

## FOREWORD

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Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Research Laboratory of the National Carbon Company located at Parma 30, Ohio, under the direction of J. C. Bowman, Director of Research, and W. P. Eatherly, Assistant Director of Research.

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Other reports issued under USAF Contract AF 33(616)-6915 have included:

WADD Technical Notes 61-18 and 61-18, Part II, progress reports covering work from the start of the Contract on May 1, 1960 to October 15, 1961, and the following volumes of WADD Technical Report 61-72 covering various subject phases of the work:

- Volume I      Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
- Volume II     Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
- Volume III    Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.
- Volume IV     Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
- Volume V      Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
- Volume VI     Creep of Carbons and Graphites in Flexure at High Temperatures, by E. J. Seldin.

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- Volume VII High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch.
- Volume VIII Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner.
- Volume IX Fabrication and Properties of Carbonized Cloth Composites, by W. C. Beasley and E. L. Piper.
- Volume X Thermal Reactivity of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.
- Volume XI Characterization of Binders Used in the Fabrication of Graphite Bodies, by E. de Ruiter, A. Halleux, V. Sandor and H. Tschamler.
- Volume XII Development of an Improved Large Diameter Fine Grain Graphite for Aerospace Applications, by C. W. Waters and E. L. Piper.
- Volume XIII Development of a Fine-Grain Isotropic Graphite for Structural and Substrate Applications, by R. A. Howard and E. L. Piper.
- Volume XIV Study of High-Temperature Tensile Properties of ZTA Grade Graphite, by R. M. Hale and W. M. Fassell, Jr.
- Volume XV Alumina-Condensed Furfuryl Alcohol Resins, by C. W. Boquist, E. R. Nielsen, H. J. O'Neil and R. E. Patcher.
- Volume XVI An Electron Spin Resonance Study of Thermal Decomposition Reactions of Organic Compounds, by L. S. Singer and I. C. Lewis.
- Volume XVII Radiography of Carbon and Graphite, by T.C. Furnas, Jr. and M. R. Rosumny.
- Volume XVIII High Temperature Tensile Creep of Graphites, by E. J. Seldin.
- Volume XIX Thermal Stresses in Anisotropic Hollow Cylinders, by Tu-Lung Weng.

## ABSTRACT

This paper concerns the electric and magnetic properties of a series of highly turbostratic pyrolytic graphite deposits. The diamagnetic susceptibility, Hall coefficient, and electron spin resonance  $g$  value are observed to have much larger magnitudes than corresponding measurements made on single crystals of graphite. The results are interpreted as being due to the turbostratic character of the deposit which brings about a decreased interaction between the randomly rotated graphitic planes. The overlap of the electron and hole bands is thereby reduced and as a first approximation one can interpret the results using the simple two dimensional model of Wallace. McClure's diamagnetism formula, which is based on the Wallace model, yields a maximum trace value of  $-39$  emu/g. The largest observed value is  $-33.5$  emu/g, a diamagnetism almost 50 per cent greater than the normal single crystal value of  $-22.8$  emu/g.

To obtain from theory the large variation of  $g$  shift and diamagnetism as a function of formation temperature, it is necessary that acceptors be present whose concentration decreases as the temperature of formation increases. Similar acceptors have been postulated by others to explain the properties of high temperature carbons.

This technical documentary report has been reviewed and is approved.



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## 1. INTRODUCTION

This report describes a study of the electric and magnetic properties of pyrolytic graphite. The purpose was to establish the extent to which these properties were consistent with the present understanding of single crystal graphite. The results show that, although pyrolytic graphite has many properties similar to single crystals, a proper description of the electrical properties must take into account correctly the turbostratic nature of the deposit. Turbostratic is the term used to describe stacking of the layers of graphite in such a way that successive layers are not properly oriented with respect to one another. This misorientation prevents atoms in successive layers from having their usual relationship (normally half the atoms are directly opposite one another). As a result, the interaction which produces the overlap of the electrons and hole energy bands is greatly reduced. It is the extent of overlap of the bands which is probably the most important factor in determining the electric and magnetic properties of graphite. The effect of reduced overlap in turbostratic graphite is shown most clearly by diamagnetic susceptibility. The diamagnetism, the Hall coefficient, and the electron spin resonance g shift have magnitudes in pyrolytic graphite which far exceed those of good single crystals. The decreased interaction between layer planes resulting from the turbostratic structure results in the two dimensional band model being a better description of turbostratic graphite than the three dimensional model, although this remark must be qualified as regards the g shift.

The first reported study of pyrolytic graphite was carried on in 1880 by Sawyer and Man;<sup>(1)</sup> however, use of the term pyrolytic was apparently first introduced in the middle 1950's. The studies have included investigations of densities, X-ray structure, microscopic appearance, resistivity, thermal conductivity, and more recently, the detailed electrical properties.<sup>(2, 3, 4, 5)</sup> Reports of some magnetic susceptibility measurements have also been given.<sup>(6, 7)</sup>

In this discussion, the term pyrolytic graphite will be restricted to material formed by the pyrolytic decomposition of a hydrocarbon gas on a heated substrate (ethane decomposed on graphite in our case) although it could be applied to almost any material produced by thermal decomposition of carbonaceous material. Hydrogen gas is usually added to the atmosphere to reduce gas phase decomposition with its attendant formation of soot which can be incorporated into the deposit and lead to an inferior product. In the pyrolytic material described in this report, argon was also added to reduce the rate of formation by hindering diffusion of hydrocarbon to the hot surface. The rate of formation of the deposit is, of course, one of the most significant factors determining the perfection of the product. Diefendorf<sup>(4)</sup> made deposits of widely different density at a given substrate temperature by simply varying the rate of formation. Had it been possible, it would have been

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advisable to fix the rate of formation of each deposit, but the operation was carried out a batch at a time and the rate undoubtedly changed during each deposit. However, we have held other conditions constant and have varied only the substrate temperature for the various members of the series. The only justification for this procedure is that it produced a fairly good deposit of uniformly high turbostratic character for the entire series.

