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ON THE PROPERTIES OF GRAPHITE

by

John P. Howe

Report No. RL-685   **April, 1952**

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ABSTRACT

The structure, thermal properties, electrical characteristics, and mechanical behavior of graphite are reviewed and the highly anisotropic character of graphite crystals emphasized. The interesting properties of graphite are due in large measure to the strong semi-metallic bonds between carbon atoms in plane layers and

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CONCLUSIONS

to the relatively weak binding between planes. Details of its structure are due in part to the Frank dislocation mechanism for growth of crystals. Thus graphite has a low vapor pressure, and approximately two-dimensional electrical and thermal conductivity. It is easily deformed in slip on the basal plane, but in polycrystalline form is relatively strong at high temperature. Its lamellar nature is emphasized by its reaction with alkali metals and bromine.

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ON THE PROPERTIES OF GRAPHITE

John P. Howe

Tetravalent carbon atoms can be bonded together to form a solid in two ways, as shown in Fig. 1. Diamond--in which classical carbon-carbon single bonds join each atom to four others, each at the corner of a regular tetrahedron--is the hardest substance known. It is, however, slightly less stable than graphite, one of the softest substances known, in which each carbon atom is bonded to three others to make up a large plane molecule. These planes in turn are stacked together relatively loosely to make a crystal in a manner to be described later.

That tetravalent carbon atoms could be bound as firmly with three bonds as with four was first suggested by Kekulé, although he used the idea of double bonds. Quantum mechanical descriptions have been offered showing the main features of such bonds, which are so important in the chemistry of aromatic carbon compounds. The large amount of work on the description of carbon and carbon compounds from first principles makes it interesting to see to what extent one can understand the important properties of graphite. For this discussion, the structure of the ideal graphite crystal and its deviations are useful. The thermodynamics or energetics of the more important changes graphite can undergo are also required. Finally, the properties that are important in the uses of graphite can be discussed. No attempt is made to review completely the information on graphite, since it is very extensive. Rather, evidence for the illustrative or characteristic properties is presented.
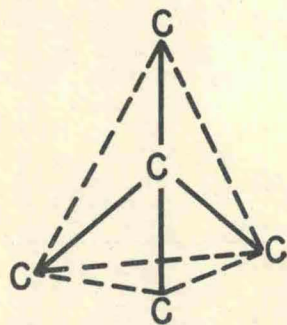
CRYSTAL STRUCTURE

The Ideal Crystal

What might be termed the ideal graphite crystal structure was proposed by J. D. Bernal[1] in 1924, and is shown in Fig. 2. The regular hexagonal ring arrangement of the atoms in each plane agrees with our knowledge about aromatic hydrocarbons and is the logical end result of building larger and larger molecules in the series: benzene, naphthalene, anthracene, coronene, etc. Why the planes stack as they appear to is not clear. In fact, one might like to believe that the structure in Fig. 3 is to be preferred. P. Debye and P. Scherrer[2] proposed this
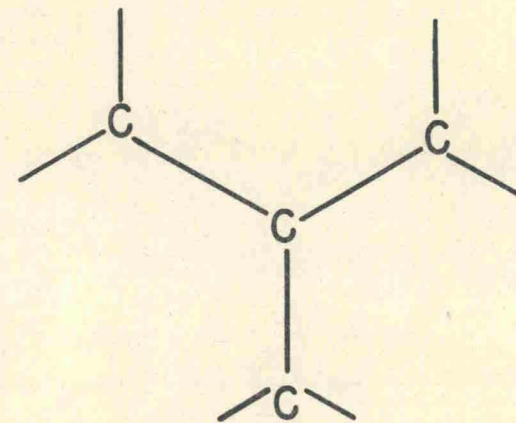
A

B

DIAMOND CRYSTALS

C

D
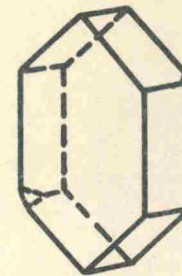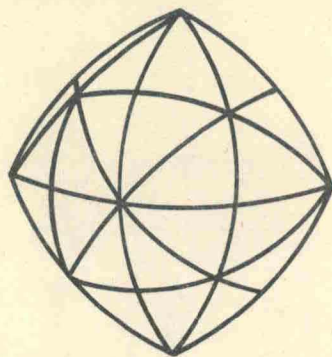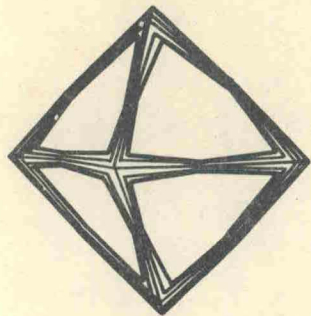
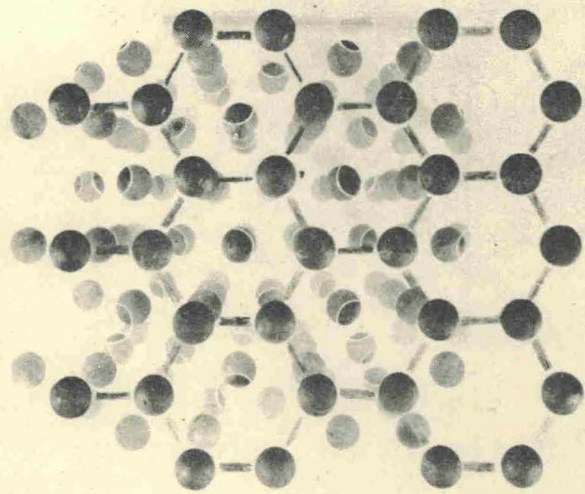GRAPHITE CRYSTALS

