zero-field Hall and magnetoresistive coefficients:

$$R_0=\left(\frac{1-b}{1+b}\right)\frac{1}{en_i}\quad[\text{cm}^3\ \text{coul}^{-1}]\tag{7}$$

$$A_0=(b/10^{16})\mu_h^2\quad[\text{gauss}^{-2}].\tag{8}$$

Here, e is the electronic charge in coulombs, n_i the number of intrinsic holes and electrons per cubic centimeter, μ_h the hole mobility in laboratory units, and $b=\mu_e/\mu_h$ the mobility ratio. The relations (7) and (8) result from a low-field approximation of the magnetoconductivity-tensor expressions for R_H and ρ_H, followed by a reduction to the two-carrier form and putting $n_e=n_h$.

In the H^2 region the magnetoresistance turns out to be proportional to $\mu_e\mu_h$, that is the square of an "average" electron-hole mobility. The individual mobilities can thus be derived from A_0 with an appropriate value for b. The mobility ratio, on the other hand, can be obtained with the help of Eq. (7), if the carrier concentration is available. Keeping in mind that in the basal planes the zero-field conductivity is expressible in terms of carrier concentrations and mobilities according to

$$\sigma_0=(b+1)en_i\mu_h\quad[\text{ohm}^{-1}\ \text{cm}^{-1}],\tag{9}$$

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[73] At lower field strengths Soule observed a Hall-coefficient drop which he attributed to the fast minority carriers associated with the trigonal band warping. Supposedly, $R_0=-0.040$ cm^3/coul represents the "zero-field" Hall coefficient at 298°K that would result if the third highly mobile type of carriers were not present. This value appears to differ by less than 10% from what we have obtained for I-65 and R-7*.

[74] J. W. McClure, Phys. Rev. **112**, 715 (1958).

[75] J. J. Donoghue and W. P. Eatherly, Rev. Sci. Instr. **22**, 513 (1951). Note that their measurement was made at a field strength of 15.88 kgauss, that is in a range where $\Delta\rho/\rho_0$ does not obey an H^2 law.

[76] It must be pointed out that Mrozowski and Chaberski (reference cited in footnote 53) do not share this belief.

TABLE II. Room-temperature transport properties of the layer planes in pyrolytic and single-crystal graphite, as derived from galvanomagnetic experimentation.

	Experimental data[b]			Transport parameters			Calculated[c]
Specimen	σ_0 (10^3 ohm^{-1} cm^{-1})	R_0 (cm^3 coul^{-1})	A_0 (10^{-10} gauss^{-2})	$n_e=n_h$ (10^{18} cm^{-3})	μ_e/μ_h	μ_h (10^3 cm^2 v^{-1} sec^{-1})	σ_0 (10^3 ohm^{-1} cm^{-1})
I-65	4.0	-0.042_5	2.5	7.9	1.11	1.5	4.0
R-7*	4.4_5	-0.045	5.0	6.2	1.09	2.1_5	4.4_5
EP-14[a]	25	-0.040	230	7.0	1.12	10	24

[a] Single-crystal graphite sample; the experimental data were taken from the reference cited in footnote 1, and the transport parameters from reference 74

[b] Presumably correct within better than 10%.

[c] According to Eq. (9).

it appears that a rough determination of n_i can be made on the basis of resistivity and magnetoresistance data alone, without recourse to the Hall effect. This is possible because we expect $b^{\frac{1}{2}}+b^{-\frac{1}{2}}$ to be approximately equal to two in pyrolytic graphite.[77] The concentration of free electrons and holes is then given by

$$n_i=\sigma_0/[(2\times10^8)eA_0^{\frac{1}{2}}] \quad [\mathrm{cm}^{-3}], \tag{10}$$

if the units are as before. This expression leads to the room-temperature carrier densities listed in Table II. They agree surprisingly well with the concentrations obtained for single crystals using other methods.[74] The mobility ratio b was found to be rather insensitive to the chosen value of n_i; for all our n-type specimens μ_e/μ_h is almost exactly as indicated by Soule's and McClure's analysis, namely 1.1 at room temperature. The magnitude of the mobility, on the contrary, reflects the structural configuration of the deposits: Their polycrystalline character accounts for the mobility reduction in pyrolytic as compared to natural graphite. Additional evidence will be introduced in the next section. In the meantime, it is easy to check that, by inserting the parameters listed in Table II into Eq. (9), we get an accurate estimate of the room-temperature conductivities. This demonstrates that Eq. (10) provides indeed correct indications on the carrier densities, assuming that the preceding interpretation of n-type PG transport data rests on valid theoretical ground.

VIII. TRANSPORT PROCESSES

The carrier densities and mobilities listed in Table II have been derived from *room-temperature* data relative to galvanomagnetic effects in the layer planes of highly-graphitized pyrolytic carbon deposits. They are fairly consistent with predictions that can be made from the generally accepted graphite band model. A detailed theoretical study of the *temperature dependence* of transport parameters in PG would require an accurate knowledge of the band structure and extensive computations far beyond the scope of this paper. We have already stressed that, since commercial graphites are made up of anisotropic crystallites with unknown orientations and because of the presence of binder material, it is rather difficult to ascertain whether a valid explanation has been given for the electrical conductance of polycrystalline graphites. This incites us to take advantage of the structural features of PG, to make use of the empirical information presented in Secs. IV–VI, and to attempt a phenomenological description of the resistivity temperature dependence within the framework of the formalism outlined by the Eqs. (7)–(9).

