THE ELECTRIC AND MAGNETIC PROPERTIES OF GRAPHITE

ΒY

RUDOLPH ROLAND HAERING

A THESIS

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INTRODUCTION.

Graphite is perhaps the most unique of all solids. It has long been known that graphite possesses a layer structure. Within a layer the carbon atoms are arranged in a continuous hexagonal array, each atom having three nearest neighbors at a distance of 1.42 A° . The distance between adjacent layers, on the other hand, is $3.3'/ A^{\circ}$. The interaction between the layers is thus very weak, a fact which results in large anisotropies in the properties of graphite. Thus the magnetic susceptibilities parallel and perpendicular to the graphite planes differ by a factor of 40, and the electrical conductivities in these directions differ by a factor of 10^{4} - 10^{5} . This large anisotropy is however not the only peculiarity of graphite. If the electronic band structure is investigated in the tight binding approximation, one finds that to a first approximation the valence and conduction bands just touch in graphite. Because of this result, graphite has sometimes been referred to as a "zero-gap semi-conductor". More detailed investigations seem to indicate that in fact the valence and conduction bands overlap slightly, and that the Fermi surface does not lie exactly at the lowest point of the conduction band. Thus a certain number of free electrons are present even at very low temperatures, and graphite should be more properly referred to as a metal.

The lamellar structure of graphite may be used as the

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basis for approximations in a theoretical treatment of the electronic band structure. For the theoreticians, the structure of graphite is therefore a simplifying feature. Unfortunately, the same is not true for the experimentalists. On the contrary, the extreme anisotropy makes the experiments very difficult. Furthermore, the peculiar band structure makes most of the properties very sensitive to impurity concentration. The wide variety of results which has been reported for the various properties of graphite is probably due to these two complicating features.

In the present study of graphite, an attempt is made to correlate the various effects which are observed in external electric and magnetic fields. We shall investigate the magnetic susceptibility, the de Haas-Van Alphen effect, the ratio of the principal electrical conductivities, the zerofield Hall effect and the low-field magneto-resistance in order to establish whether all these effects can be explained by the same model. We will be led to the conclusion that a model of graphite based on an excess number of free electrons and a small inter-planar interaction is in good agreement with experiment. Perhaps the most striking feature of this new model of graphite is its simplicity. The model, which is based on the tight binding approximation, incorporates only three independent parameters: \mathcal{X}_{o} , the nearest "in-plane" exchange integral; λ_{i} , the nearest "out-of-plane" exchange integral; and ζ_{\circ} , the position of the Fermi level at

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absolute zero of temperature.

Several attempts have been made to explain the diamagnetic susceptibility of graphite (1-3). Most of these calculations are based on the Landau-Peierls formula (4,5) which predicts a susceptibility much smaller than the observed susceptibility (2). The failure of the Landau-Peierls formula has been attributed by Adams (6) to the fact that it neglects band-to-band transitions. These transitions become important whenever there are two or more bands in the conduction band region. In graphite, where the conduction and valence bands touch to first approximation, the band-to-band transition terms must be expected to be important. McClure (3) has extended previous investigations by taking these terms into account. Using the equations of Luttinger and Kohn (7) and the two-dimensional band structure of Wallace^{\pm} (8), he has succeeded in solving the equations for the energy relation in the presence of an external magnetic field. McClure's work presents a very satisfactory explanation of the diamagnetic susceptibility of graphite at high temperatures. It will be seen that a two-dimensional model is also capable of explaining the average value of the susceptibility at low temperatures and the average period of the fluctuations in the de Haas-Van Alphen effect.

The observed average low temperature susceptibility of

ú This paper will hereafter be referred to as A.

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-30 x 10^{-6} emu/gm (1) requires the Fermi Surface at low temperatures to lie about .06 ev from the degeneracy corner, while the observed average period in the de Haas-Van Alphen effect fluctuations (9,10) of 2.15 x 10^{-5} gauss⁻¹ requires ζ_0 , the zero temperature Fermi level to lie at about .065 ev. We shall see that this rather large value of ζ_0 does not imply that the high temperature susceptibility becomes vanishingly small, as McClure supposed. The apparent discrepancy is reconciled by taking into account the shift of the Fermi level with temperature.