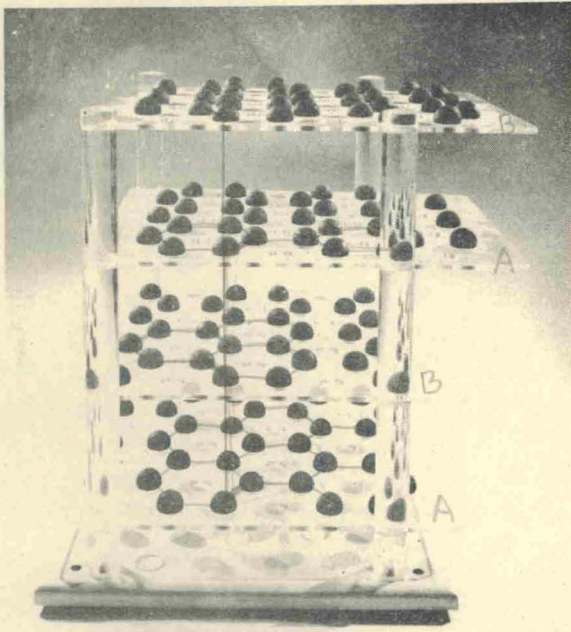Fig. 1   Two types of carbon valence bonds.
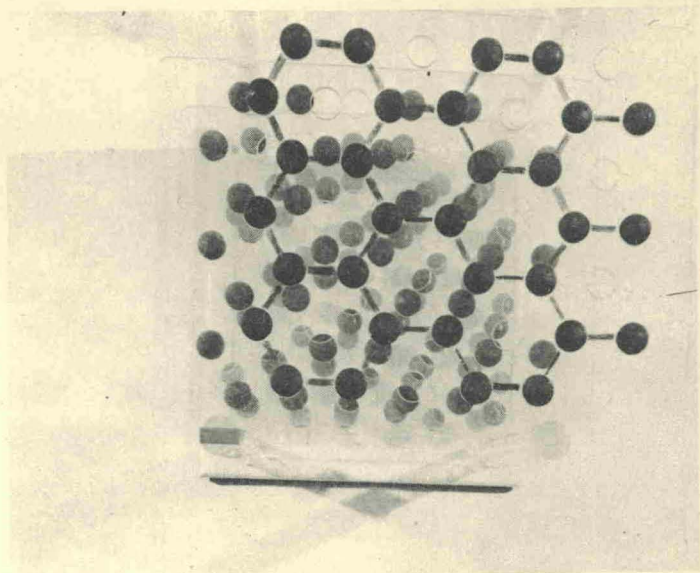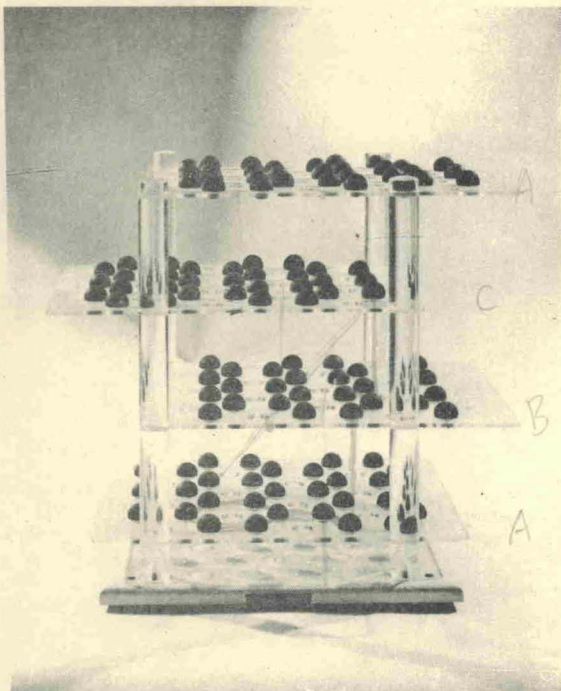
Fig. 2   The hexagonal structure of graphite.

Fig. 3   The rhombohedral structure of graphite.

structure and concluded that amorphous carbons are finely divided graphite. H. Lipson and A. R. Stokes[3] concluded that certain weak x-ray reflections, also found by G. I. Finch and H. Wilman[4a] in electron diffraction and shown not to come from the hexagonal structure, could be explained by a proper admixture of the rhombohedral structure with the hexagonal. More recently, J. S. Lukesh[5] has shown that the strongest of the reflections used by Lipson and Stokes are introduced when natural graphite is treated with bromine, thus suggesting an impurity origin of the rhombohedral structure. Also, Lukesh[6] has shown that x-ray diffraction patterns of natural graphite single crystals show reflections that are not given by either structure and that require, among other things, twinning caused by discrete rotations of parts of crystal about the c axis. Thus the details of the structure of graphite are not yet clear, although Lukesh has worked out one way of resolving the difficulties. He will publish his results soon.

It is interesting to note that still another possible structure has been proposed by Lukesh and L. Pauling,[7] as shown in Fig. 4. By a slight distortion of the hexagonal rings, observed reflections can be accounted for and, furthermore, the twin relationships can be understood. Further work by Lukesh, however, makes their interpretation dubious.

Mechanism for Growth

More recently, theories and mechanism of crystal growth having a bearing on the details of the structure of graphite have been proposed and demonstrated.[7] If graphite crystals grow, as proposed by F. C. Frank, by adding atoms to the edges of a screw dislocation in the manner shown in Fig. 5, then the stacking of the planes and the details of the structure are determined by the growth process. F. H. Horn[9] has found spirals on natural and artificial graphite crystals, as shown in Fig. 6. These spirals become visible under the microscope when a number of growth centers have combined to give a step of a few hundred Å. Areas that show no spirals may have many screw dislocations that happen to combine to give smooth areas or steps too small to be seen. Not all graphite crystals show growth spirals, but those that do not have been deformed.

