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Change in Fermi Surfaces of Graphite by Dilute Acceptor Doping

Abstract: The effect of doping graphite single crystals with the acceptor boron was studied in the dilute range from $\lesssim$0.1 ppm to 0.5% by measurements of the Hall effect and de Haas - van Alphen effect. The transition from a mixed electron and hole conduction in the narrow band overlap region (0.035 eV) to that of a single hole conduction produces a peak in the Hall coefficient that shifts to a lower boron concentration with a decrease in temperature. The increase in hole concentration is accompanied by a rapid decrease in mobility, demonstrating the importance of collision broadening. Preliminary de Haas - van Alphen results tentatively identify the major electron and hole Fermi surfaces by means of the period shift with increasing acceptor concentration. A *new*, very small ellipsoid-like Fermi surface was discovered. It is aligned along the hexagonal axis, having an anisotropy ratio of 9 with orbital masses of about 0.0023 m_0 for H $\parallel$ C and 0.017 m_0 for H $\perp$ C. Analysis strongly indicates that this surface contains minority holes. Three of these surfaces are considered to be aligned symmetrically like "outriggers" about the major hole surface, producing a total of six in the Brillouin zone. A comparison is made with the cyclotron resonance results and a possible interpretation of these minority Fermi surfaces is presented using the Slonczewski-Weiss band model.

Introduction

In a study of the change in the topology of Fermi surfaces and related electronic properties with shifting Fermi level, one must avoid undue perturbing of the host lattice in order to study reliably the gradual progression from the pure case. Boron was chosen as the acceptor because of its small size (B^{+3} ion diameter, 0.40 Å) and because it has one fewer valence electron than carbon. In addition, there have been indications in the past that boron ions occupy substitutional trigonal sites in the graphite lattice, a fact which has recently been substantiated by X-ray measurements.[1] Dilute doping is particularly important in a semimetal such as graphite because of its small band overlap (0.035 eV), making some electronic properties very sensitive to a small Fermi level shift. Finally, dilute doping minimizes the complicating, and in some cases devastating, effects of collision broadening.

The measurements of greatest interest are those which are sensitive to the *difference* in electron and hole behavior or, more importantly, those that see the effect of the *individual* Fermi surfaces themselves without being influenced by complicating scattering effects. Accordingly, we shall concentrate on the Hall and de Haas - van Alphen effects. As described previously,[2] the electrical conductivity, magnetoresistivity, and diamagnetic susceptibility have also been studied; however, these properties relate here only in a secondary way.

The boron concentration of nominally "pure" graphite single crystals purified by the conventional method in chlorine at 3000°C is $\lesssim$ 1 ppm. In this work, the technique has been improved by using fluorine at 3200°C, which reduces the boron content to $\lesssim$ 0.1 ppm. Boron was then introduced by diffusion.[2] The resulting concentration varied from the lowest level of 7 $\pm$ 2 ppm to the highest level of 0.5 $\pm$ 0.05% boron. In addition to a careful determination of the concentration, the distribution of boron throughout a crystal was checked[2] and was found to be homogeneous.

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Hall effect

The Hall coefficient was measured at 298°K and 77°K in magnetic fields up to 5 kilogauss. The acceptor behavior is demonstrated in Fig. 1, showing the transition with increasing concentration from a mixed electron and hole conduction to that of hole conduction alone. The peak, resulting from the transition to the $1/ecn_h$ behavior, occurs at 2.2×10^{-4} B/C at 298°K and shifts to 3.3×10^{-5} B/C when the temperature is lowered to 77°K. This shift is caused mainly by the narrowing of the Fermi distribution. There is a corresponding increase in height from $+0.15$ cm^3/coul to $+0.60$ cm^3/coul caused by the increase in mobility. The hole concentrations, derived from these data using the zero-field approximation to the two band model, are shown below. It will be noted that these curves coalesce at $\sim 10^{-3}$ B/C, becoming temperature independent. This region is one of comparatively high concentration where other complicating effects might enter. Since these factors have been reported previously,[2] they will not be considered further here. The lowest level is that measured earlier[3] on single crystals that were nominally "pure" ($\lesssim 1$ ppm B), plotted arbitrarily at 1 ppm B, leading to a corresponding uncertainty in the Hall coefficient curve in the lowest concentration region. The pure hole concentration value at liquid helium temperature, also plotted, is only about 10% below that observed at 77°K. A dashed curve shows its probable behavior with boron concentration. The resultant "ionization" efficiency of $75 \pm 15\%$ in the vicinity of the band edge is in agreement with that determined from the diamagnetic susceptibility measurements.[2] Such a large value indirectly supports the conclusion that the three valence electrons are covalently bound in a substitutional site in the graphite lattice.

At the bottom of the Figure, the inverse Hall mobility is shown to illustrate the rapid increase in collision broadening where, for example, the mobility at 4.2°K decreases about a factor of 10 for an increase in concentration from 1 to 10 ppm B.

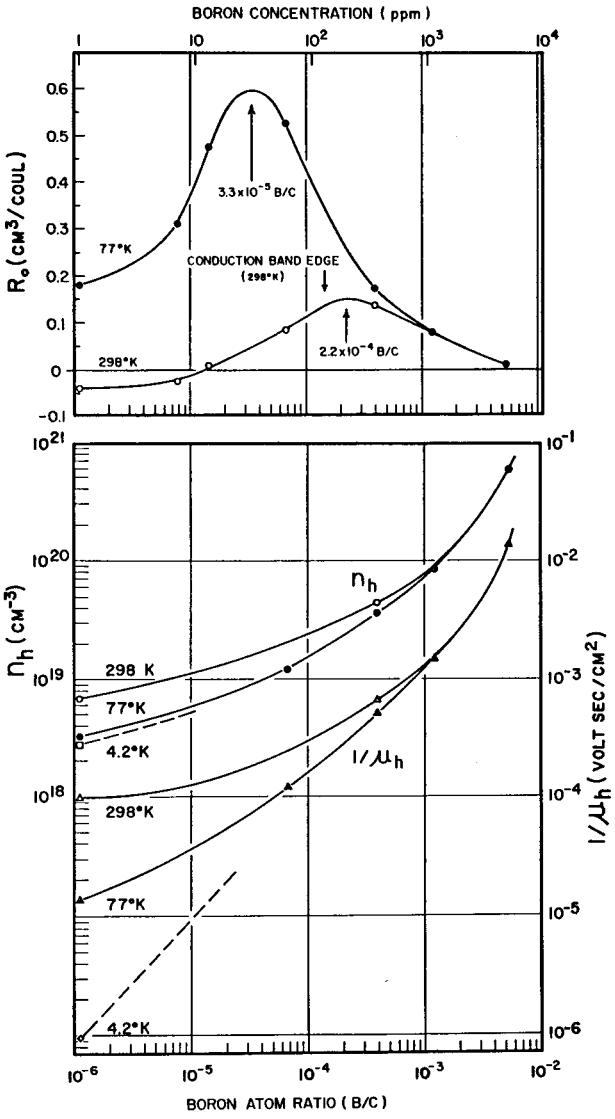

Figure 1 **Zero-field Hall coefficient, hole concentration, and Hall mobility as a function of boron concentration at 298°K and 77°K.**

de Haas - van Alphen effect

The evidence of a strong increase in collision broadening with boron concentration further emphasizes the need for remaining in the very dilute region, especially with the de Haas - van Alphen effect. Accordingly, these measurements were made on samples in the range from $\lesssim 0.1$ ppm up to 60 ppm B. In addition, since it was shown previously[4] that ΔT, the effective shift in temperature due to collision broadening, found in the susceptibility (de Haas-van Alphen effect) is about one-fifth that observed in the magnetoresistance (Shubnikov-de Haas effect), there is a distinct advantage in studying the former. The torque method, using a differentiation technique, was employed in the magnetic field range from 2 to 23 kilogauss at temperatures ranging from 2.0°K up to 4.2°K.

Figure 2 compares the oscillatory period behavior due to the major Fermi surfaces with the results obtained from the Shubnikov - de Haas effect,[4] which are shown as solid-line curves for the pure case as normalized to the present de Haas - van Alphen data. The identification as to which period is due to electrons and which to holes was made previously by an indirect reference to the cyclotron resonance results of Galt et al.[5] There is an indication here, where we can make a direct comparison with increasing concentration of a known acceptor, that the larger period

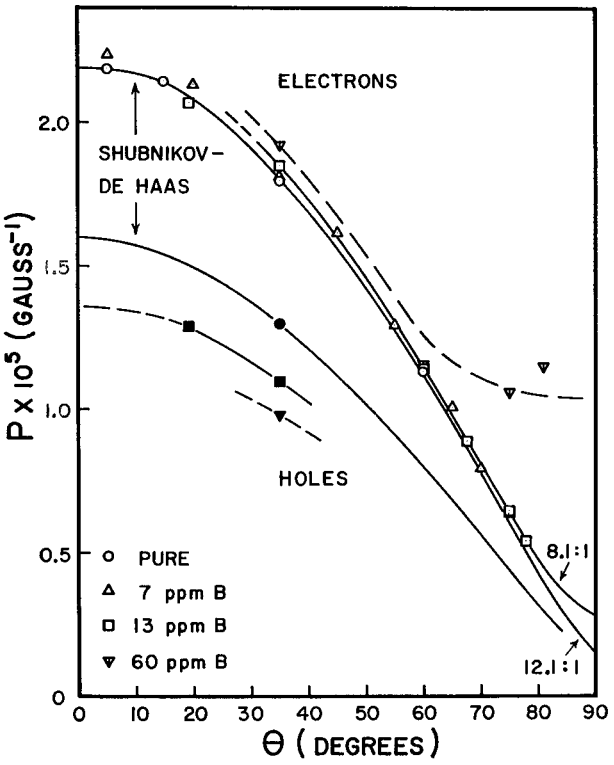

Figure 2 **de Haas-van Alphen period orientation dependence of the major electron and hole Fermi surfaces for several boron concentrations.**

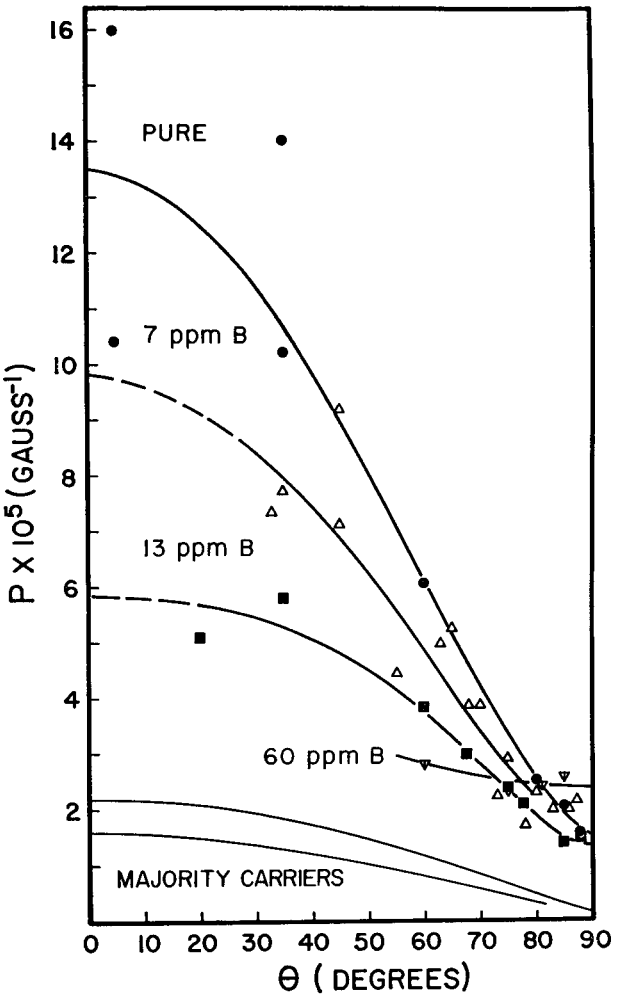

Figure 3 **de Haas-van Alphen period orientation dependence of the minority carrier Fermi surface for several boron concentrations. The majority carrier curves are also shown for comparison.**

