

effective mass of  $1.5m_0$  from a consideration of the effect of alloying on the de Haas-van Alphen periods and Galt et al.<sup>17</sup> obtained an average effective mass of  $0.16m_0$  from cyclotron resonance experiments. If the relaxation time for the holes is assumed isotropic, the ratio of the reciprocal mass components  $\beta_{33}/\beta_{11}$  is the ratio of the mobilities and the data of Abeles and Meiboom give  $\beta_{33}/\beta_{11}=0.27$ . In combination with the above estimate of  $\beta_{11}^2\beta_{33}$  this leads to the values  $\beta_{11}=2.1$  and  $\beta_{33}=0.58$ . These values of  $\beta_{11}$  and  $\beta_{33}$  may be compared with the values 1.7 and 0.13, respectively, obtained from anomalous skin effect experiments,<sup>19</sup> and 14.7 and 1.07 from cyclotron resonance experiments.<sup>17</sup>

As a result of inadequacies in the theory and the combinations in which the various quantities appear in the theoretical expressions, the de Haas-van Alphen experiments give some of the parameters for the electrons more accurately than others. Aubrey and Chambers<sup>16</sup> have suggested that  $\alpha_{11}$ ,  $\alpha_{22}$ ,  $\alpha_{33}$ , and  $\alpha_{23}$  be taken as 168, 2.0, 100, and  $-10$ , respectively, to give better agreement with the galvanomagnetic and cyclotron resonance experiments and at the same time

preserve unchanged the ratios most accurately determined in the de Haas-van Alphen experiments. With these values of the  $\alpha_{ij}$  the parameters for the holes become:  $E_h=0.0016$  eV and the average effective mass is  $0.90 m_0$ .

### 3. Lattice Heat Capacity

Over the temperature range of the measurements the lattice heat capacity is  $C_L=(12/5)\pi^4 R(T/\theta)^3$  with  $\theta$  given by  $\theta=120.4-0.6T^2$  to within a scatter of about 1%. This is in good agreement with other measurements. Kalkinkina and Strelkov<sup>8</sup> found  $\theta_0=118.5\pm 1$  and approximately the same curvature of  $\theta$  vs  $T$ . From measurements above 1°K Ramanathan and Srinivasan<sup>21</sup> found  $\theta_0=120^\circ\text{K}$  and Keesom and Pearlman<sup>22</sup> report an average  $\theta$  of  $117^\circ\text{K}$  between 1.0 and  $2.3^\circ\text{K}$ .

<sup>21</sup> K. G. Ramanathan and T. M. Srinivasan, Phys. Rev. **99**, 442 (1955).

<sup>22</sup> P. H. Keesom and N. Pearlman, Phys. Rev. **96**, 897 (1954).

*Note added in proof.*—R. R. Hewitt and W. D. Knight (private communication) have found two quadrupole resonance absorption frequencies which are consistent with the above value of the nuclear quadrupole heat capacity.

## Spin Resonance of Charge Carriers in Graphite

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The observations reported here of the electron spin resonance in quite perfect single crystals of graphite clearly establish that the resonance arises from mobile charge carriers. The line shape is of the Dysonian form which is characteristic of conduction electron spin resonance in metals. The intensity of the spin resonance agrees, both in absolute magnitude and in temperature dependence, with values calculated from the band model of graphite by McClure. The  $g$  value of the resonance shows a remarkably large anisotropy which depends strongly on temperature and on the position of the Fermi level with respect to the band edge. At room temperature in pure graphite,  $g$  varies from  $2.0026\pm 0.0002$  to  $2.0495\pm 0.0002$  as the magnetic field is shifted from perpendicular to parallel to the  $c$  axis. The  $g$ -value anisotropy increases with decreasing temperature;  $g_{\parallel}$  becomes 2.127 at  $77^\circ\text{K}$  while  $g_{\perp}$  remains constant. The line width of the resonance is a few gauss ( $T_2=2.0\times 10^{-8}$  sec) which is extremely narrow in comparison with the field shifts caused by changes of anisotropy with temperature. This indicates that for conduction states in graphite, the  $g$  value is a strong function of the wave vector and that the line is narrowed by an averaging process in  $k$  space. This averaging is similar to that which occurs in motional and exchange narrowing.

### I. INTRODUCTION

THE purpose of these experiments was to determine the nature of the unpaired spins which give rise to the electron spin resonance in graphite.<sup>1,2</sup> The investigation leads us to conclude that the spin resonance in pure, relatively perfect, single crystals is due to the mobile charge carriers. Both electrons and holes are thought to contribute to a single resonance line whose shape is described by Dyson's theory<sup>3</sup> of conduction

electron spin resonance and whose intensity agrees with the band theoretical result of J. W. McClure. The resonance shows a remarkably large  $g$ -value anisotropy which exhibits a dependence upon temperature and Fermi level similar to that predicted by Elliott.<sup>4</sup> The band structure of graphite proposed by Wallace<sup>5</sup> and elaborated by Slonczewski, Nozières, and others<sup>6,7</sup> contains a degenerate band edge. This is just the situation which, on Elliott's theory, would give rise to the

<sup>1</sup> J. G. Castle, Phys. Rev. **92**, 1063 (1953).