Most crystals of natural graphite are somewhat impure, often deformed, and show twin markings. Their density is close to theoretical, about $2.25 g/cm^3$. Artificial graphites are porous and have bulk densities of 1.6 to $1.8 g/cm^3$. They may be made highly pure. Higher densities can be achieved also.
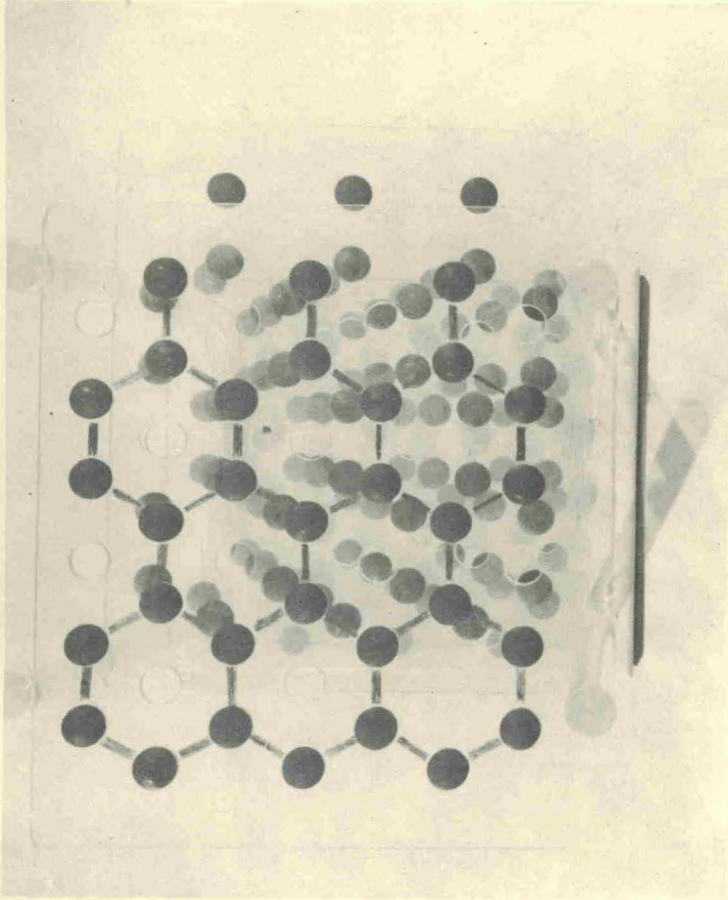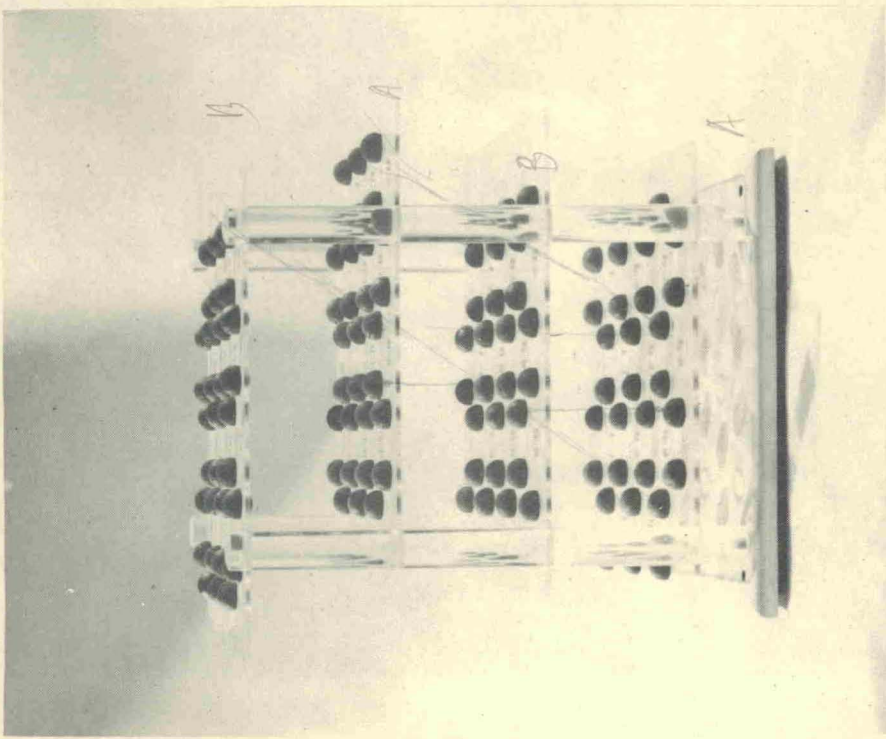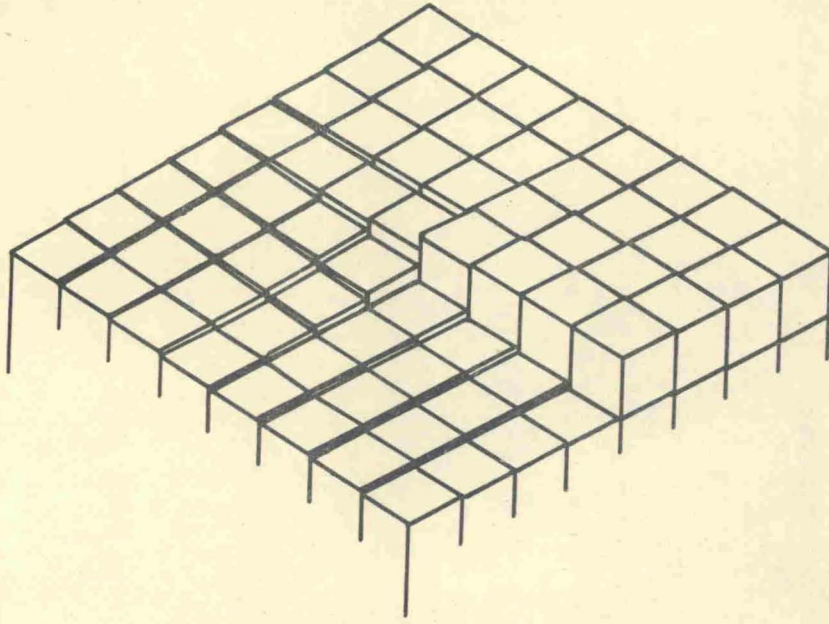
-4-

Fig. 4   An orthorhombic structure.

Fig. 5　A screw dislocation on the surface of a simple cubic crystal.

250X

500X

Fig. 6　Photomicrographs of spirals on graphite crystals.

Carbon Blacks

The formation of carbon blacks from hydrocarbons does not appear to follow the above picture of growth in the first stages. J. Biscoe and B. E. Warren[10] find that in the carbon black particles, carbon atoms are arranged regularly in hexagonal rings in the planes (a directions) and that the planes are stacked approximately equidistant and parallel. However, there is complete disorder in the orientation of the planes about their normals (the c direction), and the spacing of the planes is slightly greater than in graphite. As the carbon black in this turbostratic condition is heated above 1000°C, hydrogen is evolved, the dimensions of the regions in which parallel layer groups exist increase, and the graphitic ordering of the planes takes place; so that, at 2800°C, true graphite crystals approximately 40 x 70 Å in the c and a directions respectively are produced.

