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Energy Band Structure of Graphite*

Abstract: The energy band structure of graphite is described in the region of the Fermi surfaces by the Slonczewski-Weiss model. The electron and hole Fermi surfaces are highly elongated and are aligned along the six Brillouin zone edges which are parallel to the trigonal axis of the crystal. The energy is a non-parabolic function of wavenumber and the Fermi surfaces are not ellipsoids. Galvanomagnetic, de Haas-van Alphen, and other experiments have established that: the band overlap is about 0.03 to 0.04 eV, the carrier densities of electrons and holes are each about 3×10^{18} cm^{-3} at low temperatures, the effective masses perpendicular to the trigonal axis are about 0.04 m_0 for electrons and 0.06 m_0 for holes, and the length-to-width ratio of the Fermi surfaces is about 12. The only important effect not included in the Slonczewski-Weiss model is the correlation of electron motion due to the coulomb interaction. Though this effect is expected to be important *a priori*, it is not yet clear if it causes important discrepancies between the predictions of the model and the experimental results.

Introduction

Graphite is similar to bismuth, which is without doubt the best-known semimetal, in that it has a small band overlap, a small density of electrons and holes, and small effective masses (in certain directions). Furthermore, the anisotropies of the graphite Fermi surfaces are approximately the same as for the electrons in bismuth, the surfaces are not exactly ellipsoids, and the energy is not exactly a parabolic function of wavenumber.

In contrast to bismuth, all of the Fermi surfaces in graphite are aligned with their long axes parallel to the trigonal axis (c-axis) of the crystal, which results in large anisotropies in the measured electronic properties. For example, the electrical resistivity parallel to the c-axis is more than 100 times larger than the resistivity perpendicular to the axis. In addition, there is a degeneracy in energy between the valence and conduction bands in graphite, as opposed to a direct band gap in bismuth. Spin-orbit effects are not important in graphite, except to cause a g-shift of about 0.1, which is modest by bismuth standards! Two practical differences associated with the anisotropy of the crystal lattice are: (1) locating the Fermi surfaces in the Brillouin zone was not a difficult theoretical problem, (2) there are many difficult experimental problems.

The many experimental and theoretical contributions which have added to our knowledge of the band structure of graphite are discussed in the review by Haering and Mrozowski.[1] We shall take up only a few which seem to give the most direct information about the band structure.

The energy band model which we shall describe was derived on the assumption that each electron moves in the same static, perfectly periodic potential. It will be shown in a later section that the interaction between electrons and phonons does not produce important deviations from this model. However, the correlations between electrons due to their coulomb interaction should be important. Using the experimental results for the carrier density and effective masses, and the high frequency dielectric constant[2] $\epsilon_\infty = 4$, we estimate that the plasma frequency[3] of the carriers corresponds to $\hbar\omega_p \simeq 0.17$ eV for motion perpendicular to the c-axis, and to $\hbar\omega_p \simeq 0.01$ eV for motion parallel to the c-axis. The Fermi energies for electrons and holes are each about $\zeta = 0.015$ eV, so that the perpendicular plasma quantum is a little more than 10 times the Fermi energy. For an isotropic electron gas for which $\hbar\omega_p/\zeta = 10$ the coulomb interaction would be so strong that the ground state would be an electron solid.[4] However the parallel plasma quantum is a little less than the Fermi energy, which corresponds to the high density limit in which the coulomb interaction has a small effect.

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At this point the best guess which we can make is that graphite will be an electron liquid. In this case, the band model can be used to describe the *quasiparticle* energy spectrum, and should give a consistent account of those properties which depend only upon the quasiparticle spectrum, such as the electronic heat capacity[5] and the de Haas-van Alphen effect.[6] However, other properties such as the cyclotron resonance[7] and steady diamagnetic susceptibility[8] do not depend directly upon the quasiparticle spectrum (if the periodic potential were not present, they would depend upon the "bare" particle spectrum), and may not agree directly with the energy band model determined from the quasiparticle properties. Certain of these properties can be treated by combining Landau's theory of a Fermi liquid[9] with the present band model. At present it is not clear if the experimental results demand such a generalization.