Even though the set of samples we obtained was almost completely turbostatic, as determined from X-ray diffraction measurements, the magnetic properties varied widely as a function of the deposition temperature. This variation was presumably due to the variation of the Fermi level as a result of different amounts of imperfections at the different formation temperatures. However, we have not determined the nature of the imperfections which trap electrons and give rise to our observed changes in Fermi level, nor have we doped the samples to move the Fermi level by more conventional means; so we must regard the present work as only a preliminary investigation. In the future it may be desirable to study the entire set of pyrolytic materials of intermediate perfection between perfect single crystals and our highly turbostratic deposits.

It is clear that in the limit of highly perfect deposits, the electrical properties must approach those of single crystals. Klein, Straub, and Diefendorf<sup>(8)</sup> have attempted to achieve highly perfect deposits of pyrolytic graphite by heat-treatment to 3600°C of well oriented material. Even though these samples do show many of the characteristics of good single crystals, they also indicate significant deviations due to imperfections. It seems likely that microscopic cracks between the layers of the deposit still persist even after such extreme heat-treatment.

In the turbostratic pyrolytic graphite specimens which we prepared on substrates whose temperatures were varied from 1200°C to 2500°C, the following measurements were carried out: resistance, Hall effect, magnetoresistance, electron spin resonance, and diamagnetic susceptibility. A minor amount of metallographic and X-ray examination was also performed.

We have attempted to explain the results on our pyrolytic deposits by using Wallace's<sup>(9)</sup> band model of two dimensional graphite. The interplane interactions are expected to be considerably smaller in turbostratically stacked material than in single crystal graphite because of the larger c-spacing as well as the random rotation of the planes about the c-axis. Thus the two dimensional model, which, of course, ignores entirely the interplane interactions, appears to be a satisfactory first approximation. In fact, one does find qualitative agreement between the two dimensional model and the experimental Hall coefficient and diamagnetism if one takes the Fermi level as an adjustable parameter dependent upon the formation temperature. The observed g shift is, however, not at all accounted for by such a procedure and it is likely that only by taking account of interactions between atoms in different layers can the large g shift be adequately explained.



## 2. PREPARATION OF SAMPLES

The specimens of pyrolytic graphite here considered were formed by the thermal decomposition of ethylene from an atmosphere described below. They were deposited on a substrate from a carbon spectroscopic electrode shown in Figure 1. It was heated by electrical conduction to the desired temperature. This material was selected because of its purity and chemical compatibility and because its coefficient of expansion differed enough from that of the deposited material that the two could readily be separated mechanically.

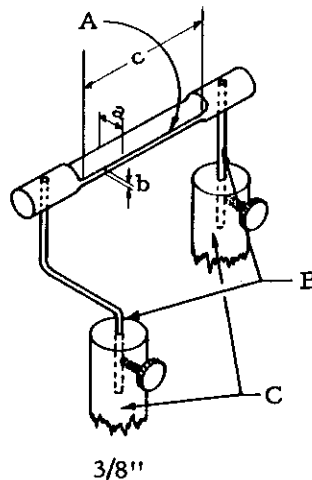


Figure 1. Substrate and Supports for the Deposition of Pyrolytic Graphite

- A - Substrate of spectroscopic carbon.  
a = ~ 4-5 mm; b = ~ 1.5 mm; c = ~ 30-35 mm.
- B - Supports of 50 mil tantalum wire.
- C - Copper connectors to Kovar rods.

The pyrolytic graphite was deposited slowly from an atmosphere of about 5-10 mm  $C_2H_4$ , 12-14 mm  $H_2$ , and 285 mm Ar. The hydrogen present reacted with any hydrocarbon radicals or carbon ions formed on the hot surface but returned to the gas phase and thus prevented the "sooting up" of the Pyrex bell jar, which would have interfered with accurate temperature measurement. The argon reduced the collision frequency between hydrocarbon and substrate, thus assuring slower growth and more perfect structure of the material. The argon also reduced the thermal conductivity of the atmosphere, thereby helping in the cooling of the bell jar system.

The preparation system is shown in Figure 2. The specimen A was mounted under the 7-inch diameter bell jar resting on the stainless steel base plate B. The plate was equipped with copper cooling coils, and the seal was made using a dry neoprene O-ring and "Q" wax on the outside of the system. Several blowers kept the wax and seal cool. Specially built

insulated leads C of  $\frac{1}{4}$ -inch Kovar rods were mounted in the plate B. A thermocouple and an NRC ionization gauge were attached at D. Ethylene and hydrogen pressures were measured on a 0-20 mm Dubrovin gauge E and the total pressure on the Hg manometer F.

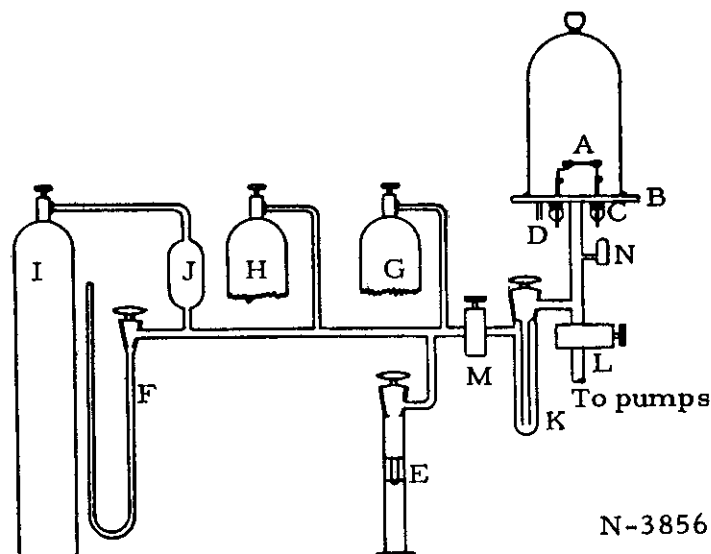


Figure 2. Vacuum System for the Preparation of Pyrolytic Graphite

Phillips reagent grade ethylene G and Linde lamp grade argon H were used as received, but the hydrogen I was passed through a Deoxo unit J. All gases were passed through the dry-ice cooled trap K.