Little grain growth appears to occur in graphite, at least under commonly attained temperatures of graphitization. It is reported, however, that each small particle[11] can be converted into a crystal. That this process is influenced by impurities is apparently the basis of Acheson's patent for making artificial graphite.

The formation of carbon blacks would appear to involve condensation of hydrocarbon molecules to form large aromatic molecules, which stack like cards, parallel, but at random otherwise. As the temperature is raised, the hydrogen at the edge of the large plane molecules dissociates and carbon atoms move, probably building up graphite crystallites by the mechanism of Frank.[8] The planes least stable because of shape or size are consumed first. Hydrogen atoms bonded to the edge of these large plane molecules can make elongated molecules more stable than square ones because, as M. Bradburn, C. A. Coulson and G. Rushbrooke[13a] show, the energy of the carbon-hydrogen bond gives a negative edge tension. Impurities can both initiate screw dislocations and provide surface media through which carbon atoms can move more easily.

A still less well-defined class of carbons results from charring sugar and other organic compounds at temperatures not over 1000°C. H. L. Riley[11] concludes that the hexagonal structure is not developed completely, but that some rings are rotated out of the planes. X-ray diffraction shows that the c spacing of the planes is even greater than in the carbon blacks and that the planes themselves are poorly defined.

In summary, the forms of carbon related to graphite that have been described are:

1. Natural graphites made up of easily distinguished crystals, which may be twinned and distorted in other ways but which consist essentially of planes of hexagonal rings stacked a b a.

2. Artificial graphites containing crystals extending 50 to 100 Å in the a direction and 20-50 Å in the c direction, but otherwise similar to the above; and artificial graphites with crystals over 1000 Å in the a direction.

3. Carbons much like very finely divided graphite but containing planes stacked with random rotations about the c axis (turbostratic). Hydrogen and other impurities on the edges of the planes are important in determining the properties of these carbons.

4. Carbons in which some disorder is present in the planes and possibly some bonding between the planes. Aromatic carbon-carbon bonds are dominant, but some single bonds may exist. Impurities such as hydrogen, oxygen, nitrogen, and boron are probably important, and their presence depends on the source of the carbon.

THE ELECTRONIC STRUCTURE OF GRAPHITE

The stability of graphite at high temperatures in the absence of oxidizing agents and carbide-forming metals is due to the very strong carbon-carbon bonds in the planes. We are now used to the type of bond in aromatic hydrocarbons in which part of the binding energy is provided by electrons not confined to any given part of the structure. The extra binding energy is usually called resonance energy, because it can be described as resulting from the superposition of two or more electronic structures or spatial distributions of electrons to approximate an actual distribution. The resonant interaction of the superposed distributions gives rise to a binding energy that may be estimated by methods of quantum mechanical perturbation theory. Thus in graphite, on the average, three electrons form standard single carbon-carbon bonds and one electron per atom provides additional binding to each of the three nearest neighbors.

When in solids the energy levels (bands) and their population are such that some of the electrons may move throughout the crystal, electrical

conductivity results and we usually think of the substance as a metal. The problem of the electronic structure of graphite has been treated by P. R. Wallace;[12] by Coulson, Bradburn, and Rushbrooke;[13a,b,c] and by J. Barriol and J. Metzger.[13d] The first-mentioned writer uses molecular electronic orbitals selected for the mobile electrons and computes their behavior, i.e., the electrical and magnetic properties. Coulson, Bradburn, and Rushbrooke consider the planes large molecules, construct molecular orbitals by taking linear combinations of atomic orbitals, and calculate stabilities of various shaped crystallites as well as the distribution of electronic states versus energy. Barriol and Metzger use molecular orbitals that satisfy the periodic boundary conditions for graphite crystals and compute binding energies. Their calculation for the heat of sublimation of graphite to carbon atoms is 124.5/kcal.

The binding between layers has been studied theoretically by R. O. Brennan.[14] He computes only the repulsive forces from the molecular orbital electronic wave functions for the crystal, and assumes a Van der Waal type of attraction of magnitude to give a correct interplanar distance. He calculates that interplanar forces contribute only 3.99 kcal per mole to the stability of the graphite crystal. The difference in energy calculated for the observed stacking versus one in which the atoms are all in register is so small as to suggest that at high temperatures no order should exist in the stacking, contrary to observation.

R. S. Mulliken[15] suggests that forces between planes may be partially due to electron transfer and that this type of binding would account for the observed stacking.

THE PROPERTIES OF GRAPHITE

The characteristics of graphite that are used to advantage are:

1. Stability at high temperatures,

2. Electrical conductivity,

3. Crystalline anisotropy and weak binding between planes.

Thermodynamic Properties

We have already given the basic reasons for the stability of graphite. Calculation alone, of course, does not yield accurate values for bond energies or heats of reaction. Accurate measurements have been made of the heat of combustion of graphite and diamond.[16] Using these values together with measured heat capacities and compressibilities, the authors mentioned in reference (16) compute the free energy difference between graphite and diamond as a function of temperature and pressure, as shown in Fig. 7. Now, rates of transformation of diamond to graphite are appreciable at temperatures of several hundred degrees. Therefore, pressures in excess of 20,000 atmospheres would be required to transform graphite to diamond.

A basic thermodynamic quantity, the heat of sublimation of graphite, is less well known, in spite of a great deal of careful work aimed at determining the value by measuring vapor pressures or rates of evaporation. Experimental work by L. Brewer, P. W. Gilles, and F. A. Jenkins[17] appears to confirm the high value of a set of three allowed by the possible values of the heat of dissociation of carbon monoxide, as shown in Table I.