First, we shall analyze the carrier motion in the basal planes of an n-type specimen (R-7*). The magnetoresistances in Fig. 15 reveal that the mobility is a smooth function of temperature which rises slowly towards a low-temperature plateau. From the shape of the curve we shall obtain quantitative indications on the scattering mechanisms. Moreover, by confronting an analytical expression of the hole mobility with the experimental Hall mobilities it is possible to deduce the temperature dependence of the electron-hole mobility ratio. The availability of this critical parameter allows us to determine the intrinsic carrier-density variations[78] and to reproduce the resistivity temperature dependence via Eq. (9). Finally, we shall make estimates of the average crystallite sizes in well-graphitized specimens by following two independent approaches: by considering the boundary-scattering relaxation time and by exploring the resistance minimum associated with the transition into a scattering range where phonon mechanisms predominate.

A. Scattering Mechanisms and Carrier Density Variations

Figure 14 shows that the Hall coefficient of graphitized PG remains negative even at the lowest ambient temperatures.[79] Since our Hall data can be considered as representative of a low-field situation, Eq. (7) is relevant and implies that b remains larger than one, in other words that $\mu_e > \mu_h$ over the whole temperature range. Hence, if the mobility ratio is a slowly varying function

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[77] There is a great deal of evidence pointing toward $b\approx 1$, throughout the temperature range, in single-crystal as well as polycrystalline graphite. For references, see for instance J. W. McClure (reference 74).

[78] As in Sec. VII, our basic assumption will be that the electron and hole concentrations are nearly equal in n-type graphitic materials.

[79] In this respect the Hall coefficient of polycrystalline products apparently does not behave as in graphite single crystals. Soule (reference cited in footnote 1) reports that for small magnetic fields R_H is positive at 77° and 4.2°K, which means that the mobility ratio changes to $b<1$.

of temperature, a plot of

$$\mu_h = \left(\frac{\Delta\rho}{\rho_0 b}\right)^{\frac{1}{2}} \frac{10^8}{H}, \tag{11}$$

with $b = 1.1$ (room-temperature value) and $\Delta\rho/\rho_0$ values taken from Fig. 15 (specimen R-7*) will yield the mobility vs temperature law in n-type PG.[80] The hole mobilities in the upper part of Fig. 18 were determined according to Eq. (11); they are approximate because of the assumption that b stays constant, but this will turn out to be a valid procedure. At room temperature, μ_h as deduced from the temperature dependence of $\Delta\rho/\rho_0$ agrees fairly well with the value previously obtained by considering the magnetic field dependence, namely 2150 cm^2/v-sec. At low temperatures, the mobility tends towards higher values and saturates at about 4000 cm^2/v-sec. This general trend demonstrates that lattice scattering mechanisms operate in pyrolytic graphite above 50°K. In the temperature range from 150°K up to at least 500°K, the mobility exhibits a $T^{-0.55}$ behavior instead of the $T^{-1.2}$ dependence obeyed by graphite single crystals[56] or the $T^{-1.0}$ law predicted for lattice scattering in a typical metal. How the temperature dependence of the mobility leads to quantitative indications on the scattering processes in polycrystalline graphite will now be discussed in some detail.

Following Bowen,[81] we shall assume that, as far as inplane transport is concerned, there are two scattering mechanisms operative in polycrystalline graphite; thermal lattice scattering and crystallite boundary scattering. If each mechanism has its own effective collision time, the hole mobility can be expressed as

$$1/\mu_h = 1/\mu_B + 1/\mu_L, \tag{12}$$

where μ_B is proportional to the average basal plane crystallite diameter, while μ_L is temperature dependent and proportional to the thermal mean-free-path. According to Bowman *et al.*,[30] the thermal mean-free-path should be linearly related to the reciprocal phonon density, and therefore, to the reciprocal specific heat of graphite, $1/C_v$. Thus we may attempt to approximate the hole mobility using a phenomenological expression such as $1/(\alpha + \beta C_v)$, where α and β are constants which depend on band-structural features and carrier relaxation times.

With decreasing temperature the mobility slope tends towards zero values indicative of a "constant" crystallite-boundary scattering (see Fig. 18). In the neighborhood of liquid-helium temperatures this type of scattering is evidently dominant, and we shall assume that for the specimen under investigation:

$$\alpha = 1/\mu_B = 2.5 \times 10^{-4} \quad [\text{v sec cm}^{-2}]. \tag{13}$$

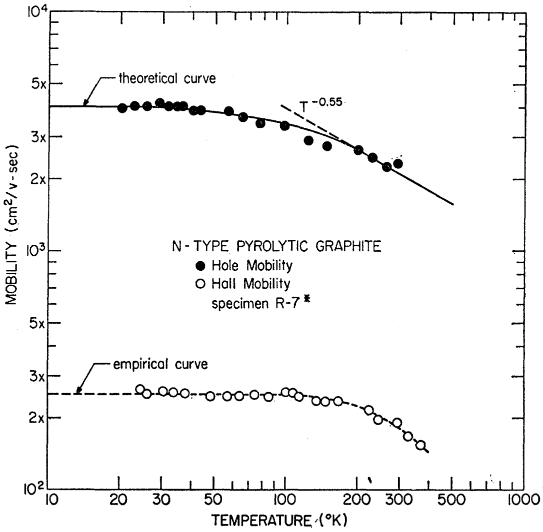

FIG. 18. Hole mobility and Hall mobility of an n-type specimen as a function of the temperature. The theoretical fit indicates that above 150°K the hole mobility decreases approximately as $T^{-0.55}$.