We shall see that if a three-dimensional model of graphite is considered, it is still possible to obtain the energy spectrum in the presence of an external magnetic field. When the high temperature susceptibility is calculated from this three-dimensional model, we will be led to the conclusion that the inter-layer interaction is much weaker than was previously supposed (8,11). If we are going to retain any susceptibility at all, we require Σ_1 , the nearest "out-of-plane" exchange integral, $\stackrel{\scriptstyle \checkmark}{\scriptstyle \sim}$.01 ev. Thus we shall find that graphite is essentially two-dimensional in structure. An independent rough estimate of **X** can be obtained from the de Haas-Van Alphen effect if one uses the semi-classical (Bohr-Sommerfeld) approximation (12). In this approximation, the two periods of the de Haas-Van Alphen effect (9,10) determine both 💪 and X. A simple calculation based on the results of Lifschitz and Kosevich (12) yields $\zeta_{0} \sim .065 \text{ ev}; \ \aleph_{1} \sim .005 \text{ ev}.$

Since ζ_{\circ} , the Fermi level at very low temperatures, now lies a considerable distance within the conduction band, the question of the origin of these excess electrons arises. A tight binding calculation of the energy band structure reveals that for an infinite crystal there are just enough states in the valence band to account for all the electrons in the crystal; that is, one finds that the Fermi level lies exactly at the degeneracy point between the valence and the conduction bands. Where then are the extra electrons coming from? Impurities are of course a possible source. However, one could hardly expect any regularity from crystal to crystal if this were the main factor. Furthermore, it would require a large amount of impurity to shift the Fermi level .06 ev in graphite. Mrozowski (13) was the first to investigate this peculiar state of affairs in graphite. By studying the resistivities of coked graphite over a wide temperature range, he came to the conclusion that the major source of the free electrons was not the impurities, but graphite itself. Let us consider an actual (finite) crystal. The carbon atoms near the surface of this crystal are unable to form proper valence bonds, because there are not sufficient neighboring atoms. If proper valence bonds were possible, the electrons forming these bonds would have their energy lowered through bonding. Thus, the electrons on these surface atoms have energies higher than the energies of the electrons in the valence band. The surface electrons may thus have energies

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which lie in the conduction band. Supposedly, it would take very little energy to free such an electron completely, so that it would become a conduction electron.

Our choice of Fermi surface is thus qualitatively explained by Mrozowski's surface bonds. Quantitatively, agreement is also good. Using the expression for the density of states near the degeneracy corner given in A, it is easily shown that $\zeta_0 \sim .06$ ev implies that there are approximately 10^{-3} free electrons per atom. Mrozowski estimates that there are 10^{-2} to 10^{-3} free electrons per carbon atom from the thermoelectric power of carbon.

Finally, the above explanation of the origin of the excess electrons implies of course, a size effect. Generally, larger crystals will have fewer excess electrons per atom, and hence a Fermi energy lower than that of smaller crystals. Such an effect could however be masked by other secondary effects, such as a change in the mean free path with crystallite size (cf. Mrozowski).

In order to test our explanation of the susceptibility and of the de Haas-Van Alphen effect, it will be desirable to investigate the consequences of our small value of & and large value of \lneq_0 on other properties of graphite. Unfortunately, the usual difficulties with the relaxation time prevent one from doing this satisfactorily. However, it should still be possible to decide whether a compatible explanation is possible, or whether a completely different

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choice of parameters is required for each effect. Using standard formulae for the electrical conductivities, the Hall coefficient and the transverse magneto-resistance, it will be shown that satisfactory agreement is obtained with the following choice of parameters:

 δ_0 = nearest "in-plane" neighbor exchange integral ~-2.5 ev. δ_1 = nearest "out-of-plane" neighbor exchange integral ~.005 ev. ζ_0 = Fermi level at zero temperature ~.06 ev.