TABLE I

Heats of Dissociation Related to the Heat of Sublimation of Graphite

$CO(g)$	$= C(g) + O(g)$	$\Delta H^{17} =$	210.82, 227.04, or 256.18 kcal/mole
$C(s) + \frac{1}{2}O_2(g)$	$= CO(g)$	$\Delta H =$	27.202
$O(g)$	$= \frac{1}{2}O_2(g)$	$\Delta H =$	58.586
$C(s)$	$= C(g)$	$\Delta H =$	125.03, 141.25, or 170.39

A. L. Marshall and F. J. Norton[19] also obtained the high value in 1933 by measuring rates of evaporation. Objection has been raised to these values on the basis that the accommodation coefficient for the condensation

of carbon atoms on graphite may be small and may vary with temperature. Although Brewer, Gilles, and Jenkins report a careful test of this point by showing that their results do not vary with the size of the orifice of their Knudsen effusion cell, many other workers in the field are still not satisfied. Future work will resolve this question.

Whatever the heat of sublimation, the vapor pressure of carbon reaches one atmosphere only at high temperatures, near 3600°C to 3700°C (6500°F-6700°F).[20] Moreover, it appears that the pressure at the triple point is approximately 100 atmospheres;[21] consequently, direct observation of a melting point is difficult.

Much of the equilibrium chemistry of graphite may be related to the extensive thermodynamic data that have been compiled.[16,22]

The heat capacity of graphite is especially interesting because the high degree of crystal anisotropy is manifested at low temperatures by the dependence of the specific heat on T^2.[23] One may think of the heat content as due to three types of vibrations in the graphite crystal:

1. Very low frequency waves involving motions of the planes as molecules, somewhat like an accordion.

2. Intermediate frequency waves with displacements transverse to the plane, like vibrations of a drum head or waves in water.

3. High-frequency longitudinal waves moving in the planes and involving displacements that stretch the strong carbon-carbon bonds.

J. Krumhansl[24] has studied the spectrum of the normal vibrational modes of a graphite crystal and has shown that, over a certain temperature range, the crystal behaves much like a two-dimensional system, requiring that the specific heat vary as the second power of the temperature instead of as the third power, as in three-dimensional solids. Qualitatively, one degree of freedom associated with the lowest frequency modes reaches its classical equipartition value at very low temperatures, leaving only two degrees of freedom per atom to contribute to the increase of the heat capacity with temperature. Figure 8 shows the logarithm of experimentally determined values plotted versus the logarithm of the Kelvin temperature. This work of W. DeSorbo and W. W. Tyler[23] has improved the value of the entropy of graphite at room temperature. Their data are presented and summarized in Fig. 9 and Table II.
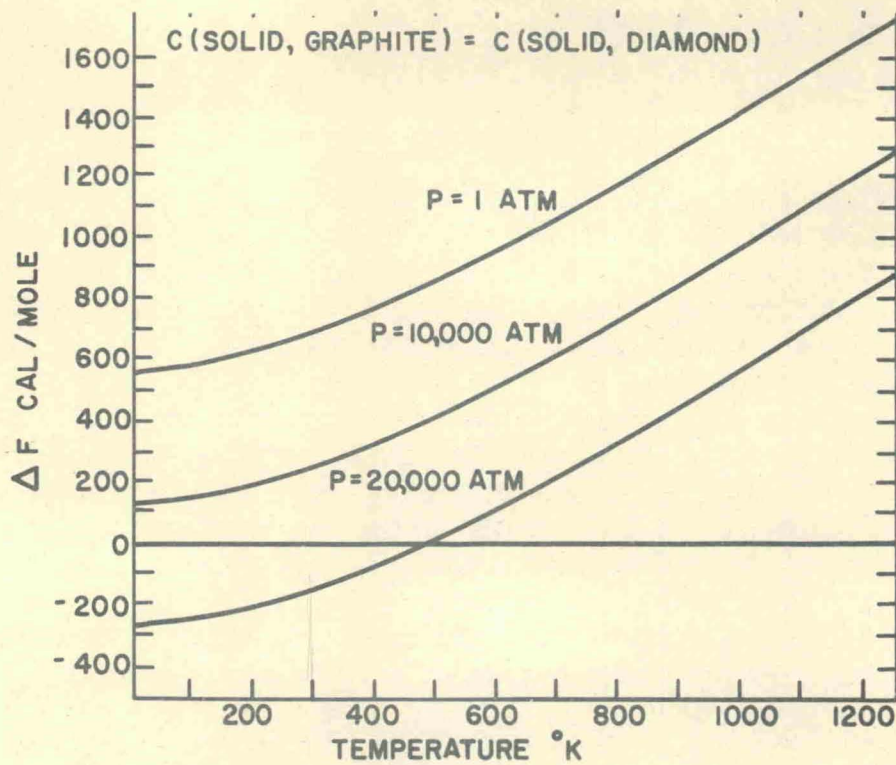
Fig. 7   The difference in free energy between graphite and
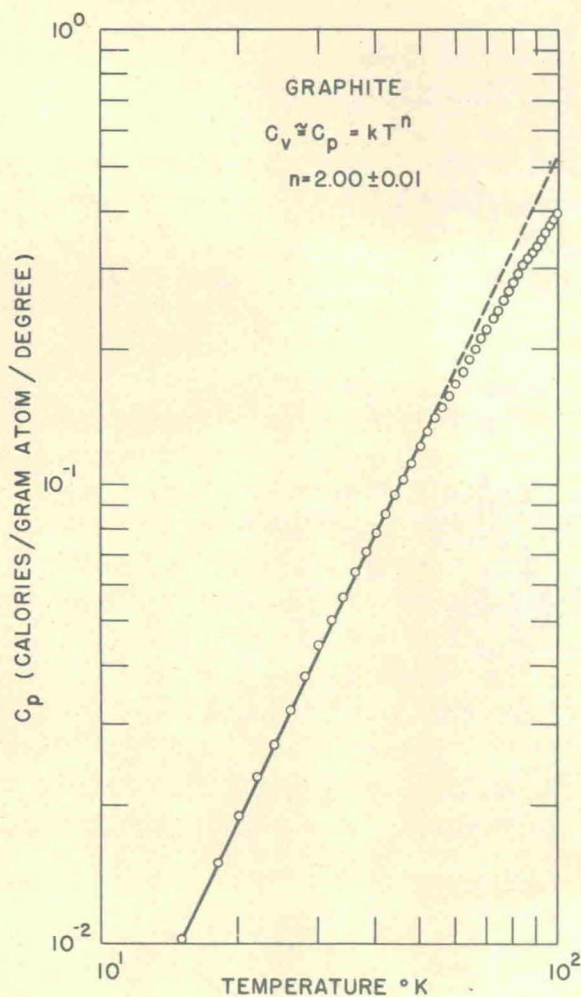diamond as a function of temperature and pressure.