In an actual experiment, the system was evacuated and the specimen degassed until the pressure in the system with the substrate hot was about  $3 \times 10^{-6}$  mm Hg. Then the Veeco valve L was closed and the reacting gases admitted in the order  $C_2H_4$ ,  $H_2$ , Ar. Veeco valve M was then also closed and the specimen A quickly brought to its predetermined temperature. This temperature was measured with a calibrated Leeds and Northrup optical pyrometer. The heating current was controlled by a Variac in the input side of the stepdown transformer used to provide the large current required by this low-resistance object. The current had to be adjusted manually as the deposit grew. The maximum current usable here was 100 amperes because of equipment limitations.

When the current, which of course rose during the deposition, had remained constant for a few minutes, valve L was opened and the heating current shut off. Then valve M was also opened and, after 10-15 minutes of pumping and cooling, the procedure was repeated until enough pyrolytic graphite had been deposited to raise the heating current required to 100 amperes. Details varied, of course, with substrate dimensions and with the desired temperature of deposition.

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In a typical deposition at 2250°C, the heating current for the empty substrate was 36 amps. The atmosphere contained 8 mm C<sub>2</sub>H<sub>4</sub>, 12 mm H<sub>2</sub>, 285mm A. Enough graphite was deposited during the next 12 minutes to bring the heating current to 50 amps. This procedure was repeated four more times -- evacuate 15 minutes, fill, deposit -- at which point the heating current was 96 amps. Then the system was pumped out once more, allowed to cool for two hours, and brought to atmospheric pressure using the bleeder valve N.

At lower temperatures, thicker deposits could be built up; however, the reactions took much longer. This method (using H<sub>2</sub>) cannot be used above 2500°C because H<sub>2</sub> will actually remove C from the deposit to form C<sub>2</sub>H<sub>2</sub>. One must remember that above 2000°C, C<sub>2</sub>H<sub>2</sub> is thermodynamically a favored species in the C-H system.

### 3. METALLOGRAPHIC AND X-RAY EXAMINATION

Metallographic examination of the specimens showed the growth cone structure characteristic of pyrolytic deposits grown at relatively rapid rates from carbonaceous gas. Fairly large regions of material result with poor c-axis orientation, indicated by the fact that the normals to the particular part of the deposit lie at 10° to 15° from the normal to the plane of the substrate. Materials with this growth cone structure also show a knobby surface and it is beneath the knobs that microcracks can reasonably be expected to form (especially after heat-treatment). Thus our examination shows that our specimens must not be regarded as adequate for orientation dependences of the material properties nor would such measurements as c-axis resistivity be meaningful because the current flow cannot be at all plane parallel. These conclusions are in accord with the magnetoresistance measurements which also showed the effects of inhomogeneities. In many cases, the magnetoresistive effect was positive and the results were generally erratic. Such magnetoresistance is to be expected in inhomogeneous samples because the current flow is not always perpendicular to the magnetic field.

A brief X-ray examination of our samples consisted of determination of the c spacings and a qualitative observation of the asymmetric (hk) lines. Both establish the highly turbostratic nature of the deposits. The basic process of formation of graphite from carbonaceous material has been studied by Franklin<sup>(10)</sup> using X-ray methods. She finds that graphitization is a process of the growth of layers which are in stacks at the expense of nonstructural material. She also finds that parallel layers which have the correct orientation in the stack have the spacing between layers of 3.35 Å, characteristic of perfect single crystals, whereas the turbostratic component with its rotated parallel layers has a spacing of 3.44 Å. The spacing measured on a given specimen yields a weighted average of the above two values with a small correction due to the c spacings intermediate between those values which occur for layers adjacent to an ordered region. She arrived at the following formula for the fraction of layers in properly oriented groups in terms of the observed c spacing,

$$d = 3.440 - 0.086(1 - p^2)$$

where d is the spacing between planes and p is the proportion of disoriented layers.\* In terms of Franklin's formula, all the pyrolytic materials in the series considered here were very highly turbostratic, c/2 ranging between 3.42 Å and 3.44 Å for all specimens. The value 3.42 Å corresponds to about 87 per cent randomly rotated planes and 3.44 Å is, of course, 100 per cent turbostratic. The measured values of interlayer spacing are given in Table 1.

\* The slight corrections to this formula by Bacon<sup>(11)</sup> are not significant for highly turbostratic material.

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Table 1. Interlayer Spacing in Pyrolytic Graphite of P1 Series

Formation Temperature °C	C/2, A	Turbostratic Percentage
1600	3.43	94
1800	3.44	100
2000	3.44	100
2200	3.42	87
2300	3.42	87
2400	3.44	100
2500	3.44	100
2600	3.43	94

From a crystallographic viewpoint, graphite occurs as hexagonal (the common form), rhombohedral (a metastable crystallographic modification which goes over to the hexagonal form on heat-treatment) and turbostratic graphite. While not strictly a crystallographic modification of graphite, turbostratic material is of interest because it is present in greater or smaller degree in all graphite and it is quite significant in the effect which it can produce in the electrical properties. The availability of these highly turbostratic samples is fortunate because it allows the study of this material in nearly pure form. In a sense these specimens are single crystals of turbostratic graphite.