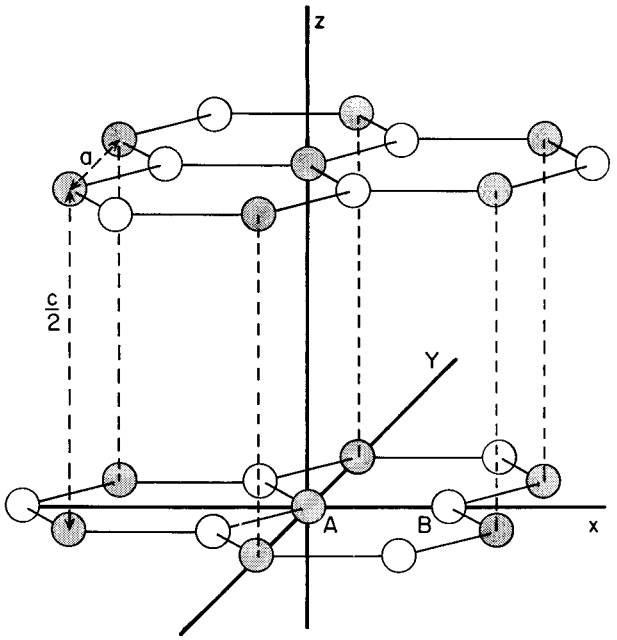

Figure 1 **The graphite crystal lattice.** *The distances between atoms are shown to scale. The distance a is 2.46 Å (the distance between nearest neighbors in a plane is 1.42 Å), and the c spacing is 6.74 Å (the distance between planes is 3.37Å).*

Energy band model

The graphite crystal lattice is shown in Fig. 1. Note that the distance between layer planes is much larger than the distance between atoms in a layer, and that each atom has three near neighbors in the same layer. The planes are stacked in *abab* order and there are two kinds of atomic sites: type A which has neighbors directly opposite in adjacent planes, and type B which does not. There are four atoms in a unit cell, an A and B atom from each plane. The Brillouin zone is a thin hexagonal cylinder, shown in Fig. 2.

Because of the large anisotropy of the crystal structure, it is a reasonable starting approximation to ignore the interaction between layers.[10] The Brillouin zone for a single layer is a two-dimensional hexagon. The $2s$, $2p_x$, $2p_y$ atomic wave functions form the familiar bonding and antibonding trigonal orbitals, which make up the σ bands. The p_z atomic wave functions give rise to two π bands, which are degenerate at the six Brillouin zone corners, the energy of degeneracy being well within the gap between the bonding and antibonding σ bands. The lower and upper π bands form the valence and conduction bands, and in the single-layer model there is no overlap or band gap between the two bands. All calculations on the two-dimensional model give the same general result, so that there is very little doubt that the Fermi surfaces will be located near the corners of the Brillouin zone.

The energy of interaction between layers is of the order of 0.5 eV, which causes very little change in the over-all character of the π bands, whose width is about 20 eV. However, the interaction between layers has a profound effect near the six vertical zone edges, which is where the carriers are located. There are four π bands (not counting spin degeneracy) in the three dimensional band structure, as there are twice as many atoms in the three dimensional unit cell. A general model for the behavior of the energy bands in the neighborhood of the vertical zone edges was developed by Slonczewski and Weiss.[11] The Fermi surfaces have very little extent in the x or y directions, so the $\mathbf{k}\cdot\mathbf{p}$ method was used in the xy plane (i.e., the elements of the Hamiltonian matrix were expressed as power series in the distance κ from the zone edge). In the z direction a Fourier expansion was made, which converges

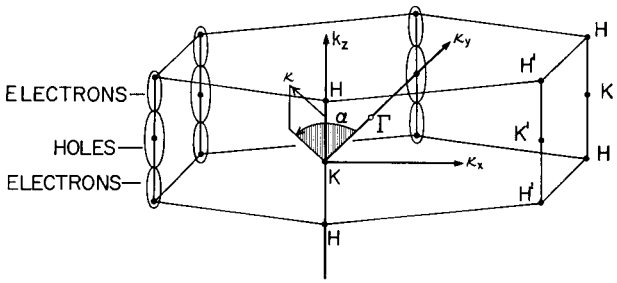

Figure 2 **The Brillouin zone for graphite, showing the positions of the Fermi surfaces.** *The Fermi surfaces are magnified in the horizontal direction by about a factor four. The surfaces are not drawn about all of the zone edges, in order to show the coordinate system more clearly.*

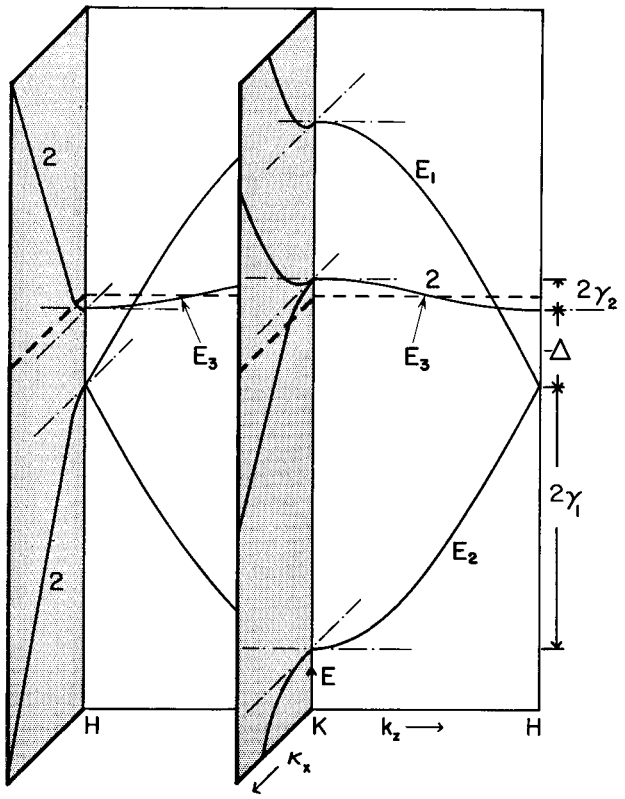

Figure 3 **Energy versus wavenumber for graphite.** *The energy is plotted vertically, and the k_x k_z plane is horizontal. The points* H, K, H *correspond to the same letters in Fig. 2. Doubly degenerate levels are indicated by the symbol 2. The dashed line indicates the Fermi level for pure graphite. The curves are constructed for* $\gamma_3 = 0$.

rapidly as the layer planes are widely separated (ideal tight binding). Group theory was used to find the most general form of the Hamiltonian, which should give a complete description of the energy spectrum, subject to the reservations discussed in the last Section.

In presenting the band model, we use the cylindrical coordinates indicated in Fig. 2, and the notation $\sigma = \frac{1}{2}\sqrt{3}\, a\kappa$. In pure graphite the maximum σ value on the Fermi surface is about 0.03. The distance from the zone corner to the zone center is 3.6 in σ units, and the height of the zone is 1.99 in the same units. For a particular choice of the zero of energy, the Hamiltonian is

$$H = \begin{bmatrix} E_1 & 0 & H_{13} & H_{13}^* \\ 0 & E_2 & H_{23} & -H_{23}^* \\ H_{13}^* & H_{23}^* & E_3 & H_{33} \\ H_{13} & -H_{23} & H_{33}^* & E_3 \end{bmatrix}, \tag{1}$$

where

$$E_1 = \Delta + \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2, \tag{2}$$

$$E_2 = \Delta - \gamma_1\Gamma + \tfrac{1}{2}\gamma_5\Gamma^2, \tag{3}$$

$$E_3 = \tfrac{1}{2}\gamma_2\Gamma^2, \tag{4}$$

$$H_{13} = 2^{-1/2}(-\gamma_0 + \gamma_4\Gamma)\sigma \exp(i\alpha), \tag{5}$$

$$H_{23} = 2^{-1/2}(\gamma_0 + \gamma_4\Gamma)\sigma \exp(i\alpha), \tag{6}$$

$$H_{33} = \gamma_3\Gamma\sigma \exp(i\alpha), \tag{7}$$

and

$$\Gamma = 2\cos(\tfrac{1}{2}k_z c). \tag{8}$$

In the above, we have gone to first order in σ, to second order in the Fourier expansion in terms which do not contain σ, and to first order in the Fourier expansion in terms proportional to σ. There seems to be no need to include higher order terms, and some of the terms included (such as γ_5) may be negligible. Spin-orbit effects have been estimated[11] to be of the order of 10^{-4} eV, and are neglected here.

Let us first inspect the variation of the energy along the vertical zone edge ($\sigma = 0$), which is plotted in Fig. 3. The level E_3 is doubly degenerate everywhere along the zone edge, while the levels E_1 and E_2 are degenerate at the zone corners H. The Figure is not drawn to scale, but reflects current estimates that γ_1 is larger than the other parameters (about 0.27 eV to 0.40 eV), that Δ is negative (about -0.02 eV to -0.1 eV), and that γ_2 is positive (about 0.015 eV to 0.02 eV). All of these parameters have to do with interaction between layer planes.

The Hamiltonian has simple solutions in certain special cases. If we neglect γ_3, we find

$$E = \tfrac{1}{2}(E_1 + E_3) \pm [\tfrac{1}{4}(E_1 - E_3)^2 + (\gamma_0 - \gamma_4\Gamma)^2\sigma^2]^{1/2}, \tag{9}$$

$$E = \tfrac{1}{2}(E_2 + E_3) \pm [\tfrac{1}{4}(E_2 - E_3)^2 + (\gamma_0 + \gamma_4\Gamma)^2\sigma^2]^{1/2}. \tag{10}$$

In this approximation, the energy is independent of the angle α. The variation of energy with σ is also indicated in Fig. 3. Note that, for any value of k_z, the two highest bands increase in energy with increasing σ, and the two lowest bands decrease in energy. Note also that the dependence of energy on σ is hyperbolic. For small σ, the dependence is parabolic, and one may define an effective mass (perpendicular to the c-axis) for zero σ by

$$m_0/m^* = 3(\gamma_0 - \gamma_4\Gamma)^2 a^2 / 2\hbar^2(E_3 - E_1) \simeq -3\gamma_0^2 a^2 / 2\hbar^2\gamma_1\Gamma, \tag{11}$$

and the similar expression involving E_2. The constant effective mass approximation is not adequate for an accurate determination of the band parameters, but does

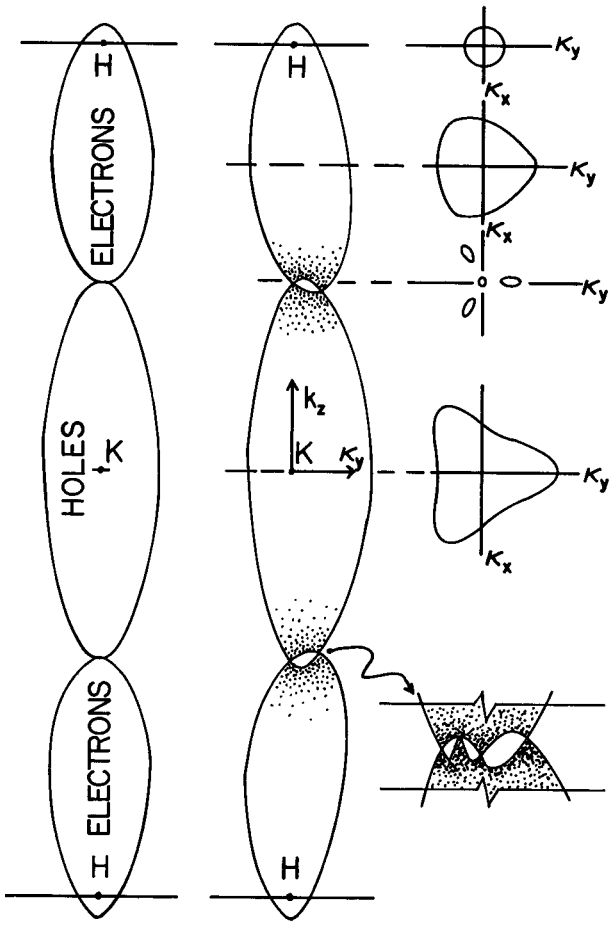

Figure 4 **Fermi surface cross sections in graphite.** *For clarity, the surfaces have been compressed by about a factor five in the z direction. The surfaces on the left are for* $\gamma_3 = 0$, *and have rotational symmetry about the zone edge* H K H. *The other surfaces are for a finite value of* γ_3, *and have trigonal symmetry about the zone edge.*

give a qualitative picture of the band structure. Note that the mass depends upon k_z, being greatest at the center of the zone. The far right of Eq. (11) represents an even more drastic approximation, assuming $|\gamma_1\Gamma| \gg |\Delta|$ or $|\gamma_5|$ and $\gamma_0 \gg |\gamma_4|$. For large values of σ the energy becomes almost the same linear function of σ as in the two-dimensional approximation, $E = \pm(\gamma_0 \pm \gamma_4\Gamma)\sigma$. The value of γ_0 is about 3 eV, while the parameter γ_4 depends upon interaction between layers and could be of about the same magnitude as γ_1.