Section I deals with the derivation of a set of coupled equations, which upon solution yield the energy spectrum of the electrons whose energies are near the Fermi energy. The results of this section are not restricted to graphite, but apply to any substance for which the approximations that are made are justified. In section II, the equations obtained in section 1 are solved in the case of graphite, for a twodimensional as well as for a three-dimensional model. It is shown that the results in the two-dimensional case agree with the results of McClure (3), and that the three-dimensional model predicts a spectrum which approaches that obtained from a two-dimensional calculation as $X \rightarrow 0$. In section III it is shown that the inter-planar interaction must necessarily be very small if one wants to retain agreement with the observed susceptibility at high temperatures. Section IV deals with the temperature variation of the Fermi level. This variation is of utmost importance in the case of graphite. We shall see that it is essentially this shift of the Fermi

level which is responsible for the observed variation of the susceptibility with temperature. In section VI the susceptibility and the de Maas-Van Alphen effect are calculated. The result is compared with that obtained from a semi-classical treatment and an interesting difference between the two approaches is noted. The ratio of the two principal electrical conductivities is calculated in section VII. We shall see that the ratio $\frac{\sigma_1}{\sigma_2}$ becomes about 10⁵ with our choice of parameters, in fair agreement with the experimental results of Krishnan and Ganguli (14) and of Dutta (15). Lower values for this ratio have also been reported, for example by Primak and Fuchs (16). It is felt however, that the largest reported experimental value should be chosen for comparison with theory, since any slight misalignment during an experiment would greatly reduce this ratio. The zero field Hall coefficient is calculated in section VIII. At low temperatures, where the difficulties due to the relaxation time are least severe, agreement with experiment is excellent. At higher temperatures, the calculation becomes doubtful because of the simplifying assumptions about the relaxation time, and the experiments become difficult to interpret. Finally, section IX deals with the low field, transverse magneto-resistance. At low temperatures, the mean free path cancels out of the expressions for the ratio of the conductivities and for the Hall effect, if one assumes that the relaxation time au depends on ${ar k}$ only through the energy. This is not true in the expression

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for the transverse magneto-resistance. In fact, $\stackrel{\text{de}}{\underset{\text{c}}{\overset{\text{de}}}{\overset{\text{de}}{\overset{\text{de}}{\overset{\text{de}}}{\overset{\text{de}}{\overset{\text{de}}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{de}}{\overset{\text{de}}}\overset{\text{d$

Summarizing, we shall find that a model of graphite based on excess electrons and a small inter-planar interaction is in good agreement with experiment. The value of the "inplane" exchange integral X_0 is determined most directly by the high temperature susceptibility. The position of the Fermi surface may be determined independently from each of the following effects:

- 1. The mean period in the de Haas-Van Alphen effect.
- 2. The average steady low temperature susceptibility.
- 3. The low temperature, zero field Hall effect.

4. The transverse magneto-resistance (only indirectly). On the other hand, the smallness of the inter-planar exchange integral follows independently from:

1. The high temperature susceptibility.

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- 2. The two periods in the de Haas-Van Alphen effect.
- 3. The ratio of the electrical conductivities.
- 4. The transverse magneto-resistance (only indirectly).

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I. THE MOTION OF ELECTRONS IN A PERTURBED LATTICE.

In reference A, the band structure of graphite was derived in the tight binding approximation. Such a calculation is always based on the assumption of a perfectly periodic lattice and a perfectly periodic potential in which the electrons move. We shall now be interested in what happens to these electrons when the periodicity of this potential is perturbed, for example through the application of an externally applied electric or magnetic field. Luttinger and Kohn (7) have developed a general theory of the motion of electrons and holes in perturbed periodic potentials. Their equations form the basis of McClure's calculation of the diamagnetism of graphite (3). McClure's equations (2.7a and 2.7b) are a special case of Luttinger and Kohn's equations after certain terms are neglected. The approximations involved are based on the following two simplifying features:

- a) Near the degeneracy point of the valence and conduction bands in graphite the $\vec{E(k)}$ relation has the form $\vec{E(k)} \sim CK$ and not $\vec{E(k)} \sim C_{L}^{2}$, which is the more usual form valid near the minimum of a band. This allows one to neglect terms quadratic in κ for all energies of interest.
- b) In graphite, the susceptibility with the magnetic field parallel to the crystallographic c-axis is about 40 times larger than the ion core susceptibility. Hence one is justified in neglecting any terms which lead to a susceptibility of the order of the ion core susceptibility

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in the calculation of this quantity.