<sup>2</sup> G. R. Hennig, B. Smaller, and E. L. Yasaitis, Phys. Rev. **95**, 1088 (1954).

<sup>3</sup> F. J. Dyson, Phys. Rev. **98**, 349 (1955).

<sup>4</sup> R. J. Elliott, Phys. Rev. **96**, 266 (1954).

<sup>5</sup> P. R. Wallace, Phys. Rev. **71**, 622 (1947).

<sup>6</sup> J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

<sup>7</sup> P. Nozières, Phys. Rev. **109**, 1510 (1958).

anomalously large  $g$  shift observed. It appears that graphite is the first material in which the interesting effects of a degenerate band edge on the spin resonance have been observed.

The first reported observation of the spin resonance in graphite was that by Castle.<sup>1</sup> In a preliminary report, he attributed the resonance to charge carriers. Doubt was later cast on this interpretation by the observations of Hennig, Smaller, and Yasaitis<sup>2</sup> who found that the resonance in finely divided samples could be destroyed, with no attendant change in the Hall coefficient, by vacuum annealing at 1500°K. The resonance could then be restored by a 1700°K anneal. These annealing effects were thought to be due to the influence of oxygen gas on the spin centers.<sup>8</sup> Experiments performed at this laboratory in collaboration with L. S. Singer lead us to propose an alternative explanation of the annealing effects. We believe that the graphite reduces the SiO<sub>2</sub> (quartz) containers in which the experiments were performed to produce chemisorbed silicon on the graphite surface. The charge carriers then undergo spin-lattice relaxation upon collision with the silicon bearing surface and the resonance line is so broadened that it becomes undetectable. The details of these experiments will be published separately.

Crystals of graphite larger than a few microns show skin effects at microwave frequencies which generally complicate the line shape in a spin resonance experiment. By using specimens very large compared to the skin depth, however, one can take advantage of the skin effect to demonstrate clearly that the resonance is due to mobile spin centers. To get a simple skin effect geometry and to simplify effects due to the large anisotropy of graphite, the observations were made on single crystal specimens. There the line shape of the spin resonance makes it possible to distinguish three cases. First, the spins may be on the surface of the conductor and the skin effect does not change the line shape (absorption) from the  $\chi''$  form (imaginary part of the complex rf susceptibility) which it normally takes in an insulating sample. Second, the spins may be distributed uniformly throughout the sample at fixed sites. Bloembergen<sup>9</sup> has treated this case in connection with nuclear magnetic resonance and has shown that the absorption has the form  $\chi' + \chi''$  if the sample size is large compared to the skin depth. Third, the spins, e.g., conduction electrons, may be uniformly distributed throughout the sample but are mobile and can diffuse through the skin depth in a time comparable with the spin lattice relaxation time. Dyson<sup>3</sup> has treated this case and has shown that the line is of a peculiar shape whose precise form depends upon the rate of diffusion. It is this third case which is observed in graphite single crystals.

The conclusion from the Dysonian line shape that the spin resonance is due to the charge carriers is strengthened by the temperature dependence of the resonance intensity. The strength of the resonance is found to increase approximately linearly with temperature in distinct contrast to the Curie law behavior which would be most likely for impurity atoms or for lattice imperfections. The linearly temperature dependent spin paramagnetism is just what one would expect for graphite at high temperatures on the basis of Wallace's two-dimensional model of graphite. (McClure's<sup>10</sup> more complete density of states expression goes over approximately to the Wallace two-dimensional value at energies on the order of 0.1 eV from the band edge.) His model shows the number of carriers to be proportional to  $T^2$  and, with a power of  $T$  removed by the Boltzmann factor, this predicts a paramagnetism proportional to temperature. Spectroscopic analysis of the graphite shows even further that the resonance is not due to impurities as the total impurity content is an order of magnitude less than the spin concentration.

The spin resonance of conduction electrons has previously been observed only in Na, K, Li, Be,<sup>11</sup> and Cs.<sup>12</sup> (In highly doped silicon and germanium, a resonance also occurs which is due to the conduction electrons in an impurity band.<sup>13</sup>) One might expect similar electron resonance in other metals but it has not been reported. Presumably the spin-orbit interaction is too great in most metals and the result is a short relaxation time and a line too broad to be detected. The most complete experimental work on conduction electron spin resonance is that of Feher and Kip,<sup>11</sup> who compared the line shapes of the above metals with Dyson's theory and the linewidths with the theories of Overhauser<sup>14</sup> and Elliott.<sup>4</sup> In none of the above materials do the electrons at the Fermi surface occupy states near a degenerate band edge and consequently the interesting resonance properties such as the temperature and impurity dependence of the  $g$  shift have not previously been observed.