Fig. 8   The dependence of
the specific heat of graphite
on temperature at low
temperatures.

TABLE II

Entropy of Graphite at 298.16°K(Cal/Mole/Degree)

Jacobs and Parks		DeSorbo and Tyler	
0-90°K extrapolated	0.182	0-13°K extrapolated	0.004
90-298.1°K graphical	1.182	13-298.16°K graphical	1.367
$S^o_{298.16}$	1.36 ± 0.02	$S^o_{298.16}$	1.371 ± 0.005

Heat capacities for graphite at higher temperatures may be obtained from the publication by the National Bureau of Standards.[16]

In addition to being more stable than diamond by virtue of binding energy, graphite also possesses the greater entropy at any temperature above 0°K because of the thermal vibrations possible and the greater volume per atom.

Electrical and Magnetic Properties

The general features of the electrical and magnetic properties may be understood in terms of the work of Wallace[12] and others.[13] The ideal infinite graphite single crystal on the basis of these calculations has the distribution of electronic energy states versus energy shown in Fig. 10. Just enough states lie below E_o to house all of the mobile electrons at 0°K. At higher temperatures, electrons are excited to states above E_o, whereupon they and the vacant states below E_o both contribute to the conductivity. According to Wallace, the number of free electrons permitted by the Fermi distribution at room temperature is 2.25×10^{-3} per carbon atom. Thus the conductivity is low. The conductivity depends not only on the number of carriers but also on their scattering as they move. Scattering by lattice waves decreases very rapidly at low temperatures and would permit the conductivity to become very large if no permanent scattering centers were present in the crystal. Measured values of the conductivity of natural graphites increase with decreasing temperature, but appear to remain finite in the range below 10°K. It must be concluded from this behavior that scattering centers for electrons are present in real crystals and that the number of carriers does not go to zero at low temperatures. From Hall effect studies[25] it can be further concluded that there is a slight excess of electrons, but their donors are not known. Graphites made by bonding

small particles with pitch followed by graphitization show increasing conductivity at room temperature. At higher temperatures a maximum is observed, followed by a decrease.

Wallace estimates that the conductivity parallel to the planes (a) is 110 times that in the perpendicular direction (c). The measured values range from 10^2 to 10^5.[26] This large anisotropy is another manifestation of the two-dimensional nature of graphite. Diamagnetic susceptibility provides another illustration of this nature also, both in theory[12] and experiment.[27]

Incompletely graphitized carbons show different electrical characteristics, their conductivities being less and, up to very high temperatures, increasing with temperature. Incompletely proved suggestions in terms of molecule size and edge impurities may be made to account for this behavior.

Although the spirals provide an additional path for current flow in the c direction, it can be shown that the effect on the anisotropy of the conductivity is negligible unless the density of dislocations should exceed 10^{10} per cm^2.

Thermal Conductivity

Two facts--(1) the value of the Lorentz, Wiederman-Franz ratio, which is the product of the electrical resistivity and the thermal conductivity divided by the absolute temperature, and (2) the low temperature dependence of the thermal conductivity--show that the thermal conductivity is not electronic as in metals. Rather, thermal energy is transported by crystal vibrations, and, while a theory is being developed, the exact reasons for the temperature dependence observed by Tyler[28] and R. Berman[29] at low temperatures are not known. A major factor, however, must be the T^2 dependence of the specific heat, and a simple theory would predict the same dependence for the thermal conductivity if boundary and permanent imperfections only scatter vibrational waves. Figure 11 shows data obtained by Tyler, which vary somewhat more rapidly than T^2. They are given here because they appear to be better than values already in the literature. A more complete account will be published later by Tyler. Energy transport by thermal vibrations in crystals falls off as T^{-1} in the high-temperature region, due to interaction of various vibrational modes. It is very likely that electronic transport becomes the more important process of the two types at sufficiently high temperature. Finely divided graphites or carbons owe their insulating value largely to the fact that conduction through the gas surrounding each particle limits the transport of heat.