We now are in a position to test the *Ansatz* (12), using for instance the specific heat data of DeSorbo and Tyler[82] in order to reproduce the mobility behavior. The fit shown in Fig. 18 corresponds to $\beta = 1.1 \times 10^{-4}$, if C_v is in calories per degree and per mole; it demonstrates that the carrier motion in the layer planes of pyrolytic graphite can be quantitatively understood in terms of elementary concepts.

In their study of defects in graphite, Bowman, Krumhansl, and Meers assert that the concentration of electrons and holes (the intrinsic carrier density) rises linearly with temperature in the helium- to room-temperature range.[30] An unqualified substantiation, which one would normally base on Hall-effect experiments, has not yet been provided. Since $b > 1$, an evaluation of the low-temperature carrier density via

$$n_i = \left(\frac{1-b}{1+b}\right)\frac{1}{eR_0} \tag{14}$$

requires an accurate knowledge of the mobility ratio as a function of temperature. This information can be obtained if the Hall mobilities μ_H and the hole mobilities μ_h are both available. From Eqs. (7) and (9) it follows that:

$$\mu_H = |R_0|\sigma_0 = (b-1)\mu_h, \tag{15}$$

and thus it should be a straightforward matter to deduce the electron-hole mobility ratio μ_e/μ_h from the Hall-hole mobility ratio μ_H/μ_h. The Hall mobilities that were

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[80] The magnetoresistance data were taken at 2.5 kgauss, that is in a field-strength region where Eq. (8) applies.

[81] D. Bowen, Phys. Rev. **76**, 1878 (1949).

[82] W. DeSorbo and W. W. Tyler, J. Chem. Phys. **26**, 244 (1957). Preliminary measurements indicate that the specific heat of pyrolytic graphite does not differ substantially from normal graphite. [High Temperature Materials Department, Raytheon Company, Final Report on Contract NOrd-18160 (FBM), March 31, 1960 (unpublished).]

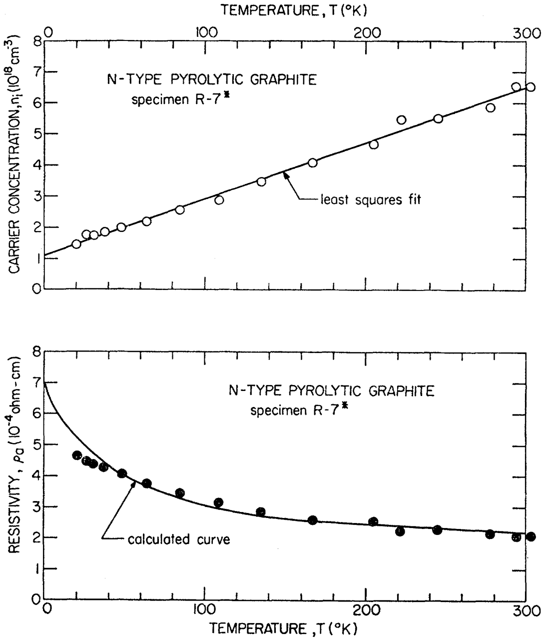

FIG. 19. Intrinsic carrier density and basal plane resistivity of an n-type specimen as a function of the temperature. The resistivity curve has been calculated assuming a linear temperature dependence for the carrier concentration, a constant mobility ratio, and a hole mobility as in Fig. 18.

measured for specimen R-7* have been plotted against temperature in the lower part of Fig. 18. The shape of the curve shows much similarity to the "true" mobility temperature dependence, in harmony with general semiconductor principles. Using an empirical Hall mobility midline together with the theoretical hole mobility curve of Fig. 18, it is found that b decreases with temperature and drops progressively from 1.09 at 300°K[83] to 1.06 at 20°K. This drop has no significance insofar as Eq. (11) is concerned but cannot be ignored in applying Eq. (14).

The intrinsic carrier density of an n-type PG specimen such as R-7*, if it is evaluated according to Eq. (14) and plotted against temperature as in Fig. 19, appears to substantiate that, within experimental uncertainty,

$$n_i \approx n_{i0} + \gamma T. \tag{16}$$

The straight line in the upper part of Fig. 19 represents a least-squares fit in the hypothesis of a strict linear temperature dependence and corresponds to a zero-degree free electron-hole concentration n_{i0} of 1.1×10^{18} cm^{-3} with $\gamma = 0.018\times10^{18}$ cm^{-3}/deg. In pure polycrystalline graphite Kinchin found the number of electrons per cubic centimeter[39] (with $n_e = n_h$) to be 1.2×10^{18} at 4.2°K and 6.2×10^{18} at 273°K. These figures are within a few percent of the least-squares fit indications, in spite of the fact that the fit refers to data acquired on oriented materials and analyzed by improved methods. A comparison with Soule's[56] and McClure's[74] single-crystal results reveals an excellent numerical agreement at 77°K ($n_i = 2.5\times10^{18}$ cm^{-3} in crystal EP-7), but the 4.2°K concentrations ($n_i = 2.1\times10^{18}$ cm^{-3} in the same single crystal) fall above those indicated for pyrolytic graphite on the basis of Eq. (16). We shall see in a moment that the discrepancy is actually of consequence.