## II. THE EXPERIMENTAL ARRANGEMENT

The experiments were all performed with 3 cm microwaves and resonant cavities of either rectangular or cylindrical shape with the sample suspended at the cavity center. An advantage of the cylindrical cavity operating in the  $TE_{01}$  mode is that the sample, as it is rotated with respect to the magnetic field, does not change its symmetry with respect to the microwave fields. The cavity  $Q$  thus remains constant or nearly so as the sample is rotated and the rf currents in the sample flow about the cylinder axis, thus avoiding

<sup>8</sup> G. R. Hennig and B. Smaller, *Proceedings of the Conferences on Carbon, The University of Buffalo, Buffalo, New York, 1956* (The Waverly Press, Inc., Baltimore, Md., 1956).

<sup>9</sup> N. Bloembergen, *J. Appl. Phys.* **23**, 1379 (1952).

<sup>10</sup> J. W. McClure, *Phys. Rev.* **108**, 612 (1957).

<sup>11</sup> G. Feher and A. F. Kip, *Phys. Rev.* **98**, 337 (1955).

<sup>12</sup> R. A. Levy, *Phys. Rev.* **102**, 31 (1956).

<sup>13</sup> G. Feher, D. K. Wilson, and E. A. Gere, *Phys. Rev. Letters* **3**, 25 (1959).

<sup>14</sup> A. W. Overhauser, *Phys. Rev.* **94**, 1067 (1954).

possible depolarizing fields. A standard scheme of video microwave detection and lock-in amplification was used. The magnetic field modulation was kept less than one-quarter of the linewidth to avoid distortion of the line shape. The static magnetic field was provided by a twelve-inch Varian electromagnet. Measurements at 77°K were made by simply inserting a quartz Dewar, with a small tip containing the sample and liquid nitrogen, into the cavity in place of the sample tube normally used. An automatic frequency control circuit was used to lock the klystron frequency to that of the cavity, thereby avoiding noise due to nitrogen bubbling. The measurements above room temperature were made in a special heater which was fitted into a water-cooled cavity. The heater was a quartz tube on which a platinum strip had been plated. A heating current was passed through the platinum and temperatures as high as 600°C were obtained.

### III. DESCRIPTION OF THE SAMPLES

The samples were mainly single crystal specimens but some observations were made on more or less finely divided specimens. The coarser grades of flake graphite (about 0.1 mm diam) gave results in full agreement with the single crystal results but, of course, with additional complications due to random crystal orientations. The finely divided specimens (50-microns diameter and smaller) did not appear to have a line shape predictable simply by averaging over the orientations of a single crystal. In this paper only the results obtained on single crystals are presented.

The graphite crystals were flakes about 5 mm in diameter and 0.1 mm thick. There were small angle grain boundaries visible on the surface of the specimens but the angles involved were estimated to be less than one degree. The samples were all purified by heating to 3000°C in a chlorine atmosphere and subsequent cooling in argon. Spectroscopic analysis showed the presence of less than 20 ppm of metallic impurities, and neutron capture cross sections of nuclear graphite purified in a similar manner show that chlorine could not be present in more than 20 ppm. It was concluded that all impurities present had a concentration an order of magnitude lower than the spin concentration.

The specimen which was most regular in form and upon which most of the measurements were made was a synthetic crystal grown from molten iron and later purified. There was no observably different behavior between this specimen and the purified natural crystals.

## IV. EXPERIMENTAL RESULTS

### 1. Line Shape

An example of a recorder tracing of the spin resonance in a graphite single crystal is shown in Fig. 1. The curve is a close approximation to the first derivative of the absorption intensity since the usual (small) field

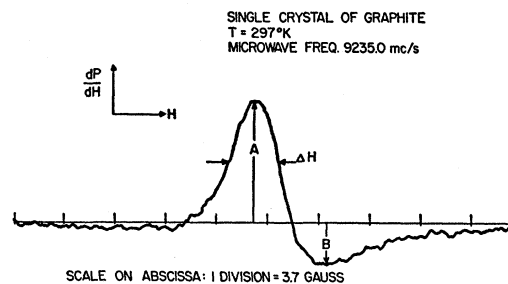


FIG. 1. Typical recorder tracing of the graphite spin resonance.

modulation and phase sensitive detection were employed. If the absorption were of the  $\chi' + \chi''$  form, the ratio of peak heights  $A/B$  would have been 2.55. As Dyson showed, diffusion of the spins out of the skin depth has the effect of increasing  $A/B$ , the limiting value being about 19 when  $T_D$  becomes very short compared to  $T_2$ .  $T_D$  is the time required for a spin to diffuse across the skin depth,  $\delta$ , and is given by diffusion theory as

$$T_D = \frac{3}{2} \delta^2 / v \Lambda,$$

where  $v$  is the mean velocity and  $\Lambda$  is the mean free path.  $T_2$  is the inverse linewidth and is equal to  $T_1$ , the spin-lattice relaxation time, for conduction electrons.<sup>15</sup> The linewidth and shape are controlled in a complicated manner by the spin-lattice relaxation time and by the diffusion of the carriers. Analysis of the resonance curves using the methods of Feher and Kip<sup>11</sup> enables one to determine  $T_2$  and  $T_D$  separately. The experimentally observed  $T_D$  may then be compared with the value computed from the mobility in graphite obtained from the dc conductivity.