SPECIFIC HEAT OF GRAPHITE
— THIS RESEARCH
□ W. NERNST ANN PHYSIK 36 395 (1911)
● A. MAGNUS ANN PHYSIK 70 303 (1923)
x C.J. JACOBS & G.S. PARKS J.A.C.S. 56 1513 (1934)
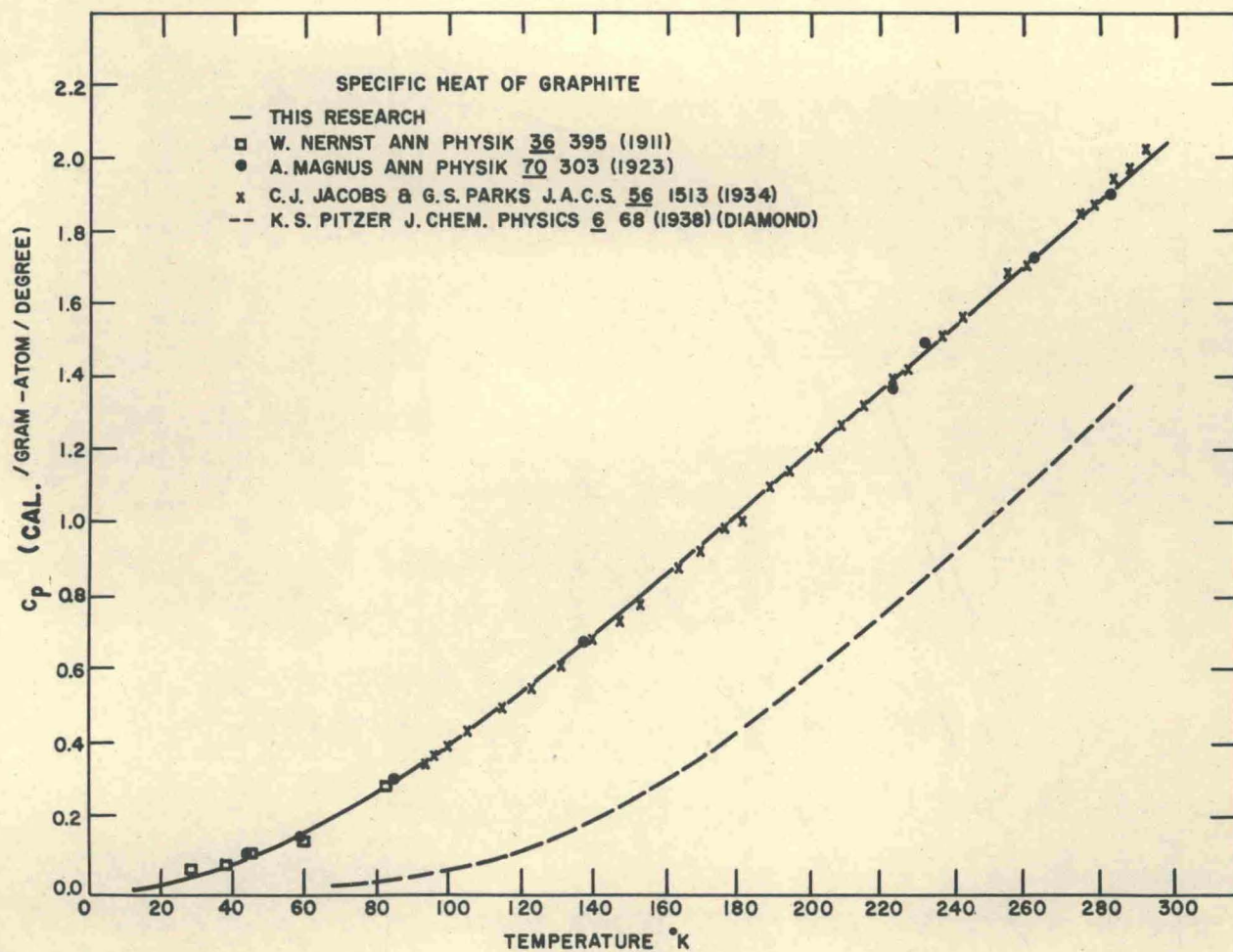-- K.S. PITZER J. CHEM. PHYSICS 6 68 (1938) (DIAMOND)

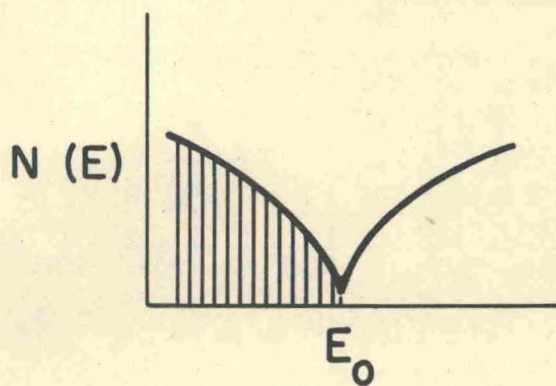Fig. 9   The specific heat of graphite.

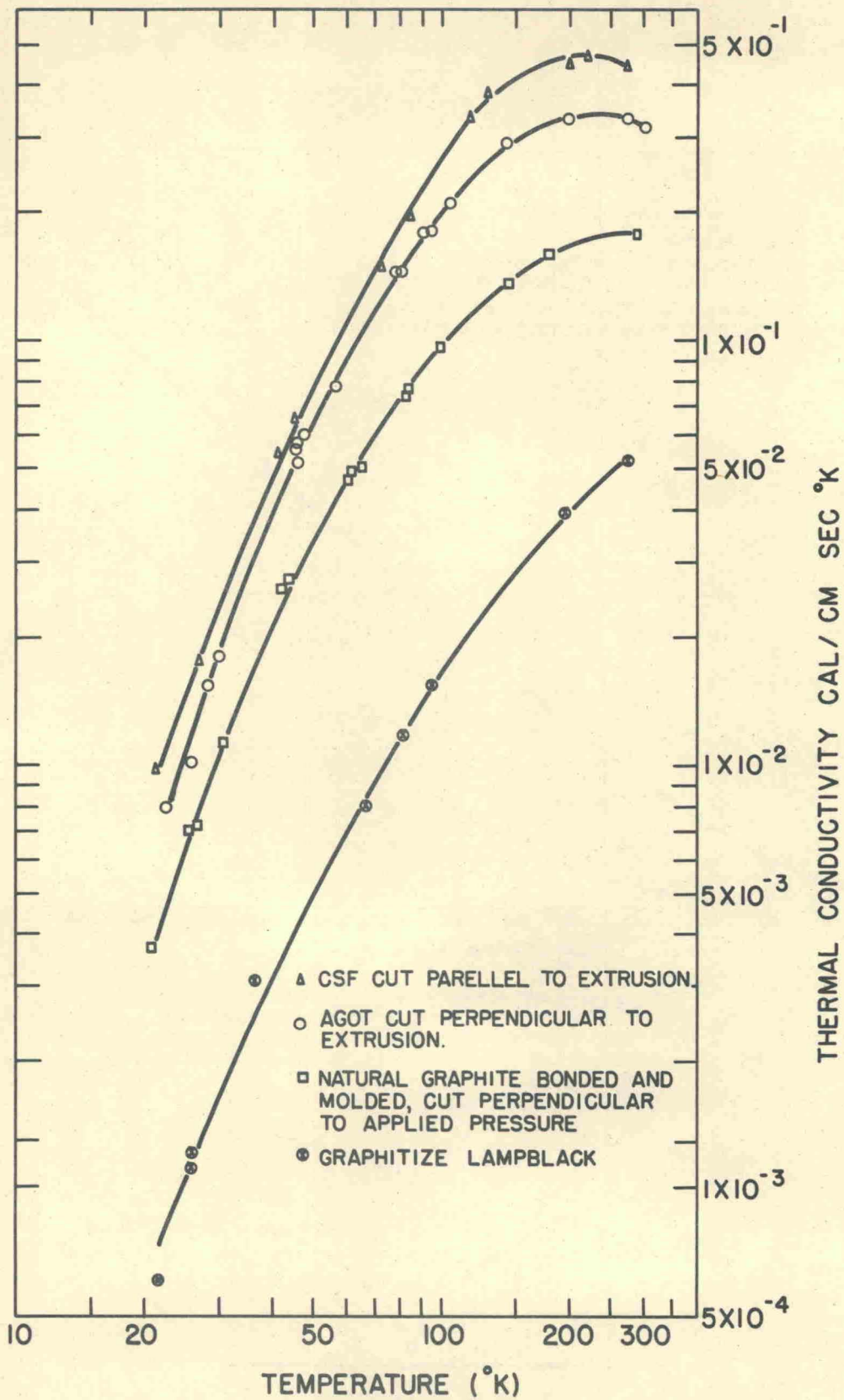Fig. 10   The distribution of electronic states versus energy.

