Effect of Pressure on the Fermi Surface of Graphite*

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Measurements of the de Haas–van Alphen effect in natural single-crystal graphite have been made at pressures up to 4 kbar. The results for the majority carriers have been interpreted in terms of the Slonczewski-Weiss band model. The minority-carrier results appear to be consistent with the interpretation given by Dresselhaus and Dresselhaus in which spin-orbit splitting at the hexagonal zone faces is included.

I. INTRODUCTION

THE success of the Slonczewski-Weiss (SW) band model[1] with adjustable parameters in describing the electronic structure and Fermi surface of graphite has prompted interest recently in testing the ability of the model to account for variations in the Fermi surface with changes in interatomic spacing. The small energy band overlap of this semimetal suggests that the Fermi surface would be quite sensitive to changes in lattice spacing. Because of the large elastic anisotropy, the effect of hydrostatic pressure is to impose an essentially uniaxial strain parallel to the hexagonal axis. This fact appreciably simplifies the analysis of the changes of band parameters with pressure as determined from de Haas–van Alphen (dHvA) studies.

In this paper we present the determination of the pressure dependences of 3 de Haas–van Alphen frequencies for hydrostatic pressures up to 4 kbar. Preliminary results were reported previously.[2] The results for the two major extremal cross sections of the Fermi surface can be described by the SW model with a suitable choice of parameters and their pressure variations. The result for the third frequency, which is nearly an order of magnitude less than the two majority-carrier frequencies, can be made consistent with an assignment made by Dresselhaus and Dresselhaus[3] for a portion of the Fermi surface attributed to minority carriers.

In Sec. II, the SW formalism and the approximations used are outlined and the model Fermi surface is described. The experimental details are outlined briefly in Sec. III. The results are given in Sec. IV and are discussed in Sec. V.

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[1] For a recent review see, J. W. McClure, IBM J. Res. Develop. 8, 255 (1964).
[2] J. E. Schirber, J. R. Anderson, W. J. O'Sullivan, and D. E. Soule, Bull. Am. Phys. Soc. 11, 222 (1966).
[3] G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. 140, A401 (1965).

II. THEORETICAL MODEL

Slonczewski and Weiss[4] have developed a model for the behavior of the energy bands of graphite in the neighborhood of the vertical edges of the hexagonal Brillouin zone. This model involves parameters generally related to the tight-binding model and leads to the Fermi surface shown schematically in Fig. 1, consisting of highly elongated hole and electron surfaces, roughly ellipsoidal in shape, with their major axes aligned along the six vertical edges of the zone.[5] Conventionally, the carriers related to these ellipsoids have been called the majority carriers. Additional very small closed sheets have been observed which contain the so-called minority carriers.[6] Dresselhaus and Dresselhaus[3] have argued that the electron tips protrude through the hexagonal faces and are closed by a splitting of the bands at this face by the spin-orbit interaction, thus forming the minority carriers. From boron-doping experiments, Soule has suggested, however, that the minority carriers are holes,[6] but this conclusion has been questioned[7] because the number of minority carriers does not increase linearly with boron concentration. (The change is linear for the majority carriers). We will show that the pressure results presented here are consistent with the Dresselhaus interpretation, and reasonable choices of the pressure dependences of appropriate combinations of the band parameters, if the zero-pressure band parameters are chosen in a rather restricted manner.

The simplified band-structure picture of graphite used in our analysis is represented by a parametrized SW band model adjusted to fit several different types of experimental results. In Fig. 2 we show a SW plot of energy versus k along the Brillouin zone edge HKH. The *abab* stacking in the hexagonal graphite lattice gives rise to two different types of atomic sites A and

[4] J. C. Slonczewski and P. R. Weiss, Phys. Rev. 109, 272 (1958).
[5] Cf: D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. 134, A453 (1964).
[6] D. E. Soule, IBM J. Res. Develop. 8, 268 (1964).
[7] S. J. Williamson, S. Foner, and M. S. Dresselhaus, Phys. Rev. 140, A1429 (1965).

TABLE I. Range of zero-pressure band parameters (in eV).

γ_0	γ_1	γ_2	E_F	$-\Delta$
2.7–3.0	0.28–0.4	0.016–0.025	0.022–0.034	0.0–0.01

B which see inequivalent potential distributions. This difference is manifested in the parameter Δ. The parameter γ_0 is the only parameter in the single-layer case and represents the overlap between wave functions centered on nearest-neighbor A and B atoms. The overlap between wave functions centered on nearest A atoms in adjacent layers is represented by γ_1, while the overlap related to B atoms two layers apart is given by γ_2.

The elastic anisotropy is exceptionally large in graphite ($C_{11}/C_{33}\approx 29$)[8] so that with the hydrostatic pressures involved in this investigation, changes in the basal-plane lattice constants are negligible and the stress can be considered uniaxial along the hexagonal axis. Because of this elastic anisotropy, we assume that the parameter γ_0 will be independent of pressure. Additional parameters γ_3, γ_4, and γ_5, which account for the axial asymmetry about the zone edges HKH, are neglected in our treatment.

The parameters that would be expected to depend most strongly on the spacing between layers are Δ, γ_1, and γ_2. In addition, as can be seen from Fig. 2, the position of the Fermi level E_F may also be very critical in the case of small band overlap and therefore may be a strong function of change in the interlayer spacing. In Table I we have listed the range of zero-pressure values of the parameters γ_0, γ_1, γ_2, Δ, and E_F considered by various investigators in fitting experimental results. These values have been obtained from analysis of diamagnetic susceptibility,[9] cyclotron resonance,[10] magnetoreflection,[11] optical transmission,[12] electron energy loss,[13] and de Haas–van Alphen effect[5,6,14] studies. An accurate fit to the dHvA zero-pressure results for majority and minority carriers (Table II) yields approximate constraining relations between different parameters within the range of values in Table I.

TABLE II.

Carriers	Frequency F (in 10^4 G)	$d\ln F/dP$ in kbar^{-1}
majority electrons	4.79±0.05	0.040 (±0.004)
majority holes	6.66±0.1	0.034 (±0.006)
minority	0.75±0.05	0.06 (±0.015)

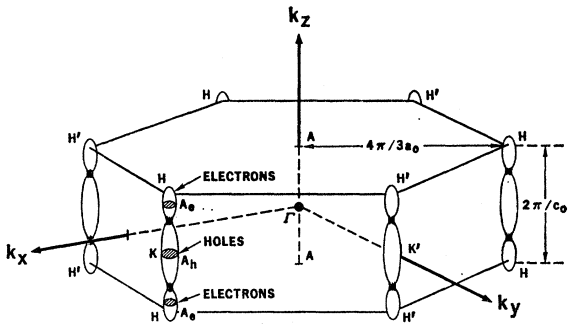

FIG. 1. The Brillouin zone for graphite, showing the electron and hole Fermi surfaces corresponding to the majority carriers. A portion of the electron "ellipsoid" may project through the horizontal Brillouin zone faces producing a small closed surface because of spin-orbit splitting. The minority carrier oscillations have been attributed to this piece of the Fermi surface.

In terms of our simplified model, the extremal cross-sectional areas, perpendicular to the hexagonal axis, of the majority hole and electron surfaces A_h and A_e are given by

$$A_h=\pi\gamma_0^{-2}\{E_F^2-E_F[\Delta+2(\gamma_1+\gamma_2)]+(\Delta+2\gamma_1)(2\gamma_2)\}, \quad (1)$$

and

$$A_e=\pi\gamma_0^{-2}\{E_F^2-E_F[\Delta-(\gamma_1-\tfrac{1}{2}\gamma_2\Gamma_e)\Gamma_e]+[\Delta-\gamma_1\Gamma_e](\tfrac{1}{2}\gamma_2\Gamma_e^2)\}, \quad (2)$$

where Γ_e is determined by the wave vector k_z at which the extremal section occurs and is given by

$$\Gamma_e=(3\gamma_1)^{-1}\{\Delta-E_F+[(\Delta-E_F)^2+6\gamma_1^2E_F/\gamma_2]^{1/2}\}. \quad (3)$$

These areas are given in units of σ^2 where $\sigma=2/\sqrt{3}a_0$ and a_0 (2.46 Å) is the lattice parameter in the basal plane. If the minority carriers are located according to the suggestions of Dresselhaus and Dresselhaus mentioned above, the extremal cross-sectional area at $k_z=\pi/c_0$ for $H\|c_0$ for the minority carrier surface is

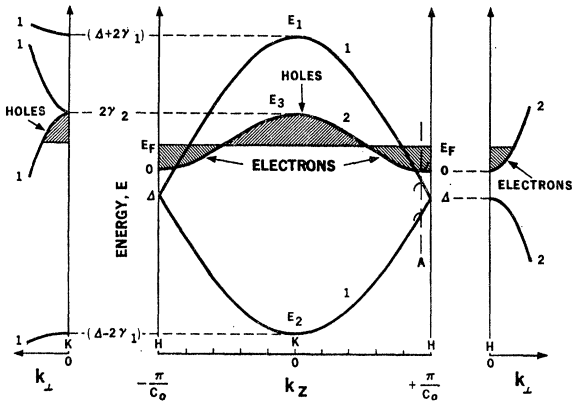

FIG. 2. Plot of energy versus wave vector along the Brillouin zone edge HKH according to the Slonczewski-Weiss model.

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[13] Y. H. Ichikawa, Phys. Rev. **109**, 653 (1958).
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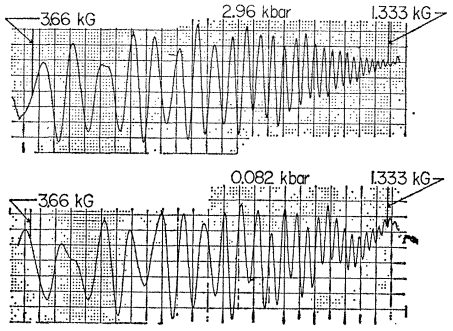

FIG. 3. de Haas–van Alphen oscillations produced by the majority electrons and holes at nearly zero pressure and 2.96 kbar.

given, also in units of σ^2, by

$$A_m=\pi\gamma_0^{-2}E_F(E_F-\Delta). \tag{4}$$

Here c_0 (6.70 Å) is the lattice parameter parallel to the hexagonal axis. The modification of the area due to the small spin-orbit splitting effects has been neglected.

It is also possible to compare the volumes occupied by the holes and electrons. In order to determine the electron and hole volumes, V_e and V_h, we have assumed an ellipsoidal model for both majority carriers, and the volumes are given by

$$V_e=2A_e(k_z{}^e-k_z{}^m), \tag{5}$$

and

$$V_h=A_hk_z{}^m, \tag{6}$$

where

$$k_z{}^e=(2/c_0)\cos^{-1}(\tfrac{1}{2}\Gamma_e),$$

and

$$k_z{}^m=(2/c_0)\cos^{-1}(E_F/2\gamma_2)^{1/2}. \tag{7}$$

The factor of 2 occurs in V_e because there are two electron ellipsoids. The contributions due to the minority carriers have been neglected.

Since graphite is a semimetal with only a small number of carriers, impurities will have an important effect upon the relative numbers of electrons and holes. Therefore, although pure graphite would be compensated, we will not make that assumption here.

III. EXPERIMENTAL TECHNIQUES

The measurements of the graphite dHvA frequencies were made at pressures up to approximately 4kbar using solid-helium pressure generation techniques described previously by Schirber.[15] No noticeable physical deformation of the extremely fragile crystals (0.1–0.2-mm-thick, 3–4-mm-diam platelets) was observed after several pressure cycles. In addition, the dHvA amplitudes, an extremely sensitive indicator of sample distortion, were not appreciably affected by pressure cycling.

The dHvA oscillations were detected using the conventional field-modulation technique in the experimental setup described previously.[16] A 55-kOe superconducting magnet was used for the majority-carrier study and a conventional copper solenoid was used to study the minority-carrier oscillations below 1 kOe. The latter oscillations were of much smaller amplitude and fewer cycles could be detected than in the case of the majority carriers; consequently the error in the minority-carrier pressure derivatives is correspondingly larger.

The samples were very thin platelets of purified natural single-crystal graphite which came from Essex County, New York. Because of the natural morphology of crystal growth, the plane of the platelet coincided with the crystallographic basal plane. Before use, these samples had been purified and annealed at 3000°C in a chlorine sweeping gas atmosphere reducing metallic impurity content to $\lesssim$10 ppm.

A phenolic rod which slip-fitted into the Be-Cu bomb was used to fix the platelet orientation. The sample was inserted into a narrow slit in this rod perpendicular to the rod axis and held gently in the slit with soft paper spacers. With this type of mounting, the magnetic field could be aligned parallel to the hexagonal axis of the crystal to within $\sim$2°. For this setting, the dHvA frequencies are relatively insensitive to orientation (varying roughly as the cos of the angle between the field and the hexagonal axis) so that any slight change in orientation resulting from pressure cycling should result in a negligible change in the dHvA frequency.

Efforts made to investigate other orientations with these samples were unsuccessful. The angle between the hexagonal axis and the field must be at least 88° in order to study the "ellipsoid" ends because of the large ratio of the major to minor axes (17 to 1 for the holes and 13.6 to 1 for the electrons).[5] At these angles, misalignment errors or orientation shifts due to pressure cycling completely mask the actual results. Furthermore, the amplitudes decrease by roughly 4 orders of magnitude as θ (the angle between the magnetic field and the c axis) goes from 75° to 90°.

IV. RESULTS

The two sets of oscillations due to the majority carriers have been studied for H parallel to the hex-

TABLE III. Pressure derivatives of X, Y, and Z in kbar^{-1}. $X=E_F(E_F-\Delta)$, $Y=\gamma_1\gamma_2$, $Z=E_F/\gamma_2$

	Our data	Reference 18
$d\ln X/dP=d\ln A_m/dP$	0.07_2	
$d\ln Y/dP$	0.03_6	0.03_6
$d\ln Z/dP$	≈ 0	0

Zero-pressure band parameters in eV:
$\gamma_0=2.85$, $\gamma_1=0.30$, $\gamma_2=0.02$, $E_F=0.026$, $\Delta=-0.006$

[15] J. E. Schirber, in *Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. F. Emrick (Academic Press Inc., New York, 1965); Phys. Rev. **140**, A2061 (1965).

[16] W. J. O'Sullivan, and J. E. Schirber, Phys. Rev. **151**, 484 (1967).

agonal axis for several pressures and the frequencies determined by least-squares analysis neglecting any possible harmonic contribution. Figure 3 shows a sample of these oscillations at zero pressure and 3 kbar. The doping experiments of Soule[6] and the cyclotron resonance results of Galt *et al.*[17] established that the 4.79×10^4-G frequency is due to the majority electrons. The results for the pressure derivatives of the majority-carrier frequencies are given in Table II together with the estimated uncertainties.

The dominant oscillations are produced by the electrons and therefore our pressure results are more accurate for these. On the other hand, Itskevich and Fisher[18] observe only the majority-hole oscillations in their pressure studies on synthetic crystals and their pressure derivative for the majority holes is in excellent quantitative agreement with ours. We have also observed the majority holes as the dominant frequency in pyrolytic graphite. The pressure derivative obtained in the pyrolytic sample agreed with our single-crystal majority-hole result. The difference between our natural single crystals and the pyrolytic and synthetic samples is not understood at present.

The minority-carrier oscillations for H parallel to the hexagonal axis are shown in Fig. 4 for zero pressure and 3.8 kbar. While the measured frequency is in good agreement with that observed by Soule,[6] the second oscillatory term he reported is not evident in our data.

V. DISCUSSION

As can be seen from Table II, the pressure changes of the Fermi-surface dimensions are quite large when compared with the compressibility (0.0025/kbar).[8] However, this might be anticipated in view of the small band overlap and its probable sensitivity to interlayer spacing.

In order to consider the effect of changes of interlayer spacings upon the band parameters, we have taken appropriate combinations of the parameters as follows:

$$X=E_F(E_F-\Delta), \tag{8}$$

$$Y=\gamma_1\gamma_2,$$

and

$$Z=E_F/\gamma_2.$$

TABLE IV. Pressure derivatives of band parameters in kbar^{-1}.

	Our data using Arkhipov assumption (see Ref. 19) and the experimental value for $d\ln A_m/dP$	Arkhipov *et al.* data and Arkhipov assumption (see Ref. 19)
$d\ln\gamma_1/dP$	0.01_2	0.01_9
$d\ln\gamma_2/dP$	0.02_4	0.03_8
$d\ln E_F/dP$	0.02_4	0.03_8
$d\ln\Delta/dP$	0.09	

[17] J. K. Galt, W. A. Yager, and N. W. Dail, Phys. Rev. **103**, 1586 (1956).

[18] E. S. Itskevich and L. M. Fisher, JETP Pisma v Redaktsiyu **5**, 141 (1967) [English transl.: JETP Letters **5**, 114 (1967)].

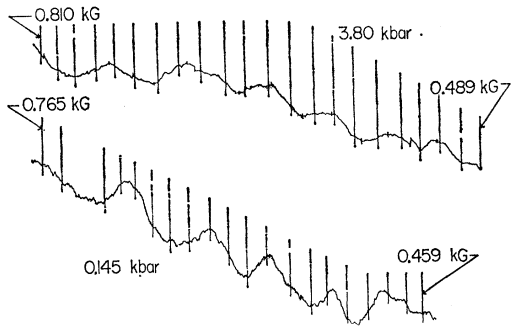

FIG. 4. Minority-carrier de Haas–van Alphen oscillations at nearly zero pressure and 3.8 kbar.

Then, since Δ, γ_2, and E_F are roughly an order of magnitude smaller than γ_1, it is a very good approximation to assume that

$$\Gamma_e\approx(\tfrac{2}{3}E_F/\gamma_2)^{1/2}=(2Z/3)^{1/2}. \tag{9}$$

With this approximation the majority- and minority-carrier extremal areas and the hole and electron volumes can be expressed in terms of only X, Y, Z, and γ_0. Therefore, the majority hole and electron areas become

$$A_h\approx\pi\gamma_0^{-2}[X(1-2/Z)-2ZY+4Y], \tag{10}$$

and

$$A_e\approx(\tfrac{2}{3})\pi\gamma_0^{-2}[X+(\tfrac{2}{3})^{1/2}YZ^{3/2}]. \tag{11}$$

The area A_m becomes simply

$$A_m=\pi\gamma_0^{-2}X. \tag{12}$$

Also for the hole and electron volumes we have

$$V_h\approx(2/c_0)A_h\cos^{-1}(Z/2)^{1/2},$$

and

$$V_e\approx2(2/c_0)A_e(\cos^{-1}(Z/6)^{1/2}-\cos^{-1}(Z/2)^{1/2}). \tag{13}$$

Because of the possibility of impurity contribution we cannot assume $V_e=V_h$, but it seems reasonable that the departure from compensation V_e-V_h is a constant independent of pressure; i.e.,