For graphite at room temperature  $A/B = 3.0 \pm 0.1$  and this gives  $T_D = 3.0 T_2$  from Fig. 7 of reference 11. Figure 5 of the same reference enables one to evaluate  $T_2 (= T_1)$  from the width at half maximum. The values we obtained for graphite are  $T_2 = 2.0 \times 10^{-8}$  sec and  $T_D = (6.0 \pm 0.6) \times 10^{-8}$  sec at 300°K. The value of  $T_2$  varies somewhat from sample to sample and is presumably set by the impurity content.  $T_D$ , on the other hand, is set by lattice scattering and for a given crystal surface (see Sec. 4) should be characteristic of graphite. The value given above was obtained on the basal planes of a single crystal and it agrees within the experimental accuracy with the value computed from the dc  $c$ -axis conductivity.<sup>16</sup>

### 2. Estimate of the $c$ -Axis Conductivity from the Line Shape

The spin resonance of only those charge carriers on the basal planes may be observed by suitably masking off the edges of a graphite single crystal (see below). The value of  $T_D$  determined from the resonance line

<sup>15</sup> D. Pines and C. P. Slichter, Phys. Rev. **100**, 1014 (1955).

<sup>16</sup> W. Primak, Phys. Rev. **103**, 544 (1956).

shape then enables one to estimate the  $c$ -axis conductivity as follows: The time taken for an electron to diffuse along the  $c$  axis across the skin depth in the basal plane is

$$T_D = \frac{3}{2} \delta_a^2 / (\Lambda v)_c.$$

The conductivity along the  $c$  direction can be written

$$\sigma_c = N e^2 (v\Lambda)_c / m_c^* v_c^2.$$

At temperatures higher than the Fermi temperature ( $T_F \sim 200^\circ\text{K}$ ) one can make the approximation that

$$m_c^* v_c^2 \approx kT.$$

These three equations combine to give

$$\sigma_c \approx \frac{3}{2} \delta_a^2 N e^2 / T_D kT.$$

Using the values  $N = 2 \times 10^{19} \text{ cm}^{-3}$ ,  $\delta_a = 3.2 \times 10^{-4} \text{ cm}$ ,  $T = 300^\circ\text{K}$ ,  $T_D = 6 \times 10^{-8} \text{ sec}$ , one obtains  $\sigma_c \approx 3.2 \times 10^2 (\text{ohm-cm})^{-1}$ . As the measured value<sup>16</sup> of  $\sigma_a$  is  $2.6 \times 10^4 (\text{ohm-cm})^{-1}$ ,  $\sigma_a/\sigma_c = 80$ .

Thus the spin resonance line shape leads one to conclude that the mobility in the  $c$  direction is a factor of about 80 lower than that in the basal planes. The uncertainty in this value is roughly a factor of two. There also may be some error in the assumption made in combining the equations for  $T_D$  and  $\sigma_c$  that the average values  $\langle v\Lambda \rangle$  and  $\langle 1/v\Lambda \rangle^{-1}$  are equal. The best ratio of  $c$ -axis resistance to basal plane resistance obtained from dc measurements is between 100 and 200.<sup>16</sup> The agreement between the dc value and the value of the ratio obtained from spin resonance is excellent if one considers the rough approximations involved. Further complications due to surface conditions may also be present and these presumably could alter the ratio  $A/B$  from its expected value.<sup>11</sup>

### 3. Resonant Intensity

The intensity of the absorption line for charge carriers is proportional to the Pauli paramagnetic susceptibility,  $\chi_0$ . It may be shown<sup>17</sup> that for a metal

$$\chi_0 = \mu_B^2 \int_{-\infty}^{\infty} g(\epsilon) \left( -\frac{\partial f}{\partial \epsilon} \right) d\epsilon,$$

where  $\mu_B$  is the Bohr magneton,  $g(\epsilon)$  is the density of states as a function of energy, and  $f$  is the Fermi-Dirac distribution function. It is convenient to express this integral in terms of an effective number of unpaired spins per cubic centimeter,  $n^*$  whence