In extending the work of McClure, we shall also make use of the fact that the susceptibility we wish to calculate is much larger than the ion core susceptibility. This allows one to derive an approximate set of equations, which upon solution yield the energy spectrum in the presence of an applied magnetic field. This approach has two advantages to recommend it whenever it is possible. The derivation shows quite clearly that the approximation corresponds to neglecting terms of the order of the ion core susceptibility, and the derivation results in a simple prescription which tells one how the equations are to be written down from the results of a tight binding calculation, such as that in A.

The derivation of these simplified equations will be carried through using Löwdin functions (17) and is thus carried out within the tight binding formalism, although one could generalize this approach. The proof given here parallels closely Luttinger's derivation of the "perturbed lattice equation" (18).

Let us for the present assume that we need to consider only one band if we wish to study the effect of the perturbation. This case would arise if our crystal had only one atom per unit cell and only one atomic orbital per atom. An actual crystal will in general have several bands, but it may still happen that the particular band of interest contains only

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electrons whose energies are far different from the energies of electrons in any other band. In such a case we expect that it is virtually impossible for an electron in the chosen band to jump to any other band, so that we are justified in ignoring the presence of these other bands.

If band-to-band transitions can be neglected and if in addition the applied perturbation is slowly varying (i.e. if the perturbation changes only slightly over the dimensions of one unit cell), then Luttinger's perturbed lattice equation applies. This equation may be written

$$\left[E_{o}(-i\vec{\nabla}-\frac{e}{\pi c}\vec{A})+U(\vec{r})\right]c(\vec{r})=Ec(\vec{r}) \qquad (1.1)$$

when the perturbation is due to an electric and a magnetic field. Here, \overrightarrow{A} is the vector potential for the magnetic field \overrightarrow{H} , and for an electric field $\bigcup(\overrightarrow{r}) = e \varphi(\overrightarrow{r})$. $E_0(\overrightarrow{k})$ is the energy in the absence of any perturbation and $E_0(-i\overrightarrow{\nabla} - \underbrace{e}_{\overline{k}} \cdot \overrightarrow{A})$ is the same function with the argument \overrightarrow{k} replaced by $-i\overrightarrow{\nabla} - \underbrace{e}_{\overline{k}} \cdot \overrightarrow{A}$. In what follows we shall always use the Landau gauge for the magnetic vector potential, that is we shall take: $A_x = -yH$; $A_y = A_z = 0$.

It may sometimes be convenient to transform equation (1.1) by defining:

$$c(\vec{r}) = \int e^{i\vec{k}\cdot\vec{r}} d(\vec{k}) d^{3}k \qquad (1.2)$$

$$\mathcal{U}(\vec{k}) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\cdot\mathbf{r}} \mathcal{U}(\vec{r}) d^3\mathbf{r} \qquad (1.3)$$

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Using the relation

$$E_{0}\left[-i\frac{\partial}{\partial x}+sy,-i\frac{\partial}{\partial y},-i\frac{\partial}{\partial z}\right]e^{i\vec{k}\cdot\vec{r}}=E_{0}\left[k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z}\right]e^{i\vec{k}\cdot\vec{r}} \quad (1.4)$$

equation (1.1) may be rewritten as:

$$E_{o}\left[k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z}\right]d(\vec{k})+\int \mathcal{U}(\vec{k}-\vec{k}')d(\vec{k}')d^{3}\vec{k}' = Ed(\vec{k}) \quad (1.5)$$
where $s = \frac{eH}{\hbar c}$.

This equation may sometimes be more convenient from the point of view of solution.

We now turn to the generalization of equations (1.1) and (1.5) in the case when one is no longer justified in neglecting band-to-band transitions. For simplicity, we shall only treat the case where two bands need to be considered. Furthermore, we shall assume that these two bands are due to the fact that there are two atoms per unit cell in our crystal, and that we are still justified in using just one orbital per atom. The results will then be directly applicable to two-dimensional graphite, if we restrict our treatment to the p_z -bands. The above simplification is only made to avoid notational difficulties. We shall see that the generalization to the case of n atoms per unit cell and m orbitals per atom is a trivial one.