For the parameter values used in Fig. 3, the top of the valence band is at point K ($E = E_3 = 2\gamma_2$) and the bottom of the conduction band is at point H ($E = E_3 = 0$). Thus there is a band overlap equal to $2\gamma_2$, and the Fermi level for pure graphite will be between 0 and $2\gamma_2$. Figure 4 shows the cross sections of the Fermi surfaces for a representative set of band parameters. Both electron and hole surfaces have been drawn in the same zone. The two surfaces touch at their ends because of the double degeneracy of the E_3 level. Also, the exploded zone scheme has been used to show the part of the electron Fermi surface in the higher conduction band. This part, which appears as an overlap in Fig. 4, matches smoothly onto the rest of the surface because of the time reversal degeneracy on the horizontal zone faces. Note that the surfaces are not quite ellipsoids, the electron surface has a pear-shaped distortion and the hole surface has a diamond-shaped distortion. If γ_2 were negative, the positions of the electrons and holes would be reversed from that shown in Fig. 4. The theoretical estimates of γ_2 are not accurate enough to establish the sign, as it is due to two competing effects. The experimental evidence for the sign of γ_2 will be discussed in the next Section.

The inclusion of the parameter γ_3 in the Hamiltonian causes the energy to have three-fold symmetry about the zone edge. The value of γ_3 is not well known, but the theory indicates that it is almost equal to γ_4, which can be of the order of γ_1. In the planes $\alpha = n\pi/3$, a simple solution of the Hamiltonian exists,

$$E = \tfrac{1}{2}(E_1 + E_3 + \gamma_3\Gamma\sigma \cos n\pi) \pm [\tfrac{1}{4}(E_1 - E_3 - \gamma_3\Gamma\sigma \cos n\pi)^2 + (\gamma_0 - \gamma_4\Gamma)^2\sigma]^{1/2}, \quad (12)$$

and the similar expression with E_1 replaced by E_2 and the sign of Γ changed. Equation (12) has been used to construct the Fermi surface cross-section in the k_yk_z plane, shown in Fig. 4. If E_1 and E_2 are well separated from E_3, then a perturbation treatment yields, for the levels near E_3,

$$E = E_3 + A\sigma^2 \pm [B^2\sigma^4 - 2B\gamma_3\Gamma\sigma^3 \cos 3\alpha + \gamma_3^2\Gamma^2\sigma^2]^{1/2}, \quad (13)$$

$$A = |H_{13}|^2 / (E_3 - E_1) + |H_{23}|^2 / (E_3 - E_2), \quad (14)$$

$$B = -|H_{13}|^2 / (E_3 - E_1) + |H_{23}|^2 / (E_3 - E_2), \quad (15)$$

for all values of α. Fermi surface cross sections in the k_xk_y plane derived from Eq. (13) are also shown in Fig. 4. Note that in addition to having trigonal cross sections in the k_xk_y plane the Fermi surfaces have four "pips" on the ends which touch, one central "pip" and three symmetrically placed "outriggers."

Experimental evidence for the band model

We shall briefly discuss a selection of experiments which seem to give the most unequivocal information generally available before the present conference. It is anticipated that following papers will contribute considerably to our

knowledge. First it should be pointed out that if the parameter Δ were so large that the E_1 and E_2 band system never crossed the E_3 bands, then graphite would be a semiconductor. However, simultaneous holes and electrons are observed at low temperatures in the Hall effect[12] and in the cyclotron resonance.[13] This also requires that the parameter γ_2 be finite, and that the Fermi level lie between 0 and $2\gamma_2$.

The best evidence for the size and shape of the Fermi surfaces comes from the de Haas - van Alphen[14] and Shubnikov - de Haas[12,15] experiments. For a magnetic field parallel to the c-axis, two de Haas - van Alphen periods are observed. One corresponds to carriers with an effective mass of 0.039 m_0 perpendicular to the c-axis, and the other to a mass of 0.057 m_0. Soule[15] has measured the period due to the lighter carrier for all angles between the magnetic field and the c-axis. Comparison of the volume of the experimentally determined Fermi surface with the carrier densities determined from the analysis[16] of the nonoscillatory galvanomagnetic data ($n \simeq p \simeq 2.9 \times 10^{18}$ cm^{-3}) showed that there must be four such Fermi surfaces in the zone (not counting spin). This means that there are two such surfaces on a zone edge, such as the surfaces labeled "electrons" in Figs. 2 and 4. (There are effectively two complete zone edges in the zone, one third of the region around each of six zone edges.) The period due to the heavier carrier was not observed at all orientations, but the results are consistent with its Fermi surface being on the center of the zone edge, such as that labeled "holes" in Figs. 2 and 4.

The identification of the signs of the carriers has been based on the cyclotron resonance results. The cyclotron resonance experiment[13] was performed in the classical skin effect region, with the magnetic field perpendicular to the sample surface (and parallel to the c-axis), and with circularly polarized microwaves. Thus the majority carriers do not produce peaks, but a broad absorption. Lax and Zeiger[17] analyzed the broad absorption and concluded that it was due to electrons of mass about 0.05 m_0 and holes of mass about 0.07 m_0. As their results indicate that the holes are heavier than the electrons, it was concluded that the light carriers in the de Haas - van Alphen effect were electrons, and that the heavy carriers were holes. With this identification, the two types of mass measurements differ by about 20%. This difference could be due either to the difficulty of analyzing the resonance data or to the effect of electron correlation. The cyclotron resonance experiment also showed harmonic structure, which was analyzed by Nozières.[18] He concluded that the harmonics were due to an electron of mass 0.054 m_0, whose Fermi surface has three-fold symmetry about the c-axis. He made the same identification of electrons and holes as in Figs. 2 and 4, and argued that the region near the pips on the electron Fermi surface was the source of the harmonics. From this identification, and using the approximation in Eq. (11), he *calculated* that the de Haas-van Alphen masses should be 0.031 m_0 for electrons and 0.066 m_0 for holes. However, Eq. (11) is quite inaccurate. For a representative set of band parameters we have calculated that setting the mass at the end of the electron Fermi surface equal to 0.054 m_0 implies that the de Haas-van Alphen mass for electrons is 0.025 m_0 and that for holes is 0.041 m_0. It may be that adjustments of the values of the band parameters could lead to better agreement, but we feel that it is best to wait and use the best values of the band parameters from other experiments. Recently Inoue[19] has also analyzed the harmonic structure in the cyclotron resonance and claimed that the harmonics are due to a *hole* with a mass of 0.053 m_0, which he placed at point K (also agreeing with the assignment in Figs. 2 and 4). He argued that the incomplete circular polarization of the microwaves allows each harmonic to appear for both signs of the magnetic field. However, his interpretation does not agree well with the relative strengths of the harmonics. It seems most likely to us that the harmonics are due to an electron of mass 0.054 m_0, but we point out the possibility that the electron may be at point K. In this case the positions of the electrons and holes would be interchanged and γ_2 would be negative. If this were so, the mass of 0.054 m_0 would be associated with the de Haas - van Alphen mass of 0.057 m_0. Also, the trend of the Hall coefficient with temperature and doping would be easier to explain[20] with a negative γ_2. As has been pointed out by Soule,[12] a more reliable identification of the carriers will come from observing the change of the de Haas - van Alphen periods as a function of doping.

Information about the values of the band parameters can be gained from the de Haas - van Alphen type effects. The band overlap $2\gamma_2$ is approximately equal to the sum of the partial Fermi energies of electrons and holes. If the energy were a parabolic function of wave number, the partial Fermi energies could be obtained directly from the measured periods and masses, yielding an estimate of 0.028 eV for the band overlap. Using the band model one finds an overlap of 0.03 eV to 0.04 eV, depending upon the values chosen for the other band parameters. The values of the effective masses yield a value of about 26 eV for the combination γ_0^2/γ_1. The de Haas - van Alphen effect also gives some other, less definite information about the band parameter values, which we will not discuss here.

The de Haas - van Alphen results and the carrier density determined from the non-oscillatory galvanomagnetic properties can be used to obtain the density of states. Assuming parabolic energy dependence, we find $N(\zeta) = 5.5 \times 10^{-3}$ eV^{-1} atom^{-1}. Calculations using the band model indicate that assuming parabolic dependence may cause the estimate to be too high by as much as 10%. The linear coefficient in the electronic heat capacity ex-

pected from this density of states is $13\mu J/mole\text{-}deg^2$, in good agreement with the most recent experimental value[21] of $13.8\mu J/mole\text{-}deg^2$. It is shown in the next section that the contribution to the heat capacity due to the electron-phonon interaction is very small. As was pointed out in the Introduction, the agreement between the de Haas-van Alphen effect and the heat capacity is not disturbed by the many-body effects.

None of the experiments discussed above can give a good estimate of γ_0, as Eq. (11) shows that the effective mass is mostly determined by the quantity γ_0^2/γ_1. However, the large steady diamagnetism of graphite is due to virtual transitions between bands caused by the magnetic field. An analysis of the diamagnetism[22] yielded a value of 2.8 eV for γ_0, and a value of 0.27 eV for γ_1. These results give a value of 29 eV for γ_0^2/γ_1, which is about 10% higher than the best value from the de Haas - van Alphen effect. It is not yet clear if the disagreement is significant.

We will learn in one of the following papers about the information which can be gained from magneto-optical experiments. Optical measurements in the absence of a magnetic field have been carried out by a number of investigators. Of particular interest is the work in the infrared by Boyle and Nozières.[23] They observed a minimum in the emissivity at about 4 microns, and a sharp increase for shorter wavelengths. They argued that the increase was due to the onset of transitions from the E_2 to the E_3 bands at the point K, and deduced a value of 0.14 eV for γ_1. This value is very much smaller than the one deduced from the analysis of the diamagnetism. We would like to suggest that the increase comes when the frequency of the radiation exceeds the plasma frequency of the carriers. At the temperature of their experiment (523°K) the carrier density is about ten times that at low temperatures. Thus the plasma frequency for oscillation in the layer plane corresponds to about 0.50 eV. The experimental data are consistent with a plasma edge at about 2.5 microns. More recently, Ergun[24] has reported preliminary measurements of the absorption at shorter wavelengths. He found a peak which he interprets as being due to the transitions from E_2 to E_3, and derived a value of about 0.4 eV for γ_1.

Electron-phonon effects

We will show here that the effects of the electron-phonon interaction in graphite are small, mainly because of the small density of states. According to Engelsberg and Schrieffer,[25] the effect on the quasiparticles is not much when the dimensionless parameter $\eta = D^2N(\zeta)/Mu^2$ is small. In the expression, D is the deformation potential constant; $N(\zeta)$ is the electronic density of states per atom; M is the atomic mass; and u is the appropriate speed of sound. The deformation potential constant[26] in graphite is about 30 eV, and the velocity of sound[27] is 2.3×10^6 cm/sec for the in-plane vibrations, which are most effective in scattering the electrons. The calculated value of η is then about 0.08.

The same parameter appears in the expression for the correction to the electronic heat capacity[28] due to the electron-phonon interaction,

$$\delta C/C = [\eta/(1 - 2\eta)](T/T_D)^2 \ln (T_D/T),$$

where T_D is the characteristic temperature of the phonons effective in the scattering process, $kT_D = \hbar k_F u$, in which k_F is the Fermi wavenumber. For graphite $T_D \simeq 25°K$, and $\delta C/C \simeq 5 \times 10^{-3}$ at 1°K.

Another electron-phonon effect has been discussed by Fan,[29] who showed that it explained the temperature dependence of the optically measured energy gap in semiconductors. In a direct transition the number of phonons is conserved, but the frequency of each is changed as the elastic constants are different with an extra excited electron. Thus the energy necessary to make the transition contains a term proportional to the phonon density. This effect causes energy shifts in semiconductors of the order of 10^{-4} eV deg^{-1}, and may be important in graphite.

Finally, the rather large thermal expansion in the c-direction is rather easily taken into account.

Some of the interesting questions concerning the energy band structure of graphite which need clarification are: (1) Which Fermi surfaces belong to the electrons and which to holes? (2) What is the extent of the trigonal warping and what is the value of γ_3? (3) Is it possible to explain all experiments with the present band model which ignores many-body effects, or must it be generalized?

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Discussion

J. K. Galt: Your Figure 4 shows the cross sections of the Fermi surface as having large trigonal distortion throughout most of the length of the surface. The interpretation by Nozières of our experiments indicated that the cross sections were significantly trigonal only over a short range of k_z. Is there any other experimental evidence for the amount of warping you show in this Figure?

J. W. McClure: Until recently the main experimental evidence for trigonal warping was the observation of harmonics in the cyclotron resonance experiment. The magneto-optical experiment reported in the next paper also presents evidence for trigonal warping.