$$\chi_0 = n^* \mu_B^2 / kT.$$

McClure<sup>10</sup> has evaluated the band parameters of graphite by fitting the predictions of the theory to the experimental observations of de Haas-van Alphen effect, magnetoresistance, etc. The band parameters

thus determined enable him to evaluate  $n^*$  as a function of temperature as<sup>18</sup>

$$n^* = [0.0432T + 0.0000425T^2] \times 10^{18} \text{ cm}^{-3}.$$

This expression for  $n^*$  includes the contributions of both holes and electrons to the spin paramagnetism. The value of  $n^*$  at temperatures above the degeneracy temperature should, of course, agree with the total number of carriers observed in the Hall effect and magnetoresistance and this is observed to be the case<sup>19</sup> (within about a factor of two). The curve in Fig. 2 shows the theoretical spin paramagnetism as a function of temperature. Also shown in Fig. 2 are two experimental determinations of the absolute value of the spin paramagnetism at  $77^\circ\text{K}$  and at  $300^\circ\text{K}$ . The temperature dependence and the absolute magnitude of the measured values agree within the experimental accuracy of about 30% with the theoretical curve. This agreement is considered quite satisfactory in view of the difficulty of measuring absolute spin susceptibilities.

To determine the number of spins per cubic centimeter, we have taken the electrical conductivity in the  $c$  planes (basal planes) of graphite to be  $2.6 \times 10^4 (\text{ohm-cm})^{-1}$  at room temperature which, together with a frequency of 9.3 kMc/sec, yields a skin depth of  $3.2 \times 10^{-4} \text{ cm}$ . For convenience of calculation the line was assumed to be of the  $\chi' + \chi''$  form, from which it deviates by only a small amount, and the appropriate corrections were applied to compare it with the resonance of a known amount of diphenyl picryl hydrazyl. The volume susceptibility was obtained from the resonance signal by the use of Eq. (3.8) of reference 11 which applies to graphite and Eq. (3.2) which applies to hydrazyl. [Note: there is a factor of  $\frac{1}{2}$  missing in Eq. (3.8) as published.]

$$\begin{aligned} \frac{dP}{d\omega} &= \frac{\omega H_1^2}{2} \frac{\chi_0 \omega_0 T_2}{2} \frac{2T_2^2(\omega_0 - \omega)}{[1 + T_2^2(\omega_0 - \omega)^2]^2}, \\ \frac{dP}{d\omega} &= \frac{\omega H_1^2}{2} \left( \frac{\delta A}{2} \right) \frac{\chi_0 \omega_0 T_2}{2} \frac{T_2}{2} \\ &\quad \times \frac{[1 - 2T_2(\omega_0 - \omega) - T_2^2(\omega_0 - \omega)^2]}{[1 + T_2^2(\omega_0 - \omega)^2]^2}, \end{aligned}$$

where the top equation is (3.2) of reference 11, and the bottom equation is (3.8) of reference 11.

When observing the resonance of a single crystal suspended in the center of a microwave cavity one may encounter complications in measuring the absolute spin susceptibility which arise from the fact that the conductivity of graphite along the  $c$  axis is 100 to 200 times smaller than the conductivity in the basal plane. Thus, even though the crystals are very thin flakes with an aspect ratio approaching 100, the volume of sample

<sup>17</sup> A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), p. 151.

<sup>18</sup> J. W. McClure (private communication).

<sup>19</sup> D. E. Soule, *Phys. Rev.* **112**, 706 (1958).

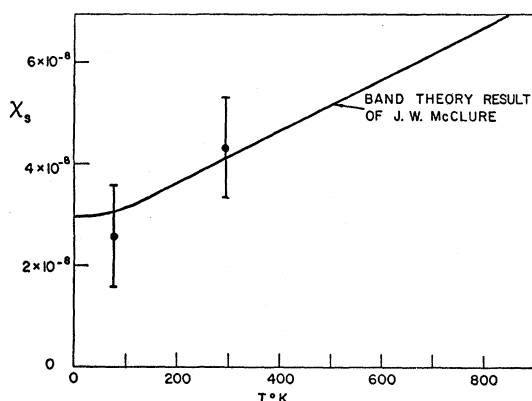


FIG. 2. Spin paramagnetism of graphite as a function of temperature.

seen by the microwave from the crystal edge is about equal to the volume of sample seen from the planes. Furthermore, the skin depth on the crystal edge is about one-third of the height of the sample so the electromagnetic plane wave approximation will not be valid for computing the resonant absorption intensity. To avoid these difficulties, a graphite crystal was prepared with its edges plated with copper and overcoated with solder to shield from the microwaves all regions of the specimen except the two exposed sides which consisted entirely of basal plane. The reference hydrazyl crystal was affixed to the center of one of the plane faces of the crystal to insure that  $H_1$  was the same for the sample and the reference. We believe that the absolute spin susceptibility obtained after observing these precautions is accurate to  $\pm 30\%$ . The room-temperature experimental point in Fig. 2 is that given by this method, whereas the value of  $\chi$  at  $77^\circ\text{K}$  is determined relative to the room-temperature result on an unplated crystal.