$$\frac{d}{dP}(V_e-V_h)=0. \tag{14}$$

From Eq. (14) and the pressure derivatives of Eqs. (10) and (11), the relative pressure derivatives of X, Y, and Z can be determined. For a given set of zero-pressure band parameters, the compensation equation [Eq. (14)] is a function only of the known experimental results, the majority-carrier dHvA pressure dependences and the change in c_0 with pressure[8] ($d\ln c_0/dP=-2.82\times10^{-3}$ kbar^{-1}), and $d\ln Z/dP$. With zero-pressure parameters chosen to be roughly the same as given in Table III in order to give an approximately compensated structure, we find $|d\ln Z/dP|\lesssim0.003$. The actual value is extremely dependent upon the zero-pressure band parameters as well as upon the model chosen and the experimental uncertainties. In view of this we have

taken for the following analysis $d\ln Z/dP=0$, as indicated in Table III. This same assumption has been made by Arkhipov *et al.*,[19] in their analysis of pressure effects in graphite. Consequently, the logarithmic pressure derivatives of X and Y are obtained from Eqs. (10) and (11), and are also shown in Table III. From the relative pressure dependence of X the pressure dependence of A_m is immediately obtained as $d\ln A_m/dP\approx 0.07$. This is in good agreement with the experimental result for the logarithmic pressure derivative of the minority carrier dHvA frequency given in Table II and lends credence to the Dresselhaus suggestion. However, it must again be mentioned that this result is quite dependent upon the zero-pressure parameters and the value assumed for $d\ln Z/dP$.

Also, in Table III, the result obtained here for $d\ln Y/dP=d\ln\gamma_1/dP+d\ln\gamma_2/dP$ has been compared with the value obtained by Itskevich and Fisher[18] based upon their de Haas–Shubnikov pressure studies of the majority holes in synthetic graphite. As our value for the pressure dependence of the hole frequency is in excellent agreement with theirs, it is not surprising that the two determinations of $d\ln Y/dP$ are essentially the same.

Without an additional assumption it is not possible to obtain the pressure dependences of the individual band parameters. However, Arkhipov *et al.* have utilized the similarity in γ_1 and γ_2 by postulating that they will be of the form

$$\gamma_1\sim\gamma_e^{-\beta c_0},$$
$$\gamma_2\sim\gamma_e^{-2\beta c_0},$$

where γ and β are constants. It then follows that

$$d\ln\gamma_2/dP=2d\ln\gamma_1/dP. \tag{15}$$

If we use Eq. (15) along with the pressure derivatives of X, Y, and Z (Table III), we obtain the pressure derivatives of the band parameters given in Table IV. Here we have determined $d\ln\Delta/dP$ from the experimental value for $d\ln A_m/dP$. The results for γ_1, γ_2, and E_F have been compared with the values obtained by Arkhipov *et al.*[19] from their high-temperature measurements of resistivity under pressure, and the agreement is probably reasonable in view of the simplicity of the model and the uncertainties in the zero-pressure parameters and the experimental values.

It can be seen that the value obtained for the relative change of Δ with pressure is quite large, but this result is very dependent upon the experimental pressure derivative for the minority carriers; variations within the experimental uncertainty can double the value of $d\ln\Delta/dP$ or reduce it to zero.

It is tempting to view the agreement of the experimental minority-carrier pressure result with the prediction of the pressure derivative of the minority-carrier area obtained from the majority-carrier measurements and a "reasonable" choice of zero-pressure band parameters as an indication of the validity of the Dresselhaus assumption. It is important, however, to point out that since the values obtained fro the pressure dependences of the band parameters E_F, γ_1, γ_2, and Δ depend *critically* upon the numerical values of the zero-pressure parameters; variations of these parameters well within the uncertainties in their magnitudes easily destroy the apparent quantitative agreement shown in Tables III and IV. Therefore, we conclude that the minority-carrier assignment is at best consistent with our pressure results within the framework of our simple model for the Fermi surface of graphite.

ACKNOWLEDGMENTS

We are indebted to L. Brubaker and D. Shanfeldt for valuable technical assistance. We wish to thank Dr. R. G. Arkhipov for a very helpful discussion. We also wish to thank Dr. A. G. Beattie for several valuable suggestions.

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