Let us define:

$$S_{ij}^{\alpha\beta} = \int \chi_{i\alpha}^{*} \chi_{j\beta} d\sigma - \delta_{ij} \delta_{\alpha\beta} \qquad (1.6)$$

Here lpha and eta label the two different atoms in the unit

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cell, and i and j label the ith and jth unit cell in the crystal. The χ 's are atomic orbitals centered on the appropriate atoms. Thus $\chi_{i\alpha}$ is an atomic orbital centered on the \ll th atom in the ith unit cell. Equation (1.6) could also be written:

$$(1+S)_{ij}^{\alpha\beta} = \int \chi_{i\alpha}^{*} \chi_{j\beta} d\tau \qquad (1.7)$$

It is easily checked that the functions defined by

$$\varphi_{i\alpha} = \sum_{j,k} \chi_{jk} (i+s)_{ji}^{\frac{1}{2}k\alpha}$$
 (1.8)

obey

$$\int \varphi_{i\alpha}^* \varphi_{i\beta} d\tau = \delta_{ij} \delta_{\alpha\beta} \qquad (1.9)$$

provided the expansion of the matrix $(1 + S)_{ij}^{-\frac{1}{2}} \stackrel{\prec \beta}{\rightarrow}$ in powers of $S_{kl}^{}$ is convergent. We also note that $S_{kl}^{}$ is not really a fourth order tensor but simply a matrix. However, it is more convenient to label the atoms in the indicated manner. The matrix $S_{ij}^{\stackrel{\prec \beta}{\rightarrow}}$ has the property that:

$$s_{ij}^{\alpha\beta} = s_{ji}^{\beta\alpha} \neq s_{ij}^{\beta\alpha} \text{ or } s_{ji}^{\alpha\beta}$$

Let us first consider the case of a perturbation other than a magnetic field. The latter case requires special treatment and will be considered later. We now denote the two atoms in the unit cell by 1 and 2. The Löwdin function centered on atom number 1 in the unit cell labelled by the lattice vector $\vec{R_j}$ is denoted by $\varphi_{1j} = \varphi_1(\vec{r} - \vec{R_j})$. Similarly, the Löwdin function centered on atom number 2 in the same cell is denoted by $\varphi_{2j} = \varphi_2(\vec{r} - \vec{R_j})$. Following the tight binding procedure we now construct an approximate Bloch function for our problem by taking

$$\psi = \lambda \psi_1 + \lambda_2 \psi_2 \tag{1.10}$$

where

$$\psi_{1} = \sum_{R_{j}} e^{i\vec{k}\cdot\vec{R_{j}}} \varphi_{1j} ; \quad \psi_{2} = \sum_{R_{j}} e^{i\vec{k}\cdot\vec{R_{j}}} \varphi_{2j}$$

and λ_i and λ_2 are constants to be determined. The relation (1.10) is now substituted into the Schrödinger equation

$$H_{o} \Psi = E_{o} \Psi \tag{1.11}$$

Here H_0 is the one-particle Hamiltonian operator in the absence of any perturbation. We now multiply (1.11) alternately through from the left by ψ_1^* and by ψ_2^* and integrate all resulting terms over \vec{r} . The two resulting equations can be written:

$$\lambda_{i} \sum_{\mathbf{R}_{s}} e^{i\vec{k} \cdot \vec{R}_{s}} \gamma_{i}(\vec{R}_{s}) + \lambda_{2} \sum_{\mathbf{R}_{s}} e^{i\vec{k} \cdot \vec{R}_{s}} \gamma_{i2}(\vec{R}_{s}) = \lambda_{i} E_{o} \qquad (1.12a)$$

$$\lambda_{1} \sum_{\mathbf{R}_{s}} e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}_{s}} \chi_{21}(\vec{\mathbf{R}}_{s}) + \lambda_{2} \sum_{\mathbf{R}_{s}} e^{i\vec{\mathbf{k}} \cdot \vec{\mathbf{R}}_{s}} \chi_{22}(\vec{\mathbf{R}}_{s}) = \lambda_{2} \mathbf{E}_{o} \qquad (1.12b)$$

where:

$$\mathcal{X}_{\alpha\beta}(\vec{R}_{s}) = \int \psi_{\alpha}^{\dagger}(\vec{r} + \vec{R}_{s}) H_{o} \psi_{\beta}(\vec{r}) d^{3}r$$