An attempt was made to determine if a large error resulted from the assumption of plane electromagnetic waves on the edge of an unplated crystal. The line shape and the measured spin susceptibility of an unplated crystal were compared with that of the crystal with its edge plated. All results were in agreement well within the experimental error for the crystal tested which was unusually regular. As the next section shows, irregular specimens would not be expected to give agreement, as their line shape indicates faster diffusion which would reduce the resonance intensity.<sup>11</sup>

#### 4. Anisotropy of the Diffusion Time

Dyson, in his theory of the line shape of the spin resonance of conduction electrons, assumed for simplicity that the electrons diffuse like free particles. The carriers in graphite, however, have highly anisotropic Fermi surfaces with the mobility along a crystallographic  $a$  axis about 100 to 200 times that along the  $c$  axis. The anisotropy was accounted for in the estima-

tion of the  $c$ -axis conductivity by simply assuming an anisotropic diffusion constant  $D = \frac{1}{3}(v\Lambda)$  with principal values  $\frac{1}{3}(v\Lambda)_c$  and  $\frac{1}{3}(v\Lambda)_a$  along the  $c$  and  $a$  directions.

The anisotropy of the diffusion in graphite may be expected to have a marked effect on the value of  $T_D$  observed in spin resonance measurement on a surface other than a basal plane. For a surface on a graphite single crystal whose normal lies at an angle  $\psi$  away from the  $c$  axis,

$$T_D = \frac{kTc^2}{2\pi\omega Ne^2(v\Lambda)_\psi(v\Lambda)_{\psi+\pi/2}}.$$

$T_D$  is the time it takes for a spin to diffuse in the direction normal to the surface through a distance equal to the penetration depth and it is this parameter which determines the line shape of the spin resonance. The magnitude of the penetration depth  $\delta$  is determined by the mobility in the direction  $\psi + \pi/2$ , parallel to the sample surface. It is possible to evaluate crudely the expression for  $T_D$  as a function of  $\psi$  by assuming

$$(v\Lambda)_\psi = (v\Lambda)_c + [(v\Lambda)_a - (v\Lambda)_c] \sin^2\psi.$$

Then

$$T_D(\psi) \approx \frac{kTc^2}{2\pi\omega Ne^2(v\Lambda)_a \{ [(v\Lambda)_c / (v\Lambda)_a] + \sin^2\psi \cos^2\psi \}}.$$

From the ratio of the electrical conductivity in the  $c$  direction to that in the  $a$  direction one knows that  $(v\Lambda)_c / (v\Lambda)_a \approx 10^{-2}$ . The value of  $T_D$  is thus a highly anisotropic function of the angle  $\psi$ .

The general validity of the above result was demonstrated by observing the spin resonance of a sandblasted graphite crystal. The effect of sandblasting is to make the surface wavy on a microscopic scale. This exposes to the microwaves regions of surface with values  $\psi$  intermediate between  $\psi = 0^\circ$  and  $90^\circ$ . Such surfaces should have  $T_D$  values very much shorter than those surfaces with  $\psi = 0^\circ$  or  $90^\circ$ , and the shorter value of  $T_D$  should increase the ratio of peak heights  $A/B$  for the resonance curve. The experiment qualitatively confirmed these expectations in that the resonance curve for the undisturbed crystal had a ratio  $A/B = 3$  while the same crystal after sandblasting yielded  $A/B = 6$  showing clearly the enhancement of diffusion.

The expression given above for  $T_D$  as a function of  $\psi$  is a fairly rough approximation in that scalar values of  $(v\Lambda)$  as a function of  $\psi$  are used, whereas in actual fact  $(v\Lambda)$  (and also the conductivity) is a tensor. A proper solution of the problem would include a solution of the wave equation with the appropriate boundary conditions and a correct accounting for the effects of the tensor diffusivity. We have not attempted to do this at the present time as it is not possible to obtain graphite crystals with exposed surfaces having a single definite intermediate value of  $\psi$  with which to compare the theory.

The linewidth of the spin resonance did not change when the surface was sandblasted showing that the spins do not relax strongly through surface states and are thus relatively unaffected by surface conditions.

### 5. The $g$ Value

The most remarkable feature of the spin resonance in graphite is the large  $g$ -value anisotropy. The spectroscopic splitting factor  $g$ , which satisfies the resonance condition  $\hbar\omega = g\mu_B H$ , shows a strong dependence on the angle between the crystallographic  $c$  axis and the magnetic field. The magnitude of the anisotropy of  $g$  also depends strongly on temperature and on the position of the Fermi level with respect to the band edge. The deviation of  $g$  from the free electron value of 2.0023 is governed by the contribution of orbital angular momentum in the electronic states of spins giving rise to the resonance. A detailed theoretical treatment for the graphite spin resonance has not yet been worked out, but it appears that the general theory of Elliott<sup>4</sup> accounts qualitatively for the observations.