term is indeed due to electrons since its radius about the hexagonal axis *decreases*, and that the smaller period term, to a lesser degree since it is not as well known, is due to majority holes since its radius *increases*. The most accurate data are at $\theta = 35°$ (θ being the angle between the magnetic field and the hexagonal c-axis), where a direct comparison was carefully made under identical experimental conditions. Ellipsoidal fits were made to the electron term data at $\theta = 0$ and at high θ. An extrapolation to $\theta = 90°$ for the 13 ppm B level is shown in the Figure. The Shubnikov - de Haas measurements taken on a pure crystal at all values of θ established an anisotropy ratio of 12:1 for the major electron surface. Here, however, for the 13 ppm B level, a ratio of 8:1 was obtained. Dimensions in both the k_x and k_z directions are evidently decreasing with increasing concentration. These preliminary results are in reasonable agreement with those predicted from the Slonczewski-Weiss band model[6] parameterized by McClure.[7] Further work is in progress, however, to establish this result unequivocally.

The most striking feature of this study is the discovery of a *new* very small Fermi surface in graphite. The exceedingly large period observed is compared in Fig. 3 with those of the major Fermi surfaces just discussed and is shown at the bottom of the Figure. The period shift with increasing acceptor concentration shows that the cross section of this Fermi surface at $\theta = 0$ *increases* with a lowering of the Fermi level. In fact, this behavior is very sensitive to a very small Fermi level shift where, for example, it increases by a factor of two at the 13 ppm B level, a shift of only 0.001 eV. The occurrence of oscillatory periods at θ approaching 90° shows this surface to be *closed* in the k_z direction. Although the trend with boron concentration of the cross section containing k_z is still indefinite, there is rather strong evidence for identifying this large period as originating from a separate minority hole Fermi surface. The extreme size of these periods made accurate resolution difficult. They are, in fact, among the largest observed in any material. In addition, evidence for a still larger

period, $>25 \times 10^{-5}$ gauss^{-1} and possibly due to minority electrons, was seen but could not be evaluated quantitatively.

The existence of minority carriers in graphite has been demonstrated previously by the low-field Hall effect[3] and cyclotron resonance.[5] The effects of both electron and hole minority carriers were seen. These carriers were associated with the small trigonal warping of the major Fermi surface tips as predicted from the band theory.[7,8] Analyses by Lax and Zieger[9] and by Nozières[8] of the cyclotron resonance results showed that these minority carrier pockets in the zone have twofold symmetry and should be located, as shown in Fig. 4, in the planes BOΓ, AOΓ or a vertical zone face, the latter being the most probable. There is some question, however, that such large peaks observed on the power absorption derivative curve could arise from such a small number of carriers associated with the surface pips.

The present results differ in that such minority carriers, in this case holes, are associated with *closed* ellipsoid-like Fermi surfaces, which for the pure case have an anisotropy ratio of 9 and orbital masses (determined from the temperature dependence of the oscillatory amplitude) of about 0.0023 m_0 for **H** || **C** and 0.017 m_0 for **H** ⊥ **C**. If we assume from the trigonal symmetry of the band structure and by analogy with the cyclotron resonance results that these consist of three "outrigger" surfaces placed symmetrically 120° apart when reduced about the zone edge, and aligned along k_z as shown in Fig. 4, the total number of Fermi surfaces in the Brillouin zone will be $Q = 6$. Each surface contains 0.0322×10^{18} cm^{-3} carriers, giving a total of 0.19×10^{18} cm^{-3} as shown in Table 1, where values for both the majority and minority carriers are shown for comparison. In the Shubnikov - de Haas work,[4] the major hole period could be fitted as far as it was observed