Fig. 11 The thermal conductivity of several types of graphite
at room temperature and below.

Mechanical Properties

The weak forces between planes permit graphite to slip on the basal plane readily. This slip probably occurs without the benefit of moving dislocations. The lubricating properties of graphite have been attributed to this phenomenon, although R. H. Savage[30] has shown that another condition must be met also; namely, the presence of adsorbed films of water, ammonia, or hydrocarbons. When such adsorbed materials are absent, graphite bearings wear rapidly and the resulting dust is a very strong adsorber of nearly any gaseous substance.

Since most pieces of graphite put to practical use have a preferred orientation due to fabrication, the over-all strength of the material is anisotropic and is greatest in the direction of working. Although not a strong material, graphite is a useful high-temperature structural material in applications not requiring the presence of oxygen--in particular in certain metallurgical and ceramic equipment and apparatus. Perhaps the most interesting and valuable feature is the increase in strength with temperature to above 2400°C (4350°F).[31]

TABLE III

Types of Graphite on Which Strengths Have Been Measured at High Temperatures

Graphite Grade*	Method of Manufacture	Graphitization Temperature ($^\circ$C)	Approx. Amount of Oriented grains (%)
AUF	Extruded	3000	60
AWG	Molded	3000	30
SA-25	Molded	3000	1
C-18	Molded	2600	30
AGX	Extruded	2600	40

* National Carbon Company terms

note increase !!
with temp

7000
6000
5000
4000
AUF
AWG
3000
2000
1000

BREAKING STRESS (PSI)

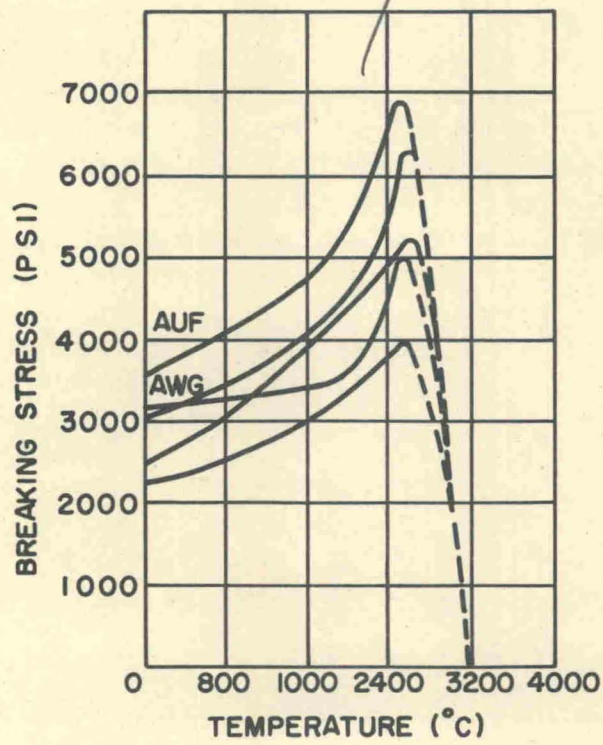0   800 1000 2400 3200 4000
TEMPERATURE (°C)

Fig. 12   The strength of several forms
of graphite as a function of temperature.

Figure 12, taken from reference (31a), illustrates the properties of several commercial artificial graphites listed in Table III. Few readily available materials are stronger than graphite above 1600°C (2900°F).

The anisotropy of thermal expansion and the resultant internal stresses in polycrystalline material must be important in explaining the variation of strength with temperature. It must also be remembered that the pores in artificial graphites provide stress concentrations. At temperatures sufficiently high for grain boundary flow, some relaxation of stress can occur. For some local stress to exceed the point required for fracture, therefore, the average stress has to be greater at high temperatures than it need be at low temperatures. S. Mrozowski[32] gives a similar explanation for the variation of strength with temperature.

Deformation due to the motion of the screw dislocations required for growth would be shear in the c direction. The author is not aware of evidence that this deformation mechanism operates.

Lamellar Compounds

There is not space in this article to discuss fully the subject of lamellar compounds of graphite. Two cases, however, illustrate the nature of the substance very interestingly and are therefore mentioned briefly.

Potassium metal reacts readily with graphite to form at least two compounds, $C_{16}K$ and C_8K.[33] It has been shown that the plane arrays of carbon atoms remain intact, and that the potassium atoms that are probably at least partially ionized are placed in regular positions between the planes. Thus one can think of an ionic compound with large plane molecule ions having a negative charge held together by positively charged ions; both electrostatic and exchange forces provide bonding. Other alkali metals react in somewhat similar although less clear-cut fashion with graphite.

Bromine also forms lamellar compounds, one of which appears to be C_8Br, although the stoichiometric relation is not definite. Riley[33] states that the bromine cannot be present as ions. However, bisulfate and nitrate ions may be introduced by electrolytic or chemical oxidation of the graphite in the presence of these ions.

Thus it is attractive, if not strictly accurate, to think of graphitic planes as plane amphoteric macro-molecules forming compounds with both electron donors and acceptors.

In summary, the unique electrical, mechanical, and chemical properties of graphite are those of large plane molecules in which the strong bonding power of the carbon atom is nearly, but not quite, satisfied by bonds lying in the planes.

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