The lower half of Fig. 19 exhibits basal plane resistivity data, as taken on specimen R-7*, in confrontation with a resistivity curve calculated according to Eq. (9), that is

$$\rho_0 = \frac{6.25\times10^{-4}(2.5+1.1C_v)}{(1+b)(1.1+0.018T)} \quad [\text{ohm cm}], \tag{17}$$

if we combine our previous results. Here, C_v must be considered as an empirical temperature-dependent quantity expressed in calories per degree and per mole, whereas b can be considered as temperature independent and equal to about 1.1. Above 40°K the calculated resistivity reproduces the experimental indications. We know that in respect to temperature dependence well-graphitized deposits behave strictly in accordance with common synthetic graphites (see Fig. 9). Our treatment of transport processes in the layer planes of n-type PG has, therefore, a rather general significance; this invites a certain number of remarks.

1. When the temperature is lowered, the resistance of a polycrystalline graphite sample increases owing to the decreasing carrier concentration and *not* to enhanced scattering. An explanation for the flattening out of the resistance curve at "higher" temperatures must be formulated as follows: Below approximately 77°K the resistivity variations are essentially generated by carrier-density variations, while above that temperature the rate of resistivity decrease appears to be slowed down by the onset of phonon scattering.[84] In this context, it will be remembered that the curvature is conspicuously absent in low-temperature deposits (see Fig. 9). These specimens have small crystallites, and their Fermi level is shifted deep into the valence band. Observations on lampblack-base materials and bromine-doped graphites[30] explain that for these reasons I-63 ought to behave as in Fig. 9.

2. The semi-empirical resistivity formula (17) does not reproduce the leveling off which has been noted for highly-graphitized PG (Sec. V) as well as for highly heat-treated carbons (Reynolds *et al.*[45]) in the vicinity of liquid-helium temperatures. We have already pointed out that the 4.2°K carrier concentration deduced from a least-squares fit assuming the validity of Eq. (16) over the whole temperature range may well be too low. In fact, McClure's calculations for pure grapihte[74] indicate that in the relatively narrow range of temperature where our analysis fails to agree with the experiment (Fig. 19), the carrier concentration should be essentially constant

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[83] In agreement with the room-temperature determination made in Sec. VII on a different basis (see Table II).

[84] Phonon scattering becomes a factor when the thermal mean-free-path becomes comparable to the average in-plane crystallite size.

or at most a slowly varying function of temperature. If this is also true for polycrystalline materials, then, as the temperature is lowered, the resistivity would indeed reach a plateau or even a maximum beyond which it might decrease, the exact behavior being dependent on counteracting trapping and scattering effects. The presently available Hall and magnetoresistance data do not allow us to draw firm conclusions in this respect; further work is in progress.[49]

3. In the boundary scattering range the basal plane resistivity of a polycrystalline graphite sample appears to be conditioned by the average in-plane crystallite size, if the Fermi level does not lie too deep within the lower π band. A striking illustration of the correlation between ρ_a and L_a has been given by Bowman *et al.*, who plotted the resistivity of various graphites, all fulfilling the above-mentioned Fermi level restriction, against the reciprocal crystallite size as determined by x rays, and thereby established a linear dependency.[30] It follows that μ_B must be closely related to L_a, and conversely, that it might be feasible to estimate the crystallite diameter from the boundary-limited mobility value. Such an attempt will be made in the next paragraph.

B. Crystallite Sizes

Introducing the boundary-scattering relaxation time, τ_B, we may write

$$\mu_B = e\tau_B/m^*, \tag{18}$$

if m^* represents the effective mass of carriers moving along graphitic layer planes. The temperature-independent character of μ_B implies that in polycrystalline graphite τ_B must remain essentially constant,[85] and since

$$\tau_B = L_a/v, \tag{19}$$

that the average carrier velocity v should not change much, at least up to 77°K. This is precisely what McClure inferred from the galvanomagnetic properties of graphite single crystals; the velocity of holes, for instance, remains equal to 0.54×10^8 cm/sec at the Fermi surface.[74] In combination with the de Haas-van Alphen masses derived by Soule, namely $m^*/m_0 = 0.060$ for holes at 4.2°K, this allows us to calculate the average crystallite size according to:

$$L_a = \mu_B m^* v/(e\times10^7) \quad [\text{cm}], \tag{20}$$

where e is in coulombs, μ_B in laboratory units, and m^*v in gram-centimeters per second. For specimen R-7* ($\mu_B = 4000$ cm^2/v-sec), Eq. (20) indicates that $L_a \approx 740$ A. This result can only be approximate, because it does not take into account the repercussions of polycrystallinity in terms of effective masses and carrier velocities. Nevertheless, if we refer to Fig. 12, which "locates" a pyrolytic graphite with respect to heat-treated carbons, and if we recall Mrozowski's statement quoted in footnote 59, we realize that the Hall coefficient of the specimen under consideration is characteristic of crystallites with diameters of about 700 A or more.[86] While the figure of 700 A should not be taken too seriously, it does encourage further attempts along these lines.