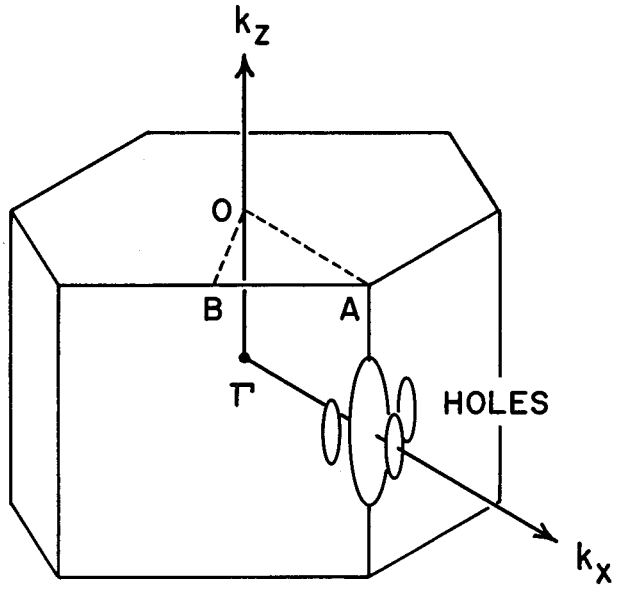

Figure 4 **Brillouin zone with possible location of minority hole "outrigger" Fermi surfaces as reduced about the zone edge.**

($\theta = 84°$) by a 12:1 ellipsoid giving a total majority hole concentration of 2.2×10^{18} cm^{-3} for $Q = 2$. The non-oscillatory galvanomagnetic results[3,10] yielded concentrations of 3.0×10^{18} cm^{-3} for the majority electrons and 2.8×10^{18} cm^{-3} for majority holes. Although there is good agreement for the electrons between these two carrier concentration numbers showing that $Q = 4$, the hole results are not so good. If we assume, however, that the non-oscillatory value is actually the *total* hole concentration, then it should be compared to the sum $n(\text{osc}) = 2.4 \times 10^{18}$ cm^{-3} due to both majority and minority holes. This considerably improves the agreement.

Table 1 **Electron and hole parameters in pure graphite.**

Fermi Surface	$P \times 10^5$ (gauss^{-1}) H || C	$P \times 10^5$ (gauss^{-1}) H ⊥ C	*Orbital mass Ratio* H || C	*Orbital mass Ratio* H ⊥ C	n(osc) $\times 10^{-18}$ (cm^{-3})	n(non-osc) $\times 10^{-18}$ (cm^{-3})
Electron						
Majority	2.19	0.15†	0.039‡	0.47‡	2.9 ($Q = 4$)‡	3.0 ± 0.3
Minority (?)	$\gtrsim 25$		—	—	—	
Hole						
Majority	1.60	0.13*	0.057‡	0.68*	2.2 ($Q = 2$)‡	2.8 ± 0.3
Minority	13.5 ± 3	1.5	~0.0023	~0.017	0.19 ($Q = 6$)	

† From the Shubnikov - de Haas effect. (Ref. 4)
* For an anisotropy ratio of 12. (Ref. 4)
‡ See Reference 4.
Q = number of Fermi surfaces in Brillouin zone.

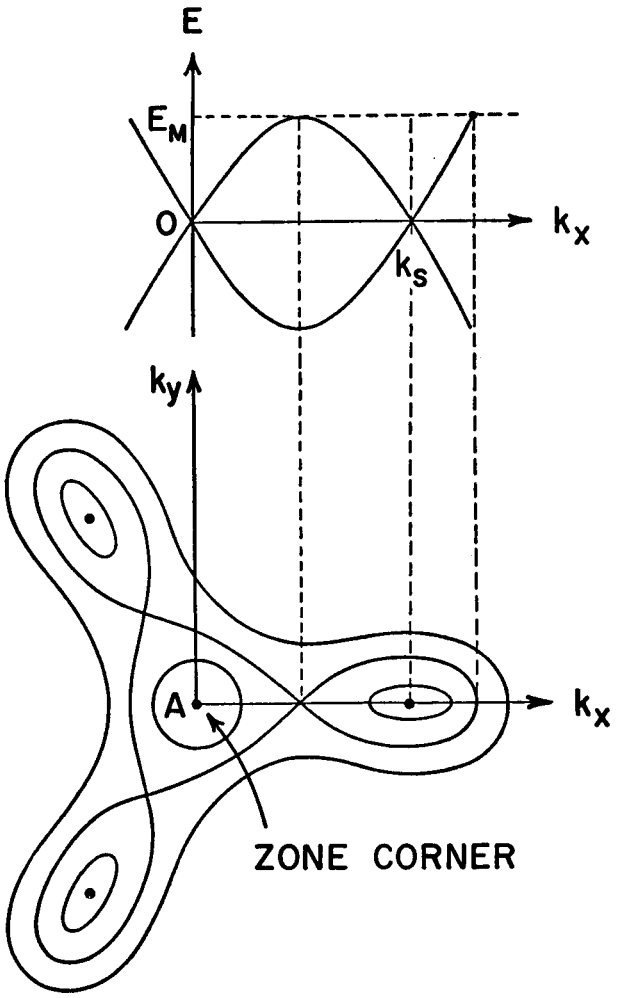

Figure 5 **Fermi surface cross sections derived (Nozières[8]) from the Slonczewski-Weiss band model for the case of E close to E_s and k_z away from $\pm\pi/c_0$.**

It would be interesting to see if these separate minority hole surfaces can be reconciled in some way with the existing Slonczewski-Weiss band model. From the four-parameter secular equation for the case where the energy E, measured from the bottom of the conduction band, is close to $E_3 = 2\gamma_2 \cos^2 (c_0 k_z/2)$ and for values k_z away from $\pm\pi/c_0$, the top or bottom of the zone, Nozières[8] has derived the anisotropic energy surface cross sections shown in Fig. 5. The variables k_s and E_M are given by

$$k_s = \frac{4}{\sqrt{3}a_0} \frac{\gamma_1\gamma_3}{\gamma_0^2} \cos^2 (\tfrac{1}{2}c_0 k_z)$$

and

$$E_M = \frac{\gamma_1\gamma_3^2}{2\gamma_0^2} \cos^3 (\tfrac{1}{2}c_0 k_z).$$

Using the accepted values for these parameters of

$\gamma_0 \simeq 2.8$ eV,

$\gamma_1 \simeq 0.27$ eV,

and

$\gamma_3 \simeq 0.14$ to 0.28 eV,

at $k_z = 0$, $E_M = 0.00034$ eV (using the lower limit for γ_3 as derived recently by Dresselhaus and Mavroides[11]). Since the electron Fermi energy is 0.014 eV, the trigonal warping is restricted to the tips of the major Fermi surfaces. The value of γ_3 is not considered to be as reliably known as γ_0 and γ_1. If we take the reverse procedure and equate E_M to the electron Fermi energy, the resultant γ_3 is 0.86 eV. This value seems large in the light of other accepted features of the band structure. Therefore, a more drastic modification of the Slonczewski-Weiss band model in this critical region appears necessary.

Acknowledgments

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Discussion

G. Dresselhaus: Is it possible that the new de Haas - van Alphen period which you observe could be accounted for by a magnetic field dependence of the Fermi level, brought about by transfer of electrons from one band to another, similar to that reported by Smith, Baraff and Rowell?

D. E. Soule: I should think that such an oscillation of the Fermi level would give a period about the same as that of the majority carriers. The observed period is a much longer period and is not any harmonic or beat period of the majority carrier periods.

J. W. McClure: I would like to point out that Nozières' analysis of the harmonics in the cyclotron resonance experiment indicated a Fermi surface with trigonal cross sections and not three little separated pieces of Fermi surface. The disagreement of these long periods with the Slonczewski-Weiss model is serious, and should be resolved.

Unidentified questioner: Would you comment on your starting material?

Soule: The single crystals were both natural and synthetic. The natural crystals were obtained from Essex County, New York. They were purified and their structural perfection was measured by various x-ray techniques. The synthetic crystals were grown from a supersaturated iron solution at about 3,200°C and have an impurity content of about 1 ppm.

J. A. Krumhansl: The experimental work which has led to the newly observed period differs from other relevant work, such as magnetoresistance, in two respects: (1) purer samples and (2) measurement of the susceptibility by a torsion technique. Would this new period be observable in magnetoresistance measurements of these pure samples?

Soule: The impurity content is actually less important. There is no observable difference in the measurements between samples of 1 ppm and 0.1 ppm boron content. The use of the modified torsion method for oscillatory susceptibility measurements is, however, important. This technique allows one to pick out a long period in $1/H$, because the method involves differentiation of the signal and the long-period term can be preferentially amplified by tuning the filter circuit. On the other hand, in a magnetoresistance measurement, the long periods would be masked by the effect of the large dc background. I should comment at this point that these long periods are very difficult to determine quantitatively, because of the interference from the majority electron and hole periods.