The  $g$  value of graphite may be very closely fitted by the following expression

$$g = g_1 + A \cos^2 \theta,$$

where  $\theta$  is the angle between the static magnetic field and the  $c$  axis, the  $g$ -value anisotropy  $A$  is 0.047 at room temperature in pure graphite, and  $g_1$  is equal to  $2.0026 \pm 0.0002$ . The value of  $g_1$  is independent of temperature, whereas the anisotropy  $A$  is very strongly dependent on temperature and changes drastically upon the addition of a small amount of electrically active impurity. Figure 3 shows the fit of the anisotropy expression to the experimentally measured  $g$  values of a pure single crystal of graphite at room temperature. The excellent agreement of the experimental points with the curve is evidence that the specimen of graphite is quite perfect and contains no large misoriented regions. The strong temperature dependence of  $A$  is shown in Fig. 4. Also given are two values of  $A$  (at 77°K and at 293°K) for a graphite sample doped with 0.037

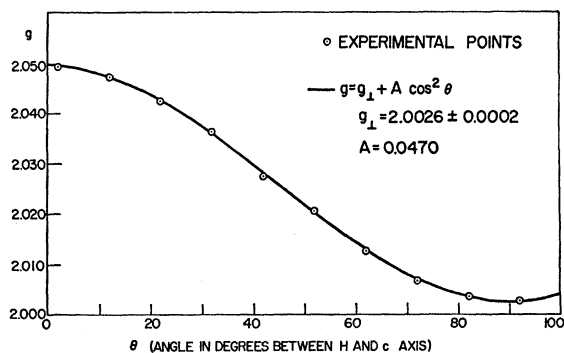


FIG. 3. The  $g$ -value anisotropy of the graphite spin resonance at room temperature.

atomic percent boron. The astonishing dependence of the anisotropy on a small change of the Fermi level is clearly demonstrated.

The order of magnitude of the  $g$  shift from the free electron value may generally be written as

$$\Delta g \sim \lambda / \Delta,$$

where  $\lambda$  is the spin orbit coupling and  $\Delta$  is the energy separation of the state being mixed in by the  $L \cdot S$  coupling. A more precise expression would include the appropriate matrix elements and an average over the states contributing to the resonances. This has been done by Elliott in his theory of the effect of spin orbit coupling on the electron spin resonance in semiconductors. In particular, he has treated the case of "electrons with kinetic energies large compared to the spin-orbit coupling energy occupying states with energies near a point where bands are degenerate." This is just the situation which prevails in graphite.<sup>5,6,7</sup> Elliott shows that it is the perturbing effect of nearly de-

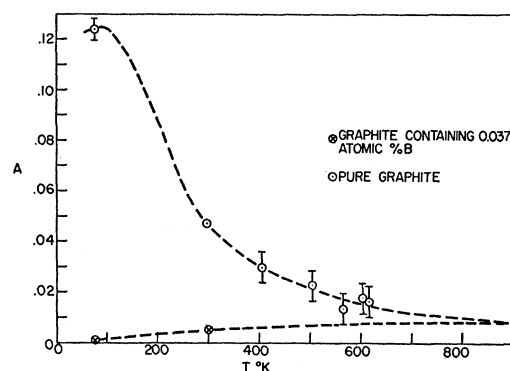


FIG. 4. Temperature dependence of the  $g$ -value anisotropy of graphite.

generate states that gives a particular state at the Fermi surface its large  $g$  shift. Thus, the degeneracy of the energy bands of graphite at the zone edge appears to be the source of the unusual  $g$  shift. Elliott's  $g$ -shift result, while not directly applicable to graphite as only wave functions with the symmetry of a diamond lattice are considered, may be expected to give the correct order of magnitude. If the dependence on the shape of the bands near the state of interest is neglected, the  $g$  shift has the order of magnitude  $\Delta g \sim \lambda / \zeta$ , where  $\zeta$  is the Fermi energy measured relative to the band edge. For graphite,  $\lambda_{sp} \approx 0.0037$  ev<sup>20</sup> and  $\zeta \approx 0.017$  ev,<sup>21</sup> and thus  $\Delta g \sim 0.2$ . The observed value of  $\Delta g$  for pure graphite at 77°K is  $\Delta g = 0.125$ . This is much better agreement than one would expect from such rough considerations.

Elliott further derives an expression which is expected

<sup>20</sup> J. C. Slonczewski, thesis, Rutgers University, 1955 (unpublished).