In Sec. V we have mentioned that the occurrence of a minimum in the resistance vs temperature curve of graphitized structures offers a relatively convenient way of estimating crystallite sizes.[38] For the sake of completeness, we shall now apply this method to the high-temperature data of Fig. 10. Owing to the additive character of the two scattering mechanisms it follows that, in graphite,

$$\rho_0 = \frac{1/\mu_B + 1/\mu_L}{e n_i(1+b)}. \tag{21}$$

The symbols are as previously defined. Introducing the mean free paths, L_a and L_{th},[87] Eq. (21) becomes

$$\rho_0 = \frac{m^* v}{e^2 n_i(1+b)}\left(\frac{1}{L_a} + \frac{1}{L_{th}}\right). \tag{22}$$

The reader will note that the symbols m^*, v, and L_{th} concern holes, if b stands for μ_e/μ_h as before, though they might as well refer to the electrons, if b is assumed to represent the μ_h/μ_e ratio. Using Kinchin's notations,[39] we shall write

$$\rho_0 = [Y + X(T)]/g(T); \tag{23}$$

Y is the reciprocal crystallite diameter, $X(T)$ a "universal" function of temperature, and $g(T)$ the function $e^2 n_i(1+b)/(m^* v)$. In Table 9 of his paper, Kinchin gives some numerical indications on $X(T) = 1/L_{th}$ and $f(T) = m^* v/n_i$, indications which he derived from conductivity and Hall-effect experiments by assuming that the crystallite sizes are reasonably well known on the basis of x-ray studies.[88] A logarithmic plot of the functions $X(T)$ and $f^{-1}(T)$ shows that, in the 600° to 1200°K range: (*a*) $X(T)$ can be approximated by ϵT^n, where ϵ is a constant; (*b*) $g(T)$ exhibits a T^m behavior, if the temperature dependence of the mobility ratio is neglected. In the neighborhood of the resistivity minima (Fig. 10), we have therefore

$$\rho_0 = (Y + \epsilon T^n)/g(T) \tag{24}$$

and

$$\frac{d\rho_0}{dT} = \frac{n\epsilon T^{n-1} g(T) - (Y + \epsilon T^n)\, dg(T)/dT}{g^2(T)}. \tag{25}$$

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[85] This feature connotes an analogy between crystallite-boundary scattering and neutral impurity scattering, as it is well known that in the latter case the relaxation time does not vary with temperature. See, for instance, R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, England, 1959), p. 152.

[86] Based on x-ray diffraction work by H. T. Pinnick, Phys. Rev. 94, 319 (1954).

[87] L_{th} refers to the scattering by thermal lattice vibrations and is strongly temperature dependent.

[88] In the liquid-nitrogen to room-temperature range, Kinchin's thermal mean-free-paths agree fairly well with the results of McClure for graphite single crystals (see reference 74). In regard to the carrier concentration, it will be remembered that Kinchin's conclusions are virtually identical to our own for pyrolytic graphite (see subsection A).

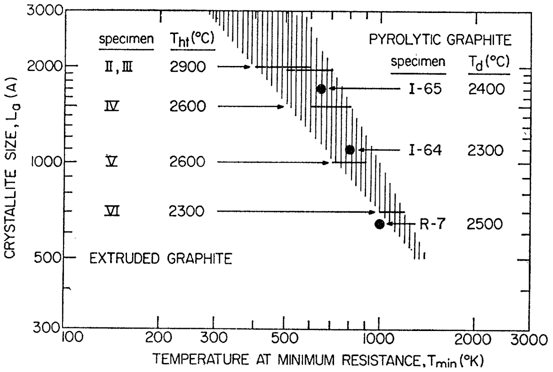

FIG. 20. Crystallite size vs the temperature at which the resistivity minimum occurs. The extruded graphite sizes were determined via x-ray methods (reference 39), and the PG sizes via Eq. (28).

There will be a minimum at the temperature $T_{\min}$ that fulfills the condition

$$\frac{Y+\epsilon T^n}{n\epsilon T^{n-1}}=\frac{g(T)}{dg(T)/dT}=\frac{T}{m}, \tag{26}$$

or

$$Y+(1-n/m)X(T_{\min})=0. \tag{27}$$

Obviously, such a minimum exists only if $n/m>1$. Kinchin's results imply that in the temperature range of interest one has $n=2.5$ and $m=1.9$. Assuming that these figures are valid for PG (see reference 88), we conclude that

$$L_a\approx 3L_{th}(T_{\min}), \tag{28}$$

if $L_{th}(T_{\min})$ designates the thermal mean-free-path in well-ordered graphitic layers at the temperature corresponding to the resistivity bottom. In Fig. 20, the herewith obtained basal plane crystallite sizes for the specimens I-65, I-64, and R-7 are plotted against $T_{\min}$ together with the "x-ray" sizes measured by Bacon on Kinchin's synthetic graphite samples.[39]

Specimen R-7 does not fit into the L_a vs $T_{\min}$ pattern delineated by Kinchin's data. This was expected because resistance-grown as-deposited material has a turbostratic layer stacking, and the preceding treatment should not apply. Detailed x-ray studies on this specific sample indicate that the average crystallite size[10] does not exceed 325 A. The specimens I-64 and I-65, on the contrary, are made up of graphitized crystallites whose L_a dimensions are very similar to those of extruded stocks after heat treatment at about 2600° and 2750°C, respectively (see Fig. 20). Considering the deposition temperatures of our samples (see Table I), this makes sense, especially because we have had a number of opportunities to substantiate our contention that the crystallites' alignment in pyrolytic deposits enhances the graphitization by an amount roughly equivalent to a heat-treatment temperature raise of a few hundred degrees.

At this stage we should reconsider the crystallite diameter value previously deduced for specimen *R*-7*, namely 740 A on the basis of the low-temperature mobility plateau. Since we have been unable to collect high-temperature data for this heat-treated specimen, we are not in a good position to confront the two methods or pass judgment on their respective merits. Nevertheless, lattice spacings and Hall coefficients indicate that from a structural point of view R-7* is superior to I-64, which entails that the crystallites should have layers of more than 1000 A. We have already emphasized that the main uncertainty in applying Eq. (20) lies with the effective mass and the carrier velocity. At low temperatures the mobility ratio in polycrystalline material differs quite appreciably from the single-crystal value (see footnote 79); a recourse to Soule and McClure's m^*v is therefore questionable. Actually, by exploiting the information that has been accumulated in the present section we have the means to determine the mass-velocity product of holes in a specimen such as R-7*. For instance, we know that below room temperature the thermal lattice mobility is given by $1/(\beta C_v)$, where β is a constant and C_v the specific heat. This implies that

$$m^*v=e\times 10^7 L_{th}(\beta C_v)\quad [\text{cm g sec}^{-1}], \tag{29}$$

if e is in coulombs, L_{th} in centimeters, and βC_v in volt-seconds per square centimeter. Pertinent indications on the thermal mean-free-path have been published by Kinchin (Table 9 of reference 39; see also footnote 88). Their use in conjunction with Eq. (29) shows that in the temperature range from 150° to 300°K, that is in the temperature range where the fit of Fig. 18 is significant (because $1/\mu_L$ becomes appreciable in comparison to $1/\mu_B$), we have

$$0.41\times 10^{-8}\leqslant m^*v/(e\times 10^7)\leqslant 0.47\times 10^{-8} \tag{30}$$

in the units of Eq. (29).[89] It follows that in the layer planes of pyrolytic graphite the holes have an average m^*v of about 7.2×10^{-21} cm g sec^{-1}, that is more than twice as large as in single crystals at 4.2°K. If we adopt this value, Eq. (20) leads to an average crystallite size of 1800 A in specimen R-7*, or a somewhat bigger size than deduced for I-65 from the location of the resistivity bottom. This is no surprise, keeping in mind that R-7* has a 2500°C history. We might "wish" to find even bigger crystallites in this exceptionally well-oriented deposit; the room-temperature magnetoresitances in Fig. 17 also point in this direction. Considering that two radically different experimental and analytical techniques were employed, the output of our crystallite-size evaluations still entails much cause for satisfaction. It must, however, be emphasized that the two methods rely on Kinchin's thermal mean-free-path determina-

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[89] In essence, the relative constancy of m^*v demonstrates the temperature independence of the crystallite-boundary scattering in graphite.

tions and are not absolute.[90] Moreover, the scattering by fixed centers such as impurities and defects has been systematically ignored. The precise meaning of an L_a as calculated here might therefore be debatable. Yet, Fig. 20 provides convincing evidence that these calculations can be very useful in helping to estimate the size of graphitic planes under circumstances where x-ray techniques demand elaborate precautions.

IX. CONCLUSION

Materials with pronounced anisotropic characteristics afford a number of attractive perspectives in the general area of solid-state physics and the related technologies. The pyrolysis of hydrocarbons ought to be particularly significant in this respect, because the products constitute a whole series of transitional structures with a great variety of electrical properties. A major objective of our study has been to explore how these properties can be correlated with specific structural features of pyrolytic carbon deposits. We have seen, for instance, that the Hall response of ***graphitized*** specimens prepared in an induction-heated furnace differs considerably from the response of ***turbostratic*** deposits produced at a similar temperature in a resistance-heated furnace; and we have shown that the difference is indeed due to structural factors. A second point of emphasis has been to exploit the structural features of PG, namely the high density, the preferred orientation, and the absence of binder, in order to attempt a phenomenological description of isothermal transport processes in the layer planes of polycrystalline graphite. This attempt has been based on the two-band model used by Soule[56] and McClure[74] in the analysis of galvanomagnetic data for single-crystal graphite. It was successful in the sense that we have obtained reasonable estimates of the carrier densities and mobilities in graphitized PG. In turbostratic graphites, on the contrary, the conventional metal or semiconductor models may well be inapplicable: A quantitative treatment of data taken on disordered pyrolytic carbons has therefore been postponed. Nevertheless, it appeared that they are consistent with Mrozowski's model,[47] that is with the concept of a variable π-band gap in conjunction with a high degree of Fermi degeneracy. We shall discuss this further after a brief review of the information elaborated in previous sections.

A. Summarizing Statements

1. If the deposition temperature of a pyrolytic carbon is raised from 1700° to 2100°C, the basal plane resistivity decreases by a factor of about 10. In accordance with Mrozowski's model, the drop appears to be caused by the transition from a one- to a two-carrier situation resulting from the growth of the crystallites. Materials deposited at 2500°C have a room-temperature resistivity of approximately 200 μohm-cm; this is much below the resistivity level of the usual synthetic graphites and must be due to the combination of preferred orientation plus lack of macroporosity.

2. The temperature dependence of the basal plane resistivity does not depend upon such "macroscopic" factors, but is essentially a matter of crystallite size and order. Below room temperature, the resistance of polycrystalline graphite increases with decreasing temperature as a result of free carrier removal processes. The resistivity vs temperature characteristics of graphitized PG specimens exhibit a typical curvature which signals the onset of phonon scattering, in contrast to the low-temperature deposits which behave like carbon blacks with crystallites of approximately 100 A diameter and therefore much smaller than the average thermal mean-free-path.

3. This is substantiated by the failure to observe indications of a resistivity minimum in the easy direction at temperatures as high as 1500°K. Graphitized PG specimens are made up of much larger crystallites whose size can be estimated from the position of the minimum on the temperature scale. Using Kinchin's high-temperature data[39] it may be concluded that $L_a \approx 3L_{th}(T_{\min})$; the procedure gives satisfactory results for induction-grown material prepared at $T_d > 2100°\mathrm{C}$.

4. In the *c* direction the resistivity of pyrolytic carbons increases with the temperature of deposition and was found to exceed 1 ohm-cm in an exceptionally well-oriented but poorly-ordered 2500°C deposit. At room temperature materials of this kind possess electrical anisotropies of the order of 3×10^3, which represents a twenty fold increase over the graphite single-crystal anisotropy measured by Primak.[23] The PG anisotropies drop fairly rapidly with the deposition temperature, in accordance with the degree of preferred orientation as measured by x rays.

5. The temperature dependence of the *c*-direction resistivity of a 2100°C deposit exhibits peculiar features; an extended low-temperature plateau coupled to semiconductor-like characteristics above room temperature. As a function of temperature the electrical anisotropy goes through a maximum of one thousand or so slightly above room temperature, and decreases sharply at high ambient temperatures. These are preliminary and partial conclusions.

6. To what extent *c-direction* measurements performed on pyrolytic carbon deposits are representative of the intrinsic *c-axis* resistivity of graphite remains debatable. Studies at microwave frequencies have been inconclusive in this respect. Heat treatment followed by partial graphitization lowers the *c*-direction resistivity of poorly-ordered PG into the half an ohm-centimeter range previously reported by other workers.[3,33]

7. As a function of the deposition temperature, the Hall coefficient of PG specimens with basal planes perpendicular to the magnetic field behaves as indicated

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[90] The evaluation of $X(T)=1/L_{th}$ requires an independent measure of L_a, for instance via x-ray diffraction studies as in reference 39.

by Mrozowski's model and shows a positive maximum in the transition region around $T_d = 1900°C$. The Hall coefficient variations with deposition temperature and heat treatment must be attributed to the closely balanced and mutually cancelling contributions of free holes and electrons. They reflect the morphological perfection of the deposit strictly in terms of rotational order: Poorly-ordered specimens ($\gamma < 0.5$) are *p* type, whereas highly-ordered specimens ($\gamma > 0.5$) have negative Hall coefficients typical of natural single crystals, namely $R_0 \approx -0.05$ cm^3/coul.

8. As a function of the ambient temperature, the Hall coefficient provides a most sensitive "description" of the structural perfection of a deposited carbon crystallite. The Hall behavior of turbostratic structures appears to be consistent with the notion of defects acting as electron traps and thereby upsetting the intrinsic electron-hole balance. Graphitized specimens remain *n* type over the whole temperature range, which implies that the upper π-band electrons move faster than the lower π-band holes, at least in the basal planes.

9. The mobility ratio μ_e/μ_h in *n*-type PG can actually be determined as a function of temperature by examining both the Hall and drift mobilities; the ratio was found to remain of the order of 1.1. On this basis it has been inferred that the free electron-hole density (assuming $n_e/n_h = 1$ at all temperatures) decreases almost linearly from a room-temperature value of 6.5×10^{18} cm^{-3} to less than 2×10^{18} cm^{-3} in the liquid-helium temperature range. These results compare favorably with Soule's and McClure's evaluations for single-crystal graphite at 77° and 300°K.

10. At high field strengths, the magnetoresistance of deposited carbons follows the $H^{1.78}$ law of single-crystal and polycrystalline graphites regardless of the deposition temperature. In as-deposited materials the magnitude of $\Delta\rho/\rho_0$, which may exceed 50% at 25 kgauss, appears to be closely related to the degree of preferred orientation and thus provides an independent indication on the structural anisotropy of a carbon deposit. On the whole, the negative magnetoresistances that have been observed in poorly graphitized PG confirm Mrozowski's measurements on heat-treated carbon blacks.

11. At low field strengths ($H < 3$ kgauss), the basal plane magnetoresistance of *n*-type PG has a quadratic field dependence which permits an evaluation of the carrier mobilities using "classical" procedures. The basal plane mobilities in well-ordered highly-oriented specimens are quite high; they rise from about 2×10^3 cm^2/v-sec at room temperature to 4×10^3 cm^2/v-sec at liquid-helium temperatures in a 2500°C deposit. The shape of the mobility curve demonstrates that in polycrystalline graphite of high perfection lattice scattering mechanisms operate in a significant way even below 77°K.

12. It has been established that the mobility can be theoretically described by combining the thermal scattering with a temperature-independent contribution that must be closely related to the crystallite size. Since crystallite-boundary scattering effects dominate the low-temperature transport picture, it was attempted to estimate the average layer-plane diameter from the boundary-limited mobility value. Trusting Kinchin's thermal mean free paths, it appears that the product of effective mass and hole velocity in the layer planes of pyrolytic graphite is approximately equal to 7×10^{-21} g-cm/sec; a figure which leads to crystallite sizes of about 2000 A in our best specimens.

B. Final Comments

In Sec. V we have seen that the electrical conductivity of graphitized PG layers has temperature characteristics reminiscent of well-known petroleum-coke based stocks. The attempt made in Sec. VIII to explain the resistivity temperature dependence should therefore be worthy of consideration, even if the theoretical *Ansatz* is not too rigorous. The yield of Eq. (17) justifies such an attitude. Nevertheless, our failure to reproduce the correct behavior at liquid-helium temperatures makes it mandatory to accumulate Hall effect as well as magnetoresistivity data in this temperature range prior to any formulation of final conclusions. A similar situation exists with respect to the crystallite-size work, which requires additional experimentation at temperatures well above 300°K.

It is quite striking that the "transition" from an extruded synthetic graphite to a natural single crystal via ordered pyrolytic deposits does not involve any significant change in the carrier concentration. Presumably, this means that in graphitized materials the major impurities remain un-ionized. The mobilities, on the contrary, show vast differences which appear to be intimately related to the degree of preferred orientation. The correlation can be established through magnetoresistivity studies for the two following reasons; magnetoresistance measurements have been found very sensitive to the relative alignment of the crystallites, and magnetoresistive effects are known to be predominantly mobility dependent. On the other hand, it was shown in Sec. VIII that the basal plane motion is to a large extent controlled by the size of the crystallites. An explanation of the situation must therefore be based on the assertion that improving the crystallites' alignment enhances their growth. In the light of many of our observations, it is actually certain that, in this respect, the pyrolytic introduction of preferred orientation has consequences similar to those which accompany an increase of the heat-treatment temperature in the case of commercial graphite.

A systematic investigation of the effects of heat treatment on the electronic properties of pyrolytic carbons and graphites has not yet been undertaken. The phenomena that we have noted in annealing some of our specimens at 2500°C are definitely of interest. It will be remembered that the high-density carbons deposited at 2500°C in the resistance-heated furnace underwent drastic transformations (they graphitized!), whereas the 1700° and 1900°C specimens behaved like carbon blacks. According to Franklin, a near-parallelism of the adjacent crystallites is the determining factor insofar as crystallite growth and graphitization are concerned.[12] This might indeed explain why a highly-oriented product such as R-7 graphitizes easily. The relative stability of I-63 and I-64 must then be attributed to morphological pecularities which harden the crystalline structure in the sense that they hamper or even inhibit the transition toward more graphitic arrangements. Much additional work is obviously required before any definitive conclusion can be reached.

More quantitative work remains also to be done if our aim is to better grasp the nature of electronic processes in poorly-graphitized pyrolytic deposits. In order to illustrate this point, it may be sufficient to say that no satisfactory interpretation of the mechanism of negative magnetoresistances can be given at present. Generally speaking, Mrozowski's model offers an explanation of the changes occurring with deposition temperature, as we have said earlier. Actually, there is little doubt that an energy gap exists in turbostratic carbons, even if it is difficult to adduce positive evidence for this because most of the effects of a variable band gap and of a shifting Fermi level are so closely coupled. Without further study the true nature of the electron traps responsible for the Fermi level anomalies also remains an open question. Whatever the answer is, we are confident that a detailed analysis of the data collected on low-temperature carbon deposits will turn out to be quite revealing.

Finally, we should like to stress once more that the galvanomagnetic experiments reported throughout this paper have been carried out with a magnetic field pointing across the deposit. With a field perpendicular to the *c* direction, the transverse magnetoresistance of good specimens was found to be too small to permit a proper measurement. This makes sense, considering that a large magnetoresistive anisotropy must be expected in pyrolytic graphite because of the effective mass as well as the relaxation-time anisotropy. In the same geometry, and using conventional techniques, Hall-effect experiments failed to yield reliable indications. Progress in this respect will probably require a major experimental effort. Success would help a great deal in clarifying the conduction mechanism along the *c* axis of graphite.

Note added in proof. This paper was completed in January, 1961. A great deal of new information has since been generated at the Imperial College in London (Professor A. R. Ubbelohde), as well as at the author's laboratory. Presentations and discussions at the "Fifth Conference on Carbon," The Pennsylvania State University, June, 1961, also focused much attention on a number of topics considered in Secs. IV–VIII. Progress has been made in describing the charge carrier behavior of graphitized PG at low temperatures,[91] in establishing that a heat treatment at 3600°C produces single-crystal material,[92] and in demonstrating that band-structural concepts can be successfully applied to the analysis of turbostratic and of boron-doped pyrolytic graphites.[93] The reader is strongly advised to take cognizance of these contributions, which cover much of the present paper's ground in a more advanced fashion. Reprints and preprints are available upon request.

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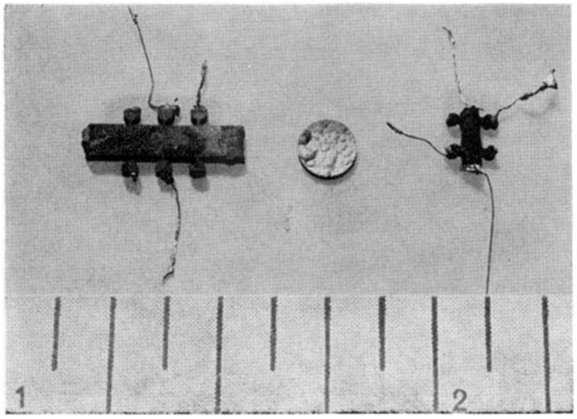

FIG. 2. Pyrolytic-graphite samples shaped for electrical and galvanomagnetic measurements. Note the high metallic reflectivity of the disc, cut from a 2400°C deposit, which is characteristic of the basal planes. The straight edge is graduated in inches.