#### 4. MAGNETIC AND ELECTRICAL PROPERTIES

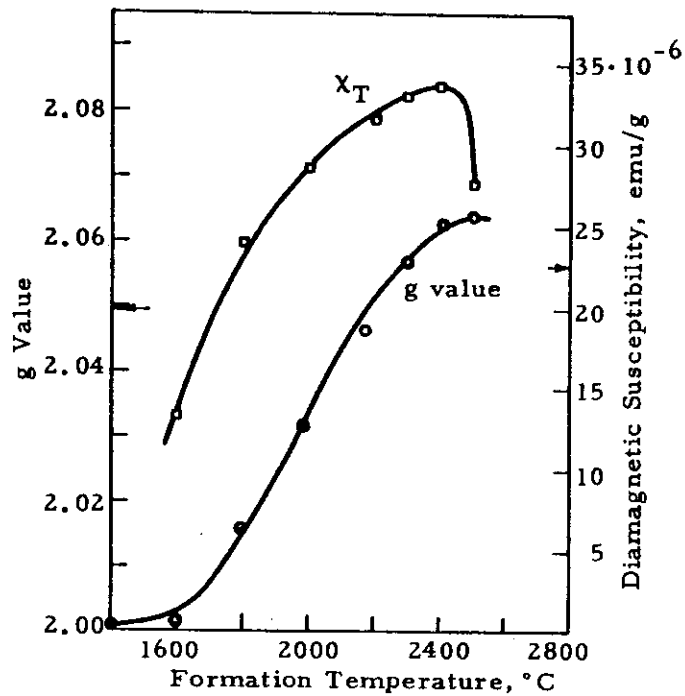
The diamagnetic susceptibility measured on these pyrolytic specimens is the largest yet reported for any form of graphite. The trace susceptibility, the sum of susceptibilities measured in three orthogonal directions, is shown in Figure 3 and has a maximum value of  $-33.5 \times 10^{-6}$  emu/g which is to be compared to  $-22.8 \times 10^{-6}$  emu/g for the best single crystal measurement. The trace susceptibility is used for comparison of polycrystalline specimens with single crystals because it does not depend on the degree of preferred orientation of the crystallites. The trace is a simple scalar quantity, a bulk property of the material. The results of the individual measurements as well as the trace susceptibility are shown in Table 2. The method of measurement and a description of the apparatus are given by Soule and Nezbeda. <sup>(7)</sup>

Table 2. Diamagnetic Susceptibility of Pyrolytic Graphites vs. Deposition Temperature

Deposition Temperature	Diamagnetic Susceptibility, $10^{-6}$ emu/gram			$\chi$ Total
	$\chi_{\perp}$	$\chi_{\perp}$	$\chi_{\parallel}$	
1600°C	-2.77	-2.81	- 7.71	-13.2 <sub>9</sub>
1800	-3.88	-3.88	-16.1 <sub>8</sub>	-23.9 <sub>4</sub>
2000	-2.87	-2.88	-21.7 <sub>7</sub>	-27.5 <sub>2</sub>
2200	-3.18	-2.91	-25.4 <sub>1</sub>	-31.5 <sub>0</sub>
2300	-2.94	-2.98	-27.0 <sub>0</sub>	-32.9 <sub>2</sub>
2400	-3.74	-3.79	-26.0 <sub>0</sub>	-33.5 <sub>3</sub>
2500	-3.10	-3.30	-21.1 <sub>0</sub>	-27.5 <sub>0</sub>

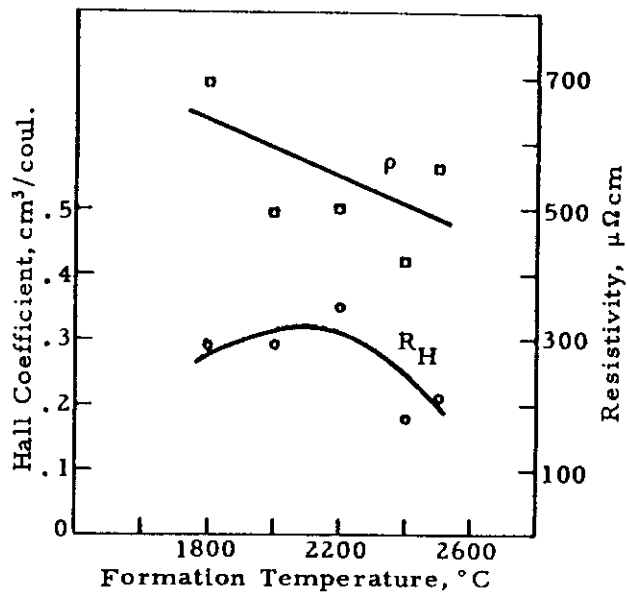
It is reasonable to ascribe the large diamagnetism of pyrolytic graphite to the effects of turbostratic stacking. McClure has made band theoretical calculations of the diamagnetism of single crystal hexagonal graphite <sup>(12)</sup> as well as that of two dimensional graphite. <sup>(13)</sup> Two dimensional graphite, which has no interlayer interactions, has a theoretical trace susceptibility of  $-39 \times 10^{-6}$  emu/g while pure hexagonal graphite where interlayer interactions cause a band overlap of 0.03 ev has a trace susceptibility of only  $-22.8 \times 10^{-6}$  emu/g. <sup>(14)</sup> Our pyrolytic graphite, whose interlayer interaction we expect to be intermediate between these extremes, also has a diamagnetism of intermediate value. McClure <sup>(15)</sup> has estimated that the diamagnetism of fully turbostratic graphite should be about 80 per cent of the value for the two dimensional form; the observed value is 86 per cent. The reason for the 14 per cent difference is that, for random orientations of planes, a certain fraction will have very nearly the required angle for interplane interaction and a certain amount of overlap will be introduced.

In addition to the diamagnetism, the Hall coefficient, resistivity, and electron spin resonance g value measured on the P1 series of pyrolytic graphites are shown in Figures 3 and 4. (The arrows in Figure 3 correspond



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Figure 3. Diamagnetism and g Value of Pyrolytic Graphite



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Figure 4. Hall Coefficient and Resistivity of Pyrolytic Graphite

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to single crystal values.) One must reconcile the relatively constant Hall coefficient and resistivity for the series of deposition temperatures with the large variation which occurs in the  $g$  value and diamagnetism. As the  $c$  spacing, and thus the turbostraticity, of the series is nearly constant it is a fair assumption that the changes are due to a shift in Fermi level. Mrozowski and Chaberski<sup>(16)</sup> and others have observed that the Hall coefficient of an ordinary coke-base graphite goes through a maximum as a function of heat-treatment temperature. Other electrical properties also confirm this shift in Fermi level as a function of heat-treatment and although the nature of the imperfections which act as electron traps is not known, their existence seems well established.

It is probable that an energy band structure applicable quantitatively to turbostratic graphite can be worked out. Although the simple two dimensional theoretical model of Wallace<sup>(7)</sup> seems to fit turbostratic graphite qualitatively, it does not fit precisely. The reason the two dimensional model agrees as well as it does is that the interplane interactions, which have a strong effect in single crystal graphite, are quite weak in the turbostratic modification and to a first approximation may be ignored. The interplane interactions are smaller in turbostratic than in either the hexagonal or the rhombohedral form because of the larger interplane distance and the effect of random rotations. However, there are small deviations of the experimental values for the diamagnetism from the predictions of the two dimensional band theory. There is also a complete inadequacy of the two dimensional band theory of the  $g$  shift to account for the magnitude or sign of the effect. Both of these discrepancies show that the three dimensional character of the material must be taken into account in a complete theory. The explanation of the magnetic properties of turbostratic graphite seems to be that the large diamagnetism and Hall coefficient have their origin in the reduced band overlap due to the turbostratic character of the deposit. The large  $g$  shift, on the other hand, seems to arise mainly from the three dimensional interplane interaction. This conclusion follows from the insufficiency of the theoretical two dimensional  $g$  shift (given in a later section) and from the adequate magnitude of the theoretical  $g$  shift in single crystals.<sup>(17)</sup> Although the single crystal theory cannot be applied directly to turbostratic graphite, it seems reasonable that the same type of interaction is responsible for the large effect in both cases.



5. COMPARISON OF PYROLYTIC GRAPHITE MEASUREMENTS  
WITH TWO DIMENSIONAL THEORY

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We now turn our attention to the quantitative comparison of the data on pyrolytic graphite to the two dimensional model. The Fermi level shift is taken as an adjustable parameter whose value depends on perfection and thus on the deposition temperature of the deposit. Because of the finite though small interaction between planes in turbostratic material, we do not expect the absolute magnitudes of the various effects to be in exact accord with the simple theory. We do, nonetheless, expect the variation of these quantities with Fermi level to be closely that of the two dimensional model. While our results cannot confirm that the electrical properties are set by the change in Fermi level alone, they are (with the exception of a detailed fit of the g shift) at least consistent with such a picture.

The g shift is given roughly by the equation <sup>(18)</sup>

$$\Delta g = \frac{\lambda_{so}}{\Delta E}$$

where  $\lambda_{so}$  is the spin orbit coupling constant and  $\Delta E$  is the Fermi level shift. The rise <sup>so</sup> in g shift with deposition temperature suggests that  $\Delta E$  is decreasing in magnitude and that the Fermi level is approaching the Brillouin zone corner. Let us now see if the other electrical properties are consistent with such a variation.

The increase in diamagnetism as a function of heat-treatment can also be accounted for by decreasing  $\Delta E$  as is shown by McClure's susceptibility formula for two dimensional graphite

$$\chi = -\frac{0.00146}{T} \gamma_0^2 \operatorname{sech}^2 \frac{\Delta E}{kT}$$

where T is the absolute temperature,  $\Delta E$  is the Fermi energy shift ( $\Delta E = 0$  for material with no acceptors or donors), k is Boltzmann's constant and  $\gamma_0$  is an energy band parameter of graphite estimated to be 2.8 ev. This expression evaluated at room temperature with  $\Delta E = 0$  is -38 emu/g. This diamagnetism, added to three times the core diamagnetism, gives the trace value of -39 emu/g. The theoretical variation of  $\chi$  with  $\Delta E$  is shown in Figure 5, which also shows the variation of the Hall coefficient with  $\Delta E$ .\*

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\* Figure 5 is very similar to Eatherly's <sup>(19)</sup> plots for the theoretical variation of these properties with change of Fermi level in two dimensional graphite. We have added the scale for the absolute value of the Hall coefficient. He used the Landau-Peierls formula for susceptibility which gives the correct dependence of  $\chi$  on Fermi level but as McClure established <sup>(13)</sup> is much too small in magnitude. The curve, which is normalized, is nonetheless correct as shown.