By virtue of the orthogonality of the Lowdin functions we also have:

$$H_{o} \varphi_{ij} = \sum_{R_{\ell}} \chi_{ii} (\vec{R}_{j} - \vec{R}_{\ell}) \varphi_{i\ell} + \sum_{R_{\ell}} \chi_{2i} (\vec{R}_{j} - \vec{R}_{\ell}) \varphi_{2\ell} \qquad (1.13a)$$

$$H_{o} \varphi_{2j} = \sum_{R_{L}} \gamma_{i2} (\vec{R}_{j} - \vec{R}_{L}) \varphi_{il} + \sum_{R_{L}} \gamma_{22} (\vec{R}_{j} - \vec{R}_{L}) \varphi_{2l} \qquad (1.13b)$$

These relations are easily verified by multiplying them through by $\Psi_{\alpha\kappa}^*$ and integrating over \vec{r} .

We now introduce the perturbation $U(\vec{r})$. The expansion of ψ_1 and ψ_2 in terms of Löwdin functions is still possible in the presence of the perturbation, but the phase factors are now replaced by arbitrary coefficients, which are to be determined. We thus take:

$$\Psi_{i} = \sum_{\mathbf{R}_{j}} c_{i}(\vec{\mathbf{R}}_{j}) \varphi_{ij} \qquad (1.14a)$$

$$\Psi_2 = \sum_{R_j} c_2(\vec{R_j}) \varphi_{2j}$$
 (1.14b)

and $\Psi = \Psi_1 + \Psi_2$ (1.1¹/₁c)

It is no longer necessary to include the constants λ_1 and λ_2 , since these may be incorporated in c_1 and c_2 respectively. Let us now operate with the total Hamiltonian operator H on the function ψ .

$$H\psi = (H_0 + U)\psi = E\psi$$
 (1.15)

It is shown in Appendix 1, that the resulting set of coupled equations for the coefficients c_1 and c_2 are:

$$H_{ii}^{\circ}(-i\vec{\sigma})c_{i}(\vec{r}) + H_{i2}^{\circ}(-i\vec{\sigma})c_{2}(\vec{r}) + U(\vec{r})c_{i}(\vec{r}) = Ec_{i}(\vec{r}) \qquad (1.16a)$$

$$H_{21}^{\circ}(-i\vec{r})c_{1}(\vec{r}) + H_{22}^{\circ}(-i\vec{r})c_{2}(\vec{r}) + U(\vec{r})c_{2}(\vec{r}) = Ec_{2}(\vec{r}) \quad (1.16b)$$

where:

$$H^{\circ}_{\alpha\beta}(\vec{k}) = \sum_{R_s} e^{i\vec{k}\cdot\vec{R}_s} \gamma_{\beta}(\vec{R}_s) \qquad (1.17)$$

Suppose that we need to take into account one band only. Then $c_2 = 0$, and the equations (1.16a) and (1.16b) reduce to:

$$\left[H_{ii}^{\circ}(-i\vec{\phi}) + U(\vec{r})\right]c(\vec{r}) = Ec(\vec{r})$$

and since

$$H^{\circ}_{\mu}(\vec{k}) = \sum_{R_{s}} e^{i\vec{k}\cdot\vec{R_{s}}} \gamma(\vec{R_{s}}) = E_{o}(\vec{k})$$

this is exactly Luttinger's result in the absence of a magnetic field \overrightarrow{H} (cf. equation 1.1).

Again, it may be more convenient to replace equations (1.16a) and (1.16b) by their Fourier transforms. Defining

$$c_{m}(\vec{r}) = \int e^{i\vec{k}\cdot\vec{r}} d(\vec{k}) d^{3}k \qquad (m = 1,2)$$

and

$$\mathcal{U}(\vