

FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Graphite Materials Development"; Project No. 7381 "Materials Application", Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administrated under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

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.

This is the eighth of a series of volumes of WADD Technical Report 61-72 prepared to describe various phases of the work. The preceding volumes of this series are:

- Volume I Observations by Electron Microscopy of Dislocations in Graphite, by Richard 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 Roger Bacon and Richard 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.
- Volume VII High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar and K. J. Zeitsch.

Contrails

ABSTRACT

The electron spin resonance of polycrystalline graphite is shown to be due to charge carriers, as for single crystals. For lampblack-base graphite, the variation in g-value with temperature agrees approximately with that for single crystal graphite if it is assumed that the spins effectively average out the anisotropic interactions by rapid intercrystallite diffusion. The magnitude and temperature dependence of the spin susceptibility are found to be in excellent agreement with McClure's theoretical predictions for the charge carriers in perfect graphite. Complications of measuring these materials are discussed, including effects of skin depth and microwave heating and the dependence upon crystallite size and sample purity. It is found that two types of impurities can affect the resonance; those which become ionized and shift the Fermi level, and large un-ionized atoms which do not shift the Fermi level but act as efficient scattering centers for shortening the spin-lattice relaxation time.

This technical report has been reviewed and is approved.



W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

TABLE OF CONTENTS

	PAGE
1. INTRODUCTION	1
2. ELECTRON SPIN RESONANCE IN ELECTRONIC CONDUCTORS	1
3. LINE NARROWING DUE TO ELECTRON MOTION	4
4. EFFECTS OF IMPURITIES	6
4.1 The "Silicon Effect"	6
4.2 Effect of Boron	7
5. SPIN RESONANCE RESULTS IN POLYCRYSTALLINE GRAPHITE	7
6. SUMMARY	10
7. REFERENCES	12

ABSTRACT

The electron spin resonance of polycrystalline graphite is shown to be due to charge carriers, as for single crystals. For lampblack-base graphite, the variation in g-value with temperature agrees approximately with that for single crystal graphite if it is assumed that the spins effectively average out the anisotropic interactions by rapid intercrystallite diffusion. The magnitude and temperature dependence of the spin susceptibility are found to be in excellent agreement with McClure's theoretical predictions for the charge carriers in perfect graphite. Complications of measuring these materials are discussed, including effects of skin depth and microwave heating and the dependence upon crystallite size and sample purity. It is found that two types of impurities can affect the resonance; those which become ionized and shift the Fermi level, and large un-ionized atoms which do not shift the Fermi level but act as efficient scattering centers for shortening the spin-lattice relaxation time.

This technical report has been reviewed and is approved.



W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

Contrails

TABLE OF CONTENTS

	PAGE
1. INTRODUCTION	1
2. ELECTRON SPIN RESONANCE IN ELECTRONIC CONDUCTORS	1
3. LINE NARROWING DUE TO ELECTRON MOTION	4
4. EFFECTS OF IMPURITIES	6
4.1 The "Silicon Effect"	6
4.2 Effect of Boron	7
5. SPIN RESONANCE RESULTS IN POLYCRYSTALLINE GRAPHITE	7
6. SUMMARY	10
7. REFERENCES	12

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	Spin resonance derivative curves for polycrystalline graphite . . .	2
2.	Microwave heating effect for a polycrystalline graphite rod. . .	3
3.	Comparison of the spin resonance of single crystal and polycrystalline graphite for different cases of electron motional averaging. (a) Single crystal, (b) Polycrystalline, no averaging, (c) Polycrystalline, complete averaging	5
4.	Comparison of the temperature dependence of the g-factor of lampblack-base graphite with that of a single crystal. (See text for legend of curve points.)	8
5.	Temperature dependence of the spin susceptibility of lampblack-base graphite	9
6.	Temperature dependence of the line width of lampblack-base graphite	10

Contrails

1. INTRODUCTION

This report presents the results of an investigation of the electron spin resonance in polycrystalline graphite¹. The resonance phenomena are dominated by such complications as the effects of microwave heating and skin depth, and the dependence upon crystallite size and sample purity. By considering these factors in detail, we have been able to obtain quantitative measurements of the temperature dependence of the spin resonance of polycrystalline graphite which had been heat-treated at 3000°C. Comparison of the experimental results with a theoretical extension of single crystal graphite behavior² clearly shows that the spin resonance in high-temperature, polycrystalline graphite is due to charge carriers.

The paper is divided into several parts. Section 2 deals with the complications which arise in making electron spin resonance measurements on any electronic conductor. Section 3 discusses line narrowing due to electron motion. Section 4 describes the effects of impurities. Section 5 presents the temperature dependence measurements for a polycrystalline graphite and compares the results with theory.

2. ELECTRON SPIN RESONANCE IN ELECTRONIC CONDUCTORS

In insulators, the ordinary resonance parameters such as the spectroscopic splitting or g-factor, line width, static spin susceptibility, and spin concentration are meaningful parameters because most spin systems in real materials are quite accurately described by the remarkably simple model of Bloch³. Means of measurement and methods for accurately determining the values of these properties in insulators have previously been discussed⁴.

In conductors, except for the insulator-like case of spins located only on the surface, the observed resonance properties are not in general similarly related to corresponding physical properties. For example, the g-factor will not be correctly obtained from the magnetic field at maximum absorption nor will the spin susceptibility or spin concentration be proportional to the integrated absorption intensity. In fact, the apparent area under a resonance absorption curve for a piece of conducting material large compared to the microwave skin depth, is infinite.

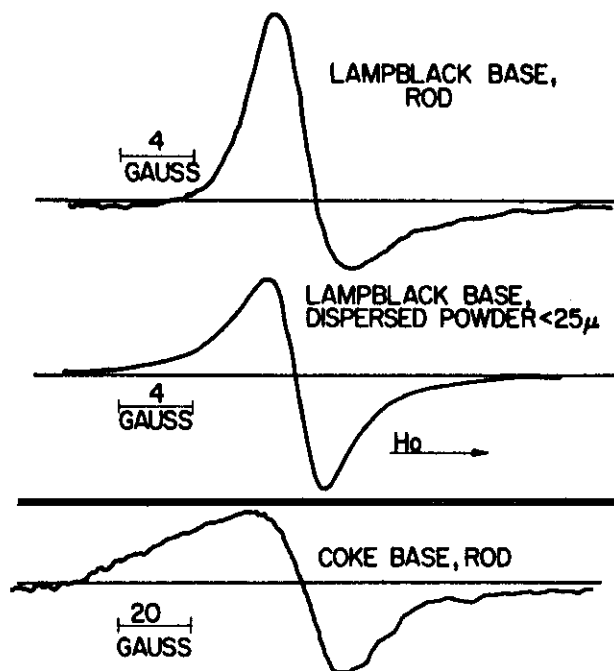
For spin resonance in conducting specimens large compared to the skin depth, the two important situations are²:

1. The spins are homogeneously distributed but can diffuse in and out of the skin depth in a time comparable with the spin-lattice relaxation time.
2. The spins are homogeneously distributed throughout the material but remain at fixed positions.

Manuscript released by the authors January 1962 for publication as a WADD Technical Report.

The first case has been treated by Dyson⁵ in connection with the conduction electron resonance in the alkali metals. The principal result of Dyson's analysis is that for rapid diffusion of the spins, the resonance absorption line shape has a peculiar asymmetric form. However, if the diffusion is slow, the spins can be considered fixed and the much simpler analysis of case 2 will apply. It can be shown from Dyson's expression for the diffusion time that this approximation is quite good for graphite.

Bloembergen⁶ has considered the second case in which the magnetic species are in fixed positions and are homogeneously distributed throughout the material. He derived an absorption curve proportional to $\chi' + \chi''$, the dispersive and absorptive parts of the susceptibility. Physically, the mixing of χ' with χ'' arises from the variation in ohmic losses in the sample as the spins within a skin depth undergo magnetic resonance absorption. In Figure 1, the top curve



N-894

Figure 1. Spin resonance derivative curves for polycrystalline graphites.

illustrates the derivative curve for such a case. As can be seen, the curve is quite asymmetric. The ratio of the heights of the two sides of the curve is 2.5 as would be predicted for the $\chi' + \chi''$ shape derived from a Lorentz-shaped absorption. It can be shown⁷ that the correct field to use for calculating a g-factor in this case is not at the crossover point but at a point between the crossover and the low-field peak where the ordinate reaches 85 per cent of its maximum value. This field differs from the crossover value by almost half the peak-to-peak line width. As mentioned previously, the apparent integrated absorption intensity for such a curve should be infinite. Any finite answer obtained by arbitrarily cutting off the wings is obviously meaningless.

1. INTRODUCTION

This report presents the results of an investigation of the electron spin resonance in polycrystalline graphite¹. The resonance phenomena are dominated by such complications as the effects of microwave heating and skin depth, and the dependence upon crystallite size and sample purity. By considering these factors in detail, we have been able to obtain quantitative measurements of the temperature dependence of the spin resonance of polycrystalline graphite which had been heat-treated at 3000°C. Comparison of the experimental results with a theoretical extension of single crystal graphite behavior² clearly shows that the spin resonance in high-temperature, polycrystalline graphite is due to charge carriers.

The paper is divided into several parts. Section 2 deals with the complications which arise in making electron spin resonance measurements on any electronic conductor. Section 3 discusses line narrowing due to electron motion. Section 4 describes the effects of impurities. Section 5 presents the temperature dependence measurements for a polycrystalline graphite and compares the results with theory.

2. ELECTRON SPIN RESONANCE IN ELECTRONIC CONDUCTORS

In insulators, the ordinary resonance parameters such as the spectroscopic splitting or g-factor, line width, static spin susceptibility, and spin concentration are meaningful parameters because most spin systems in real materials are quite accurately described by the remarkably simple model of Bloch³. Means of measurement and methods for accurately determining the values of these properties in insulators have previously been discussed⁴.

In conductors, except for the insulator-like case of spins located only on the surface, the observed resonance properties are not in general similarly related to corresponding physical properties. For example, the g-factor will not be correctly obtained from the magnetic field at maximum absorption nor will the spin susceptibility or spin concentration be proportional to the integrated absorption intensity. In fact, the apparent area under a resonance absorption curve for a piece of conducting material large compared to the microwave skin depth, is infinite.

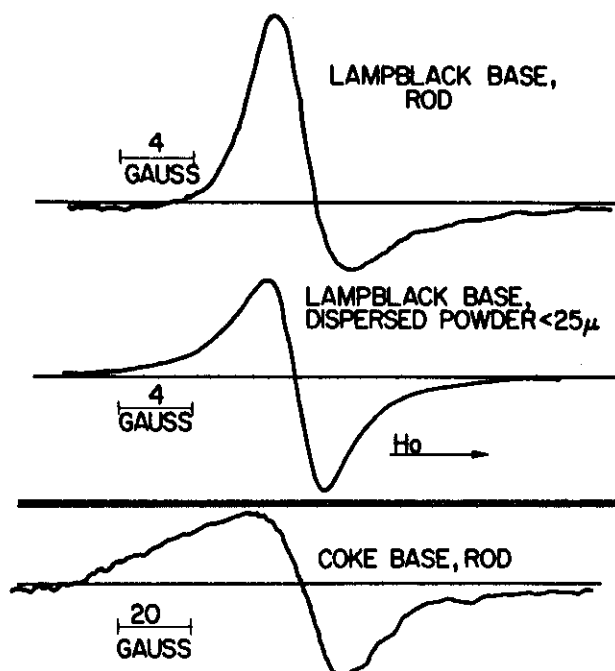
For spin resonance in conducting specimens large compared to the skin depth, the two important situations are²:

1. The spins are homogeneously distributed but can diffuse in and out of the skin depth in a time comparable with the spin-lattice relaxation time.
2. The spins are homogeneously distributed throughout the material but remain at fixed positions.

Manuscript released by the authors January 1962 for publication as a WADD Technical Report.

The first case has been treated by Dyson⁵ in connection with the conduction electron resonance in the alkali metals. The principal result of Dyson's analysis is that for rapid diffusion of the spins, the resonance absorption line shape has a peculiar asymmetric form. However, if the diffusion is slow, the spins can be considered fixed and the much simpler analysis of case 2 will apply. It can be shown from Dyson's expression for the diffusion time that this approximation is quite good for graphite.

Bloembergen⁶ has considered the second case in which the magnetic species are in fixed positions and are homogeneously distributed throughout the material. He derived an absorption curve proportional to $\chi' + \chi''$, the dispersive and absorptive parts of the susceptibility. Physically, the mixing of χ' with χ'' arises from the variation in ohmic losses in the sample as the spins within a skin depth undergo magnetic resonance absorption. In Figure 1, the top curve



N-894

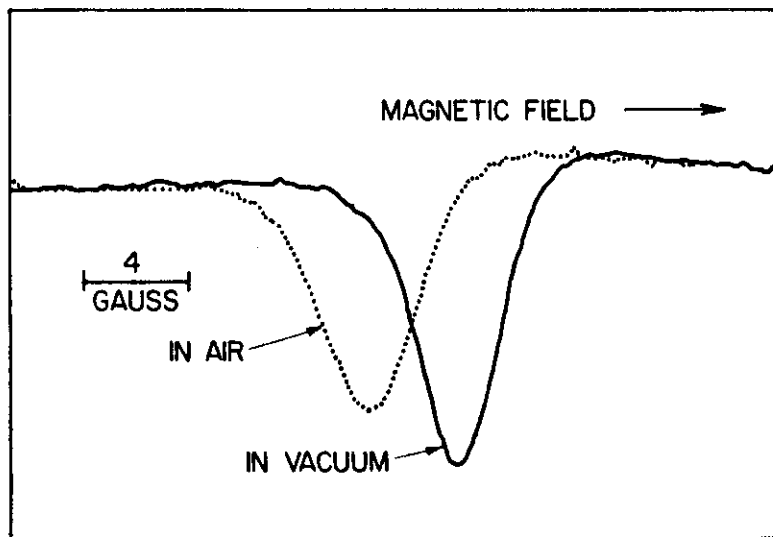
Figure 1. Spin resonance derivative curves for polycrystalline graphites.

illustrates the derivative curve for such a case. As can be seen, the curve is quite asymmetric. The ratio of the heights of the two sides of the curve is 2.5 as would be predicted for the $\chi' + \chi''$ shape derived from a Lorentz-shaped absorption. It can be shown⁷ that the correct field to use for calculating a g-factor in this case is not at the crossover point but at a point between the crossover and the low-field peak where the ordinate reaches 85 per cent of its maximum value. This field differs from the crossover value by almost half the peak-to-peak line width. As mentioned previously, the apparent integrated absorption intensity for such a curve should be infinite. Any finite answer obtained by arbitrarily cutting off the wings is obviously meaningless.

To extract the information of physical significance from a resonance experiment on a conductive material, one either takes account of the skin effect in large samples or avoids these problems by adequately grinding and dispersing the material. If one knows the shape of the true χ'' , the actual geometric area of the solid surface, and the electrical conductivity and thus the skin depth, a line width, g-value, and spin susceptibility can be computed by the methods used by Feher and Kip⁷ for the conduction electron resonance in the alkali metals, and by Wagoner² for single crystal graphite. These requirements are quite difficult to fulfill for most polycrystalline graphites. The second alternative of using a dispersed sample, each particle of which is much smaller than a microwave skin depth, is simpler for graphite. This still may be difficult, since for natural graphite with a skin depth at 10Gc of $\sim 3\mu$, the grinding and dispersal problems are serious. However, by choosing lampblack-base graphite, which has a skin depth of $\sim 40\mu$, one eliminates the difficulties of dealing with such small particles. It has thus been possible to obtain accurate g-values and spin susceptibilities for this particular polycrystalline graphite. The center curve in Figure 1 shows the resonance behavior for lampblack-base graphite when it is properly ground and dispersed to eliminate skin effects.

The bottom curve in Figure 1, which is the resonance signal of a piece of coke-base graphite, has a shape complicated not only by skin effect and electron diffusion but also by crystalline anisotropy effects which become quite marked for graphites having such a large crystallite size. This will be discussed further in Section 3.

An additional problem common to spin resonance measurements of all conductors, but particularly evident for carbons and graphites, is the microwave heating phenomenon. Figure 2 shows the derivative curve for a carbon rod



N-892

Figure 2. Microwave heating effect for a polycrystalline graphite rod.

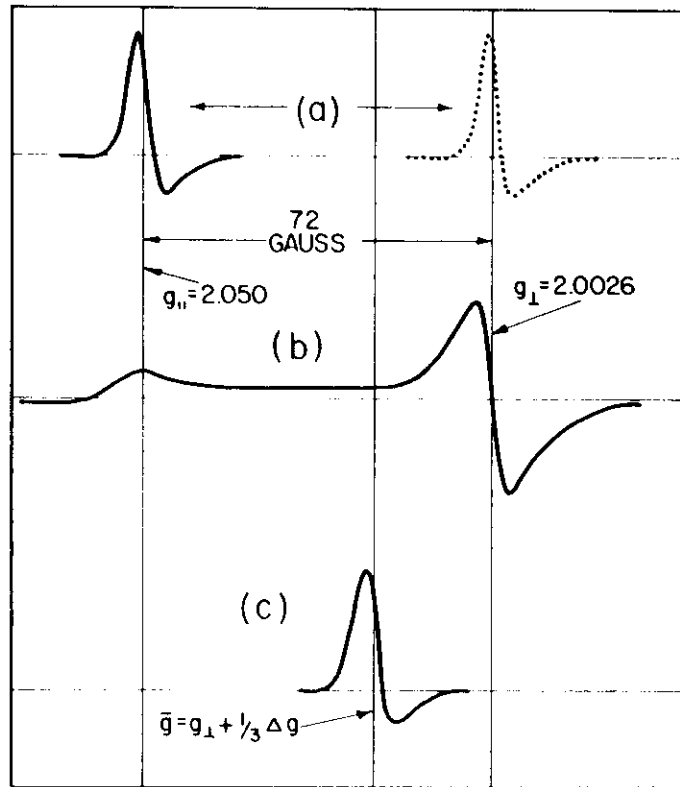
measured at a normal microwave power level of 100 mw. This curve was measured with the sample in vacuum. Upon admission of air, the curve broadened and decreased in intensity as is shown by the dotted curve. This effect of air has, however, nothing to do with "dangling bonds" or any other nebulous surface phenomenon. Not only was a similar reversible broadening phenomenon produced by argon, but the effect disappeared completely upon going to lower microwave powers. The explanation of these observations is almost trivial. The carbon is resistively heated by the microwaves in the cavity. Both the g -value and line width are known to be quite critically temperature dependent². The reason for the observed change when air or argon was introduced into the sample tube was simply that the increased thermal contact of the sample with its surroundings resulted in a slight cooling of the sample. Since temperature rises of as much as 100°C have been observed in these graphite samples at ordinary microwave powers, the necessity for going to a very low power is obvious.

3. LINE NARROWING DUE TO ELECTRON MOTION

If electron spin resonance measurements are made on a material which has a large g -anisotropy, the polycrystalline nature of the substance will tend to smear the resonance over all the resonant values of magnetic field required by the anisotropy.

If many single crystals of graphite are dispersed by an insulator, the resonance curve for this powder will be the single crystal result averaged over all possible graphite crystal orientations. The shape can be predicted from the anisotropy to be a broad, asymmetric curve with most of the absorption occurring near the field corresponding to g_{\perp} . Figure 3 illustrates this situation. In part (a) of the figure, the single crystal resonance is shown for the two magnetic field orientations, H parallel to the c -axis and H perpendicular to the c -axis. Curve (b) gives the line shape for the case of a large number of graphite crystals randomly oriented. (It would be very easy for a casual observer to mistake curve (b) for a symmetrical resonance at $g = 2.0026$.) If the spin resonance is due to charge carriers and if, in contrast to the case (b) above, a carrier can move through a large number of crystallites before flipping its spin, then a type of motional narrowing occurs which results in a narrowed resonance at the average g -value and a line width characterized by T_1 . To our knowledge, graphite is the first material to show such a time averaging of the anisotropy due to electron motion. This effect should also be observable in other cases of anisotropic charge carrier resonance. Curve (c) of Figure 3, which shows the resonance for a sample of lampblack-base graphite of dimensions large compared to the skin depth, illustrates this case.

Let us consider the situation in graphite in a little more detail by finding the distance an electron can diffuse between spin flips. The room temperature line width of the spin resonance in spectroscopic grade lampblack-base graphite is three gauss, which corresponds to a relaxation time $T_2 = 2 \times 10^{-8}$ sec. Furthermore, since the correlation time for charge carriers is the collision time $\tau_r \approx 3 \times 10^{-13}$ sec. associated with resistivity⁸, one is assured by the argument of Pines and Slichter⁹ that $T_1 = T_2$. Thus, a carrier makes $n \sim 10^5$ collisions



N-1521

Figure 3. Comparison of the spin resonance of single crystal and polycrystalline graphite for different cases of electron motional averaging. (a) Single crystal, (b) Polycrystalline, no averaging, (c) Polycrystalline, complete averaging.

with the lattice between spin flips, each collision involving a mean free path Λ of about 300 Å. Simple diffusion theory gives a diffusion length $L_0 = n^{1/2} \Lambda \cong 10 \mu$ between spin flips or, with crystallite dimensions of about $100 \text{ \AA} \cdot 10^{-12}$, an electron can diffuse across about 10^3 crystallites between flips. The g -value of such a charge carrier spin resonance will be just the average g for crystallites of all possible orientations. Thus, the resonance occurs at

$$\bar{g} = (g_{||} + 2g_{\perp})/3$$

which is the single crystal expression, $g = (g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta)^{1/2} \cong g_{\perp} + \Delta g \cos^2 \theta$, averaged over all values of θ . (θ is the angle between the magnetic field and the c -axis.) The result of such an averaging process is shown in curve (c) of Figure 3.

We have found that only by choosing lampblack-base graphite is the crystallite size small enough to give reasonably complete averaging. Petroleum coke-base graphite shows quite a broad resonance as shown in Figure 1 which we attribute

to the fact that an electron can only traverse a few crystallites before a spin flip occurs. The line shape in this material should therefore be quite dependent on crystallite size. We have not worked out a line shape for this case but we expect it to be relatively complicated, especially for solid pieces where the skin effect must also be taken into account.