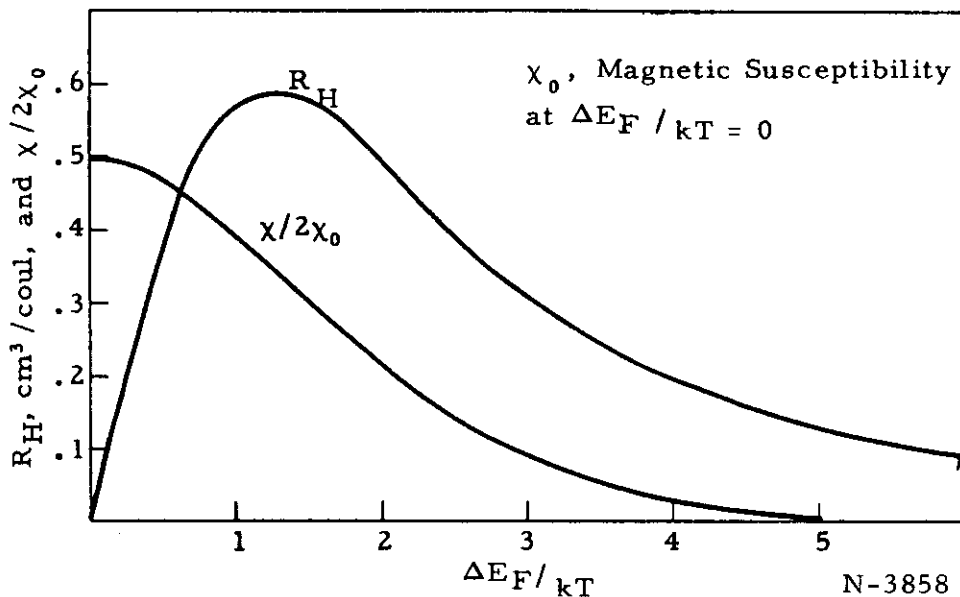


Figure 5. Susceptibility and Hall Effect of Two Dimensional Graphite vs. Fermi Level (taken from NAA-SR-146 by W. P. Eatherly)

To be consistent with the small variation in Hall coefficient, the Fermi level must be near the region where the Hall coefficient reaches its maximum (Figure 5). If, as the deposition temperature goes from 1600° to 2600° C, the parameter  $\frac{\Delta E_F}{kT}$  were to go from 2.5 to 0.75, the Hall coefficient would vary by only about 50 per cent while the diamagnetism would increase by about a factor of three. This variation is within the range observed in these properties (as shown in Figures 3 and 4).

The magnitude of the observed Hall coefficient is only about 60 per cent of the maximum value given in Figure 5. This discrepancy could be due to electrons and holes not having the same mobility, as they were assumed to have by Eatherly, or it could be, as McClure suggests, that interactions between layers prevent the two dimensional model from being strictly applicable to turbostratic material. To show how the Hall coefficient may be expected to behave as one goes from two dimensional to three dimensional graphite one proceeds as follows. The equation for the Hall coefficient (in  $\text{cm}^3/\text{coulomb}$ ) for mixed conduction given by Wilson<sup>(20)</sup> can be written

$$R = \frac{1}{e} \frac{p - b^2 n}{(p + bn)^2}$$

where p and n are the number of holes and electrons per  $\text{cm}^3$ , respectively, e is the electron charge in coulombs, and b is the ratio of electron mobility to

hole mobility. To evaluate this expression for the various levels of doping, we have taken the unpublished theoretical results of J. W. McClure for the densities of electrons and holes at 300 °K in both two dimensional and three dimensional graphite. Thus we obtain the required values of p and n as a function of Fermi level shift. The result of putting these numbers in the equation above is shown in Figure 6 where we have plotted the Hall coefficient vs. doping for two dimensional graphite and for three dimensional hexagonal graphite. Also shown is the simple one band Hall coefficient. The curves for the Hall coefficient of each type of graphite are not unique in that the Hall coefficient for mixed hole and electron conduction depends upon the ratio b of the mobility of electrons to that of holes. The curves for hexagonal graphite show three values of b, b=1.1 which is thought to apply to pure graphite, b = 1 and b = 0.5. The series shows the increasingly positive Hall coefficient one obtains as the electron mobility decreases (for a given doping level). The limit is reached when either n = 0 or the electron mobility is zero, in either case, the single band curve is obtained.

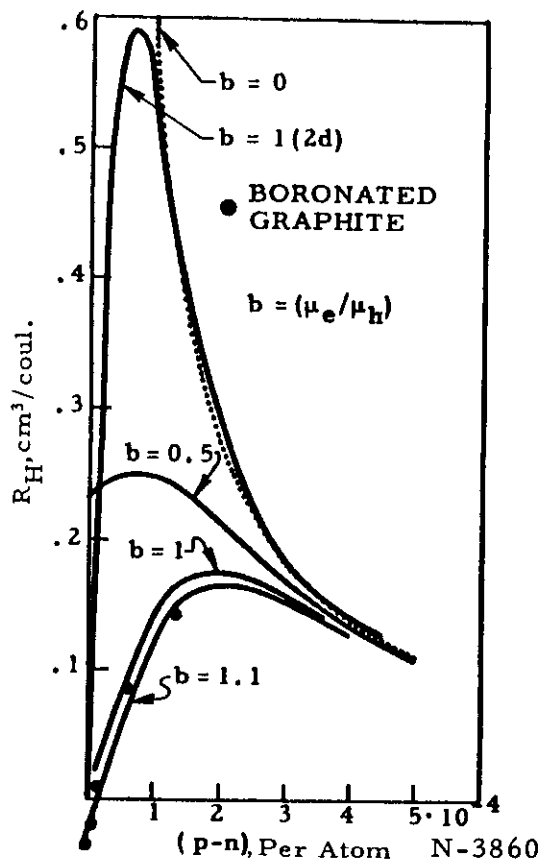


Figure 6. Hall Coefficient vs. Doping for Graphite at 300 °K

Figure 6 shows that, although the large Hall coefficients of pyrolytic graphite are not incompatible with either the two or three dimensional band models, the two dimensional model is somewhat more reasonable. It is not possible to say at this time exactly what value the mobility ratio b will have, but a value near unity is quite likely. The points for boronated single crystal graphite show that this is the case in that material.<sup>(21)</sup> In pyrolytic graphite where the disorder of the material determines the mean free path, and the effective masses of electrons and holes are expected to be very nearly the same, the assumption that b = 1 would seem to be quite justified. The Hall coefficient data thus support a model of turbostratic graphite with a band structure intermediate between the two dimensional and three dimensional hexagonal models.

The resistivity variation of Figure 5 is the result of two opposite trends; as the perfection of the deposit increases at higher deposition temperatures, the mean free path of the charge carriers increases but the number of carriers available to carry current goes down. The resistance is about an order of magnitude greater than that of single crystals which shows that the mean free path is almost completely set by the perfection of the deposit and it is thus very difficult to deduce anything about the band structure from this measurement.

## 6. EVALUATION OF THE $g$ SHIFT OF THE TWO DIMENSIONAL MODEL

We have made a detailed evaluation of the theoretical  $g$  shift of two dimensional graphite as a function of Fermi level. McClure and Yafet<sup>(17)</sup> obtain as the  $g$  shift of a state of energy  $\epsilon$  in two dimensional graphite

$$\delta g = \pm \frac{a^2 \lambda_{so}}{\epsilon}$$

where  $\lambda_{so}$  is the spin orbit coupling constant and  $a^2$  is a parameter which describes the admixture of  $d$  wave function to the  $p$  electrons which make up the conduction states. The positive sign corresponds to electron states and the minus to holes.

It is immediately apparent that there is a disagreement in sign between the two dimensional model and the observed  $g$  shift in pyrolytic graphite. The measured Hall coefficient is positive indicating a predominance of holes. The observed  $g$  shift is positive whereas the theory indicates a negative value. This factor, however, may be a simple sign error in the theory. For the moment, however, we will ignore the sign difficulty.

To evaluate the above expression for an arbitrary Fermi level, we must average over all the states which contain unpaired electrons, i. e., over all the states on the Fermi surface. Thus

$$\delta g = \frac{a^2 \lambda_{so} \int_{-\infty}^{\infty} \frac{|\epsilon|}{\epsilon} \frac{\partial f}{\partial \epsilon} d\epsilon}{\int_{-\infty}^{\infty} |\epsilon| \frac{\partial f}{\partial \epsilon} d\epsilon},$$

where we have taken the zero of energy at the point of contact between the valence and conduction bands. The density of states per atom given by Wallace<sup>(21)</sup> is

$$\frac{N(\epsilon)}{N} = \frac{2|\epsilon|}{\pi \sqrt{3} \gamma_0^2},$$

and it is this term which introduces the absolute value of  $\epsilon$  in the expression for the  $g$  shift. The Fermi function  $f$  is

$$f = \frac{1}{e^{\frac{\epsilon - \Delta E}{kT}} + 1}$$

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and its derivative is

$$\frac{\partial f}{\partial \epsilon} = \frac{-\frac{1}{kT} e^{\frac{\epsilon - \Delta E}{kT}}}{\left[ e^{\frac{\epsilon - \Delta E}{kT}} + 1 \right]^2} .$$

Rewriting the expression for  $\delta g$  to remove the absolute value signs, we have

$$\delta g = a^2 \lambda \text{ so } \left[ \frac{\int_{-\infty}^0 -\frac{\partial f}{\partial \epsilon} d\epsilon + \int_0^{\infty} \frac{\partial f}{\partial \epsilon} d\epsilon}{\int_{-\infty}^0 -\epsilon \frac{\partial f}{\partial \epsilon} d\epsilon + \int_0^{\infty} \epsilon \frac{\partial f}{\partial \epsilon} d\epsilon} \right] .$$

These integrals may all be evaluated readily, for example

$$\int_{-\infty}^0 -\frac{\partial f}{\partial \epsilon} d\epsilon = \int_0^{\infty} \frac{\partial f}{\partial \epsilon} d\epsilon = \int_0^{\infty} \frac{e^{\frac{\epsilon - \Delta E}{kT}}}{\left[ e^{\frac{\epsilon - \Delta E}{kT}} + 1 \right]^2} \frac{d\epsilon}{kT} = -2 \int_0^{\infty} \frac{d\epsilon / 2kT}{\left[ e^{\frac{\epsilon - \Delta E}{2kT}} + e^{-\frac{(\epsilon + \Delta E)}{2kT}} \right]^2}$$

$$= -2 \int_{\frac{-\Delta E}{2kT}}^{\infty} \frac{dx}{\left[ e^x + e^{-x} \right]^2} \quad \text{where } x = \frac{\epsilon - \Delta E}{2kT}$$

$$= \left. -\frac{1}{2} \tanh x \right|_{\frac{-\Delta E}{2kT}}^{\infty} = \frac{1}{2} \left( 1 - \tanh \frac{\Delta E}{2kT} \right) .$$

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Also since

$$\int_0^{\infty} \frac{\partial f}{\partial \epsilon} d\epsilon = \frac{1}{2} \left( -1 - \tanh \frac{\Delta E}{2kT} \right),$$

the numerator of the bracket in the expression for  $\delta_g$  is

$$- \tanh \frac{\Delta E}{2kT}.$$

To evaluate the integrals in the denominator of the expression for  $\delta_g$  we integrate by parts

$$\begin{aligned} \int_0^{\infty} \epsilon \frac{\partial f}{\partial \epsilon} d\epsilon &= \epsilon f \Big|_0^{\infty} - \int_0^{\infty} f d\epsilon \\ &= - \int_0^{\infty} \frac{d\epsilon}{e^{\frac{\epsilon - \Delta E}{kT}} + 1} = -kT \int_0^{\infty} \frac{\frac{d\epsilon}{kT}}{e^{\frac{\epsilon - \Delta E}{kT}} + 1} \\ &= -kT \int_{\frac{-\Delta E}{kT}}^{\infty} \frac{dx}{e^x + 1} = -kT \ln \left. \frac{e^x}{1 + e^x} \right|_{\frac{-\Delta E}{kT}}^{\infty} = +kT \ln \frac{e^{\frac{-\Delta E}{kT}}}{1 + e^{\frac{-\Delta E}{kT}}}, \end{aligned}$$

where  $x = \frac{\epsilon - \Delta E}{kT}$ .

One can experience trouble with the boundary condition at  $-\infty$  in the integral

$$\int_0^{-\infty} \epsilon \frac{\partial f}{\partial \epsilon} d\epsilon$$

but the resulting divergence is a peculiarity of filling bands to

negative infinite energy and need not concern us. The other integral in the denominator is thus obtained by replacing  $\frac{-\Delta E}{kT}$  by  $\frac{+\Delta E}{kT}$  and integrating from 0 to  $\infty$ .

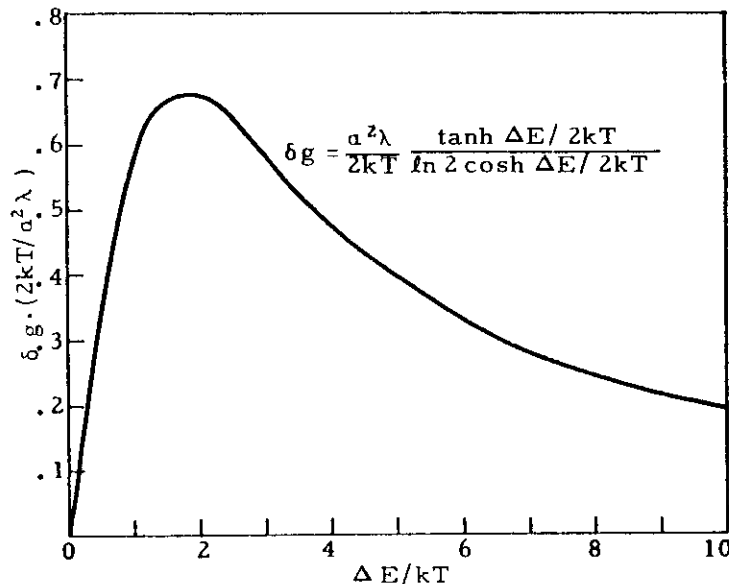
Thus

$$\delta g = \frac{a^2 \lambda}{kT} \left[ \frac{-\tanh \frac{\Delta E}{2kT}}{\ln \frac{1}{e^{\frac{\Delta E}{kT} + 1}} + \ln \frac{1}{e^{\frac{-\Delta E}{kT} + 1}}} \right],$$

or by rearranging the denominator

$$\delta g = \frac{a^2 \lambda}{2kT} \left[ \frac{\tanh \frac{\Delta E}{2kT}}{\ln 2 \cosh \frac{\Delta E}{2kT}} \right].$$

In Figure 7 we have shown the functional dependence of the g shift and the similarity to the Hall coefficient is clear. It is to be noted, however, that the variation of the two dimensional  $\delta g$  as the Fermi level is varied from  $\frac{\Delta E}{kT} = 2.5$  to  $\frac{\Delta E}{kT} = 0.75$  is not at all the variation shown by the experimental results. The theoretical result shows a maximum whereas the experiment indicates a monotonic increase. This difference between the theoretical two dimensional band model of the g shift and experiment is the second of three points of disagreement. The first was the sign difficulty mentioned earlier, and the third is the fact, discussed in the next paragraph, that the magnitude of the observed g shift is much larger than the above formula would indicate.



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Figure 7. The g Shift of Two Dimensional Graphite vs. Fermi Level Shift/kT

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The magnitude of the two dimensional g shift indicated by the preceding formula is about 0.004. In this estimate we have used pure 3 d wave functions ( $\alpha^2 = 1$ ) and we have taken  $\lambda_{3d} = 2.2 \times 10^{-4}$  ev., the value which McClure and Yafet<sup>(17)</sup> find adequate to account for the g shift of single crystal graphite. The observed g shift is 0.065, more than a factor of ten greater than the estimate. The g shift of turbostratic graphite must therefore arise from interaction between atoms in different planes. The three dimensional aspect of turbostratic graphite is thus clearly evident in the large g factor.



## 7. CONCLUSIONS

The pyrolytic graphite samples described in this report are almost perfect examples of turbostratic single crystals. The usual energy band picture of hexagonal graphite does not accurately describe the electric and magnetic properties of such turbostratic material. However, a band structure intermediate between the pure two dimensional band model of Wallace and the three dimensional band picture will at least describe some properties reasonably well.

The principal observations which show unusual properties as a result of the turbostratic nature are:

1. The diamagnetism is nearly 50 per cent greater in some of the pyrolytic specimens than in the best single crystals.
2. The Hall coefficient in the pyrolytic material is larger than expected on the basis of the band theory of hexagonal graphite (except for the unlikely possibility that the holes are many times more mobile than electrons).
3. The g shifts are larger in pyrolytic graphite than in any form of graphite yet measured. Single crystals whose Fermi levels had been shifted by various amounts had smaller g shifts than occurred in the pyrolytic material. The large g shift must consequently be due to structural differences and not simply due to acceptors.

Comparison of properties 1 and 2 with the expectations of the two dimensional model makes it appear that the properties of these highly turbostratic graphite deposits are consistent with a band structure which is almost two dimensional. That is to say, the electric and magnetic properties, which lie between the values expected from the two dimensional and the three dimensional models, are given to an accuracy of about 20 per cent by the simple two dimensional picture alone. The g shift, however, does not agree with the expectations of two dimensional graphite theory. A plausible explanation is that the g shift depends on anisotropic interaction between atoms in different planes and that the anisotropy is larger in the turbostratic structure than it is in the more symmetrical hexagonal form.

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