<sup>21</sup> D. E. Soule, Phys. Rev. **112**, 708 (1958).

to be valid at temperatures much greater than the degeneracy temperature,  $T_F$  ( $\sim 200^\circ\text{K}$  for graphite).

$$\Delta g = (T_F/T)(\Delta g)_F,$$

where  $(\Delta g)_F$  is the value of  $\Delta g$  measured at a temperature much less than  $T_F$ . Figure 5 shows  $\Delta g$  as a function of  $T^{-1}$ . The linear behavior at high temperatures is evident. The slope of the curve may be used to calculate  $(\Delta g)_F = 0.081$ . This is not unreasonable when compared to the observed value of the  $g$  shift at  $77^\circ\text{K}$  of 0.12. There is, however, one discrepancy in that  $\Delta g$  does not extrapolate to zero at high temperature, as the above formula would indicate, but instead approaches the value  $-0.009$ . Nonetheless, it is quite clear that Elliott's theory has many features at least in qualitative agreement with the observations on graphite.

That the electron spin resonance in graphite is due to both holes and electrons contributing to a single resonance absorption may be largely inferred from simple relaxation time considerations. The observed line width of about four gauss leads to a relaxation time  $T_2$  for the spins of  $2 \times 10^{-8}$  second. The collision time of the carriers with the lattice is on the order of  $10^{-13}$  second. Thus, a charge carrier with its associated spin makes  $2 \times 10^5$  collisions between spin flips. This enables it to sample the entire Fermi surface and to produce a resonance whose  $g$  value is just the average over all the states (holes and electrons) on the Fermi surface.

In connection with this averaging process, it is interesting to note that the change of  $g$  value with temperature from  $77^\circ\text{K}$  to  $600^\circ\text{K}$  corresponds to a shift in magnetic field for resonance of about 160 gauss, which is some 40 times the linewidth. This large change must be caused by the change in population of the energy states with temperature. As the temperature is increased, the population shifts from states close to the band edge to those further away which have smaller  $g$  shifts.

## 6. The Linewidth

The linewidth  $\Delta H$  (see Fig. 1) for the purified graphite crystals decreases with increasing temperature, the values being roughly five gauss at  $77^\circ\text{K}$ , four gauss at room temperature and one gauss at  $600^\circ\text{C}$ . This dependence strongly suggests spin-lattice relaxation through interaction with the spin-orbit coupling of impurity atoms. Following Pines and Slichter<sup>15</sup> one can obtain an estimated spin-lattice relaxation time of

$$1/T_1 \sim (\lambda^2/\hbar^2)(a/v)f,$$

where  $\lambda$  is the spin-orbit coupling,  $a$  the dimension of a unit cell,  $f$  the fraction of impurity atoms, and  $v$  the electron velocity. At low temperatures, the electron

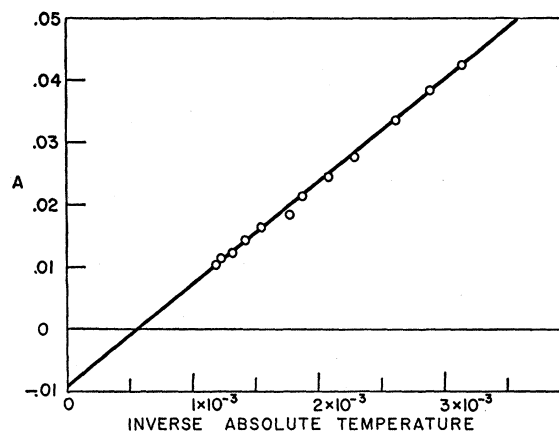


FIG. 5. The  $g$ -value anisotropy of pure graphite vs inverse temperature.

gas becomes degenerate and  $v$  is the velocity of an electron on the Fermi surface. At temperatures well above the Fermi temperature,  $v \sim [kT/m^*]^{1/2}$  and the linewidth falls off as  $T^{-1/2}$ . The above equation for the relaxation time is reasonable in magnitude as well as temperature dependence since the graphite impurity content of some 20 ppm could easily produce the observed linewidth.

It is worth noting that Elliott's expression for spin-lattice relaxation through lattice scattering, i.e.,  $T_1 \sim \tau_R(g-2)^2$  gives a value some  $10^7$  times shorter (broader line) than that observed and furthermore has the wrong temperature dependence. ( $\tau_R$  is the relaxation time characteristic of the electrical resistivity.)

The linewidth, which might be expected to be large from the spread in  $g$  values, is motionally narrowed. For a motionally narrowed line, one would expect that<sup>16</sup>

$$1/T_2 \sim \tau_R[(\Delta g/g)\omega]^2.$$

For graphite at high temperatures, this expression varies as the absolute temperature to the inverse 3.2 power, which is a much stronger variation with temperature than the experiments indicate. Moreover, the observed magnitude of  $T_2$  at room temperature is two orders of magnitude less than this expression yields. Thus, the motional narrowing must be complete and the linewidth is set by a spin-lattice relaxation mechanism, presumably the one above due to impurities.

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