4. EFFECTS OF IMPURITIES

The effects of impurities in graphite may be placed in two broad categories, those which shift the Fermi level and those which do not. The effect of small amounts of the former type can be remarkable since it is the separation of the Fermi level by only a few hundredths of an electron volt from the degenerate band edge which gives graphite its unusually large g -value. For example, ten parts per million of boron, which acts as an acceptor, gives rise to a significant g -shift (even at room temperature). The principal effect of the second type of impurity, which does not ionize in graphite, is to serve as a means of spin-lattice relaxation for the charge carriers. This effect takes place through spin-orbit coupling, which increases rapidly with higher atomic number, so that heavy elements are very effective. The presence of a few parts per million of silicon in even the purest graphite is sufficient to account for the resonance line width observed in this material. It is quite possible for an impurity to act both to shift the Fermi level and as an agent for spin lattice relaxation. Bromine is probably in this category, since not only does it act as an acceptor¹³, but also we have observed that it broadens the resonance markedly. Potassium, on the other hand, acts as a donor and although it has high Z does not greatly broaden the line. We presume that this occurs because the charge carrier wave functions are small on the potassium ion cores.

In the following sections we record in somewhat more detail some of our observations on the effect of impurities in graphite.

4.1. The "Silicon Effect"

We have observed¹⁴ that graphite reacts with SiO_2 at temperatures as low as 300°C to produce a broadening of the resonance line. The degree of broadening depends upon the particle size of the SiO_2 and upon the particle and crystallite size of the graphite. The observations suggest that Si, by forming some substitutional or surface compound with graphite, provides an additional spin-lattice relaxation mechanism for the conduction electrons which are responsible for the resonance. Similar broadening effects are observed with SiC and elemental Si and Ge. In no case was there a change of total spin concentration.

Although the detailed mechanisms for the diffusion of Si and the line broadening are not yet known, we have obtained some qualitative estimates of both the equilibrium and kinetic behavior of the silicon-graphite system. At temperatures up to 1300°C , the process is diffusion limited. That is to say, the higher the temperature and the greater the time and intimacy of contact between Si and C, the higher the concentration of Si in the graphite and the broader the resonance. For example, heating a mixture of lampblack-base graphite and SiO_2 , both of particle size less than 25 microns, to 1300°C for one hour broadens the

originally 4 gauss-wide signal beyond detection. However, the innermost portion of a 1/8" diameter rod of the same type graphite showed a broadening of only a factor of 7 when heat-treated under the same conditions. By spectroscopic analysis, it was found that these samples contained between 10 and 100 parts per million silicon.

Above 1400°C, the C-Si complex or compound is unstable and the silicon is driven off. If such a sample is then cooled rapidly through the critical region between 1000°C and 1300°C, no significant amount of Si can diffuse back in so that the room temperature resonance is again narrow. However, if the sample is cooled slowly, part of the Si can diffuse back in and the resonance remains somewhat broadened.

This behavior of graphite in the presence of Si may explain the results of Hennig and Smaller¹⁵ who attributed the disappearance of the resonance upon heat-treatment to an oxygen chemisorption effect. Their resonances were probably broadened by heating samples in quartz vessels. This broadening phenomenon points out the great importance of using pure samples as well as scrupulously clean (particularly with respect to Group IV impurities) sample containers and furnace equipment for heat-treatment studies.

4.2. Effect of Boron

The effect on the g-value of the addition of boron as a substitutional impurity in single crystal graphite has been mentioned previously². A detailed report of these effects in both single crystal and polycrystalline graphite will appear elsewhere¹⁶. It should suffice to say at this point that boron impurity in the concentration range around 0.01 atom per cent, lowers the Fermi level in graphites significantly. This becomes evident in both the electric and magnetic properties of graphites. The g-factor anisotropy is reduced and the spin susceptibility altered both in its magnitude and temperature dependence.

5. SPIN RESONANCE RESULTS IN POLYCRYSTALLINE GRAPHITE

The temperature dependence of the g-factor and spin susceptibility were determined for National Carbon L113SP, spectroscopically pure, lampblack-base graphite. Measurements were made on the powder, with particle size less than a skin depth, and on a polished rod for which the surface roughness was on the order of 1 micron. The particle size requirement was determined from the measured room temperature resistivity of the rod, viz., 5.8×10^{-3} ohm-cm. This corresponds to a skin depth of 40 microns at 10 Gc. The dispersal requirements were found empirically using SiO₂ powder of the same particle size as the graphite. No change in the quantitative resonance properties of the graphite was observed for dispersions containing at least 40 per cent SiO₂.

The following conditions of measurement were employed:

1. The fine powder was dispersed with 70 per cent SiO₂ of similar particle size. This insured a uniform microwave field throughout the sample.
2. All measurements were made at a microwave power level of 0.1 mw

using a superheterodyne detector. This low power level prevented sample heating by the microwaves.

3. A ruby single crystal was used to monitor the cavity Q¹⁷.
4. The variable temperature apparatus⁴ enabled measurements to be made between 100°K and 500°K without disturbing the sample.

The g-factor results are shown in Figure 4. The open circles denote

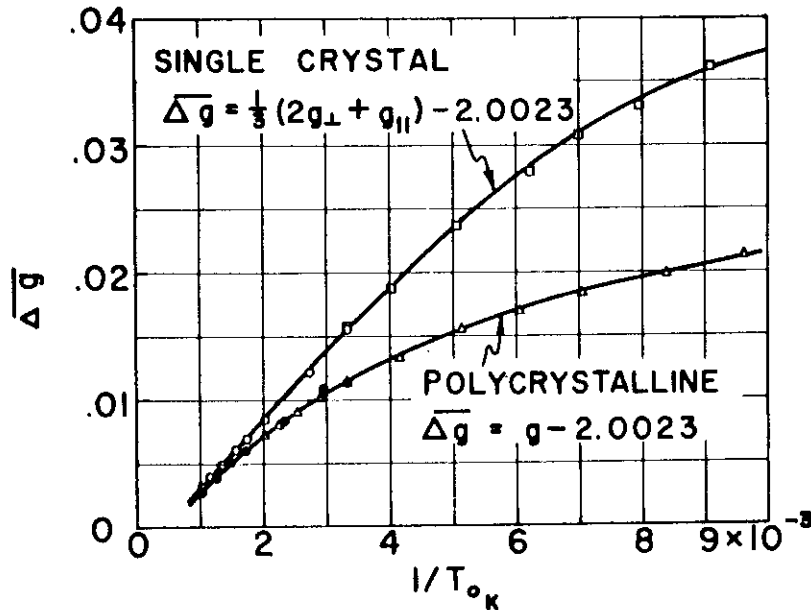
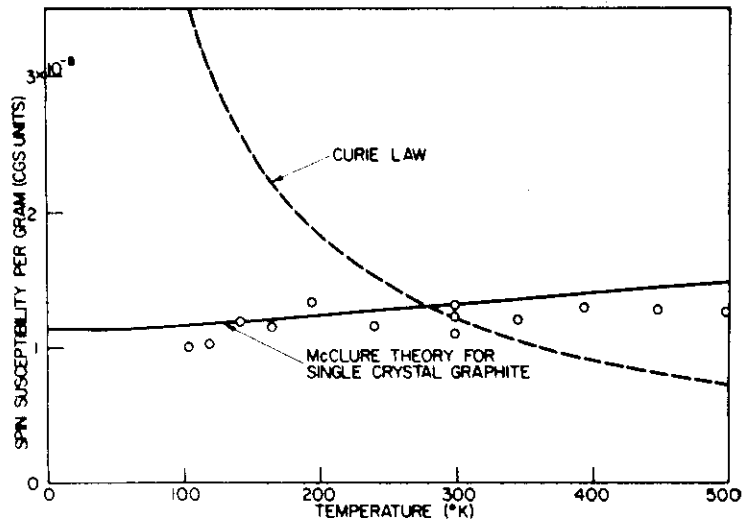


Figure 4. Comparison of the temperature dependence of the g-factor of lampblack-base graphite with that of a single crystal. (See text for legend of curve points.)

measurements on one single crystal. Because of poor signal-to-noise, it was necessary to use many carefully aligned Madagascar flakes at the lower temperature (squares). For the polycrystalline material, dispersed powder was used for the measurements below 500°K (triangles). Because of the chemical reactivity of the fine powder above 500°K, a solid rod was used for the very high temperature measurements (solid circles). It is worth noting that the g-factors are independent of the form of sample used.

It can be seen that the magnitude of the g-shift and its variation with temperature for the polycrystalline material are similar to the single crystal results. The deviations which become quite large at low temperatures, may be due to a slightly modified Fermi level resulting from imperfections in the polycrystalline material acting as electron traps. It also may be due to lattice strains which occur on cooling as a result of the anisotropic thermal expansion of graphite crystallites. The spin susceptibilities are shown in Figure 5. It can be seen that the susceptibility is approximately independent of temperature, in sharp contrast to the Curie Law dependence which would be expected for localized internal or surface spins. The results are in remarkably good agreement with McClure's theory for single crystal graphite, which was largely determined



N-1519

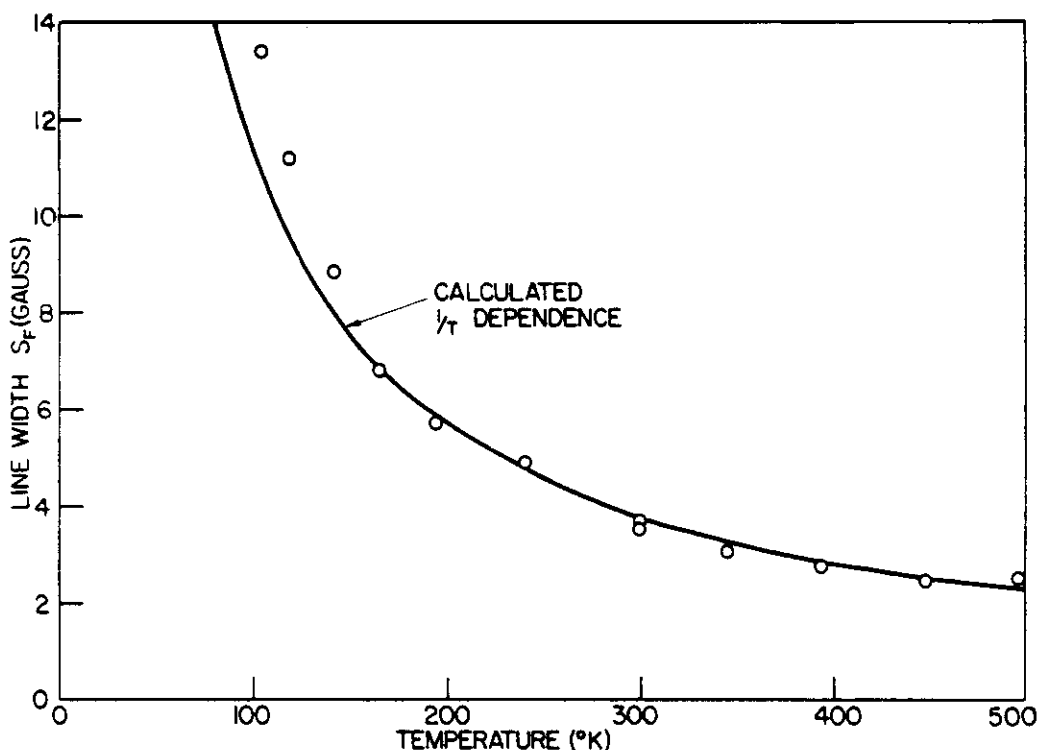
Figure 5. Temperature dependence of the spin susceptibility of lampblack-base graphite.

from a band theoretical analysis of Soule's de Haas-van Alphen data¹⁸.

The results for the smooth rods agreed within 30 per cent with those for the fine powder, using the simple geometrical surface area in computing the number of spins within a skin depth. Rods of the same diameter and material, which showed roughness on the same order as or larger than a microwave skin depth, exhibited a larger signal with no change in line shape. This is simply due to a larger volume of sample exposed to the microwaves.

Our temperature dependence measurements of the spin susceptibility for these graphites are not in agreement with the simple 2-dimensional free-electron gas model¹⁹. If one assumes that the degeneracy temperature of these 3000°C heat-treatment temperature materials is $T_0 \approx 400^\circ\text{K}$, our experiments covered the range of T_0/T from 0.8 to 4.0. The free electron gas model predicts a decrease in susceptibility with increasing temperature by almost a factor of 2 in this temperature range, whereas we actually observed a slight increase, in agreement with McClure's theory. Although it would be of interest to investigate the temperature dependence of the spin susceptibility for carbons and graphites of lower heat-treatment temperatures, there is as yet no detailed theory available for comparison.

The temperature dependence of the line width for the dispersed lampblack-base powder is shown in Figure 6. S_F is the peak-to-peak separation on the derivative curve. It is of interest that the line width very nearly follows the inverse temperature dependence curve which has been added for comparison. On the basis of quite crude arguments², one would expect impurities to give a line width varying approximately as $T^{-1/2}$ for nondegenerate graphite and an even slower variation with temperature for the degenerate case. Thus, the impurity relaxation mechanism which was tentatively suggested as accounting



N-1520

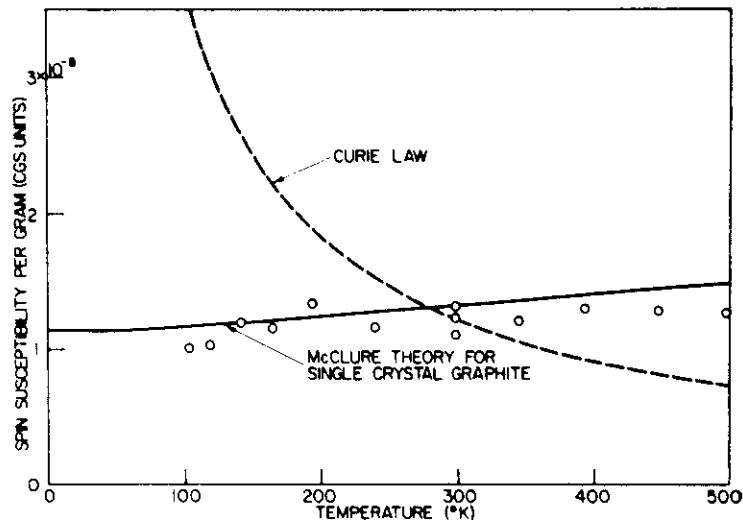
Figure 6. Temperature dependence of the line width of lampblack-base graphite.

for the spin lattice relaxation in single crystals², does not fit the polycrystalline line width data²⁰.

We have also tried unsuccessfully to fit the temperature dependence of the linewidth with Elliott's²¹ expression, viz., $T_1 \sim \tau_r / \Delta_g^2$. The values of τ_r which were used were those calculated from the single crystal data of Soule and McClure¹⁸ and the values of Δ_g were the observed polycrystalline values of Figure 4²². We interpret this lack of success as meaning that Elliott's mechanism does not apply or that a more sophisticated application of his theory to graphite must be made. The latter case is most likely in view of the anisotropic nature of graphite.

6. SUMMARY

The conclusion that the electron spin resonance in polycrystalline graphite is due to charge carriers is based on two observations. First, the magnitude and temperature dependence of the spin susceptibility agree with McClure's theoretical expectation; and second, the magnitude and temperature dependence of the g-shift are approximately the average single crystal value. It is believed that adequate accounting has been made for the effects of sample conductivity and impurities so that the results are quantitatively meaningful. A very significant departure of the polycrystalline g-shift from the average single crystal value is noted. This is attributed to a slightly altered band structure or a



N-1519

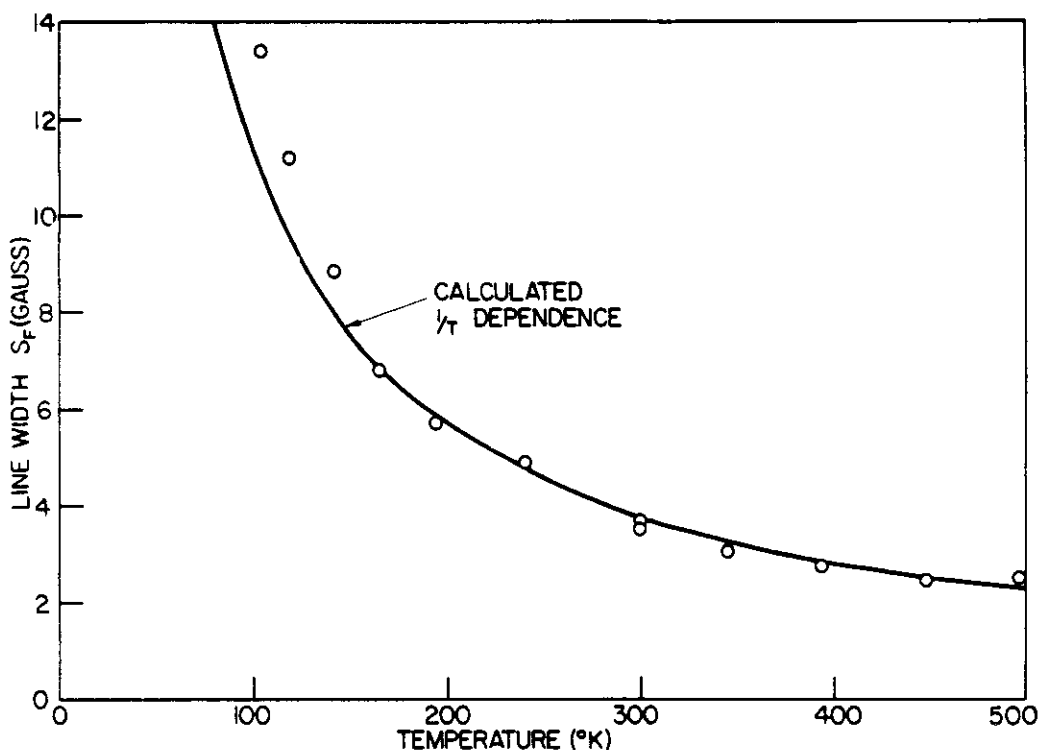
Figure 5. Temperature dependence of the spin susceptibility of lampblack-base graphite.

from a band theoretical analysis of Soule's de Haas-van Alphen data¹⁸.

The results for the smooth rods agreed within 30 per cent with those for the fine powder, using the simple geometrical surface area in computing the number of spins within a skin depth. Rods of the same diameter and material, which showed roughness on the same order as or larger than a microwave skin depth, exhibited a larger signal with no change in line shape. This is simply due to a larger volume of sample exposed to the microwaves.

Our temperature dependence measurements of the spin susceptibility for these graphites are not in agreement with the simple 2-dimensional free-electron gas model¹⁹. If one assumes that the degeneracy temperature of these 3000°C heat-treatment temperature materials is $T_0 \approx 400^\circ\text{K}$, our experiments covered the range of T_0/T from 0.8 to 4.0. The free electron gas model predicts a decrease in susceptibility with increasing temperature by almost a factor of 2 in this temperature range, whereas we actually observed a slight increase, in agreement with McClure's theory. Although it would be of interest to investigate the temperature dependence of the spin susceptibility for carbons and graphites of lower heat-treatment temperatures, there is as yet no detailed theory available for comparison.

The temperature dependence of the line width for the dispersed lampblack-base powder is shown in Figure 6. S_F is the peak-to-peak separation on the derivative curve. It is of interest that the line width very nearly follows the inverse temperature dependence curve which has been added for comparison. On the basis of quite crude arguments²⁰, one would expect impurities to give a line width varying approximately as $T^{-1/2}$ for nondegenerate graphite and an even slower variation with temperature for the degenerate case. Thus, the impurity relaxation mechanism which was tentatively suggested as accounting



N-1520

Figure 6. Temperature dependence of the line width of lampblack-base graphite.

for the spin lattice relaxation in single crystals², does not fit the polycrystalline line width data²⁰.

We have also tried unsuccessfully to fit the temperature dependence of the linewidth with Elliott's²¹ expression, viz., $T_1 \sim \tau_r / \Delta_g^2$. The values of τ_r which were used were those calculated from the single crystal data of Soule and McClure¹⁸ and the values of Δ_g were the observed polycrystalline values of Figure 4²². We interpret this lack of success as meaning that Elliott's mechanism does not apply or that a more sophisticated application of his theory to graphite must be made. The latter case is most likely in view of the anisotropic nature of graphite.

6. SUMMARY

The conclusion that the electron spin resonance in polycrystalline graphite is due to charge carriers is based on two observations. First, the magnitude and temperature dependence of the spin susceptibility agree with McClure's theoretical expectation; and second, the magnitude and temperature dependence of the g-shift are approximately the average single crystal value. It is believed that adequate accounting has been made for the effects of sample conductivity and impurities so that the results are quantitatively meaningful. A very significant departure of the polycrystalline g-shift from the average single crystal value is noted. This is attributed to a slightly altered band structure or a

Contrails

shifted Fermi level or both in the polycrystalline material. It is hoped that the explanation of this discrepancy will further clarify the character of these materials.

7. REFERENCES

1. For the purposes of this paper, "polycrystalline graphite" is defined as any carbonaceous material which has been heat-treated above 2500°C.
2. G. Wagoner, Phys. Rev. 118, 647 (1960).
3. F. Bloch, Phys. Rev. 70, 460 (1946).
4. L. S. Singer and J. Kommandeur, J. Chem. Phys. 34, 133 (1960).
5. F. J. Dyson, Phys. Rev. 98, 349 (1955).
6. N. Bloembergen, J. Appl. Phys. 23, 1379 (1952).
7. G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955).
8. J. W. McClure, Phys. Rev. 112, 715 (1958).
9. D. Pines and C. P. Slichter, Phys. Rev. 100, 1014 (1955).
10. B. E. Warren, "Proceedings of the Second Conference on Carbon," (Waverly Press, Baltimore, 1956), p. 49.
11. J. C. Bowman, *ibid*, p. 59.
12. L. D. Loch and A. E. Austin, *ibid*, p. 65.
13. G. R. Hennig, J. Chem. Phys. 20, 1443 (1952).
14. G. Wagoner and L. S. Singer, Bull. Amer. Phys. Soc., Series II, Vol. 4, No. 7, 415 (1959).
15. G. R. Hennig and B. Smaller, "Proceedings of the Second Conference on Carbon," (Waverly Press, Baltimore, 1956) p. 113.
16. G. Wagoner, to be published.
17. L. S. Singer, J. Appl. Phys. 30, 1463 (1959).
18. D. E. Soule and J. W. McClure, J. Phys. Chem. Solids 8, 29 (1959).
19. A. Pacault and A. Marchand, "Proceedings of the Third Conference on Carbon," (Pergamon Press, New York, 1959) p. 37.
20. Recent line width measurements on a single crystal at high temperatures also indicate a $1/T$ temperature dependence which is not consistent with an impurity relaxation mechanism.

7. REFERENCES CONT'D.

21. R. J. Elliott, Phys. Rev. 96, 266 (1954).
22. The single crystal collision time τ_r is used rather than the much smaller value observed for lampblack-base graphite because the crystallite boundaries, which are effective as scattering centers for conduction, are not effective in inducing spin relaxation. This must be the case since the line widths for polycrystalline and single crystal graphite are observed to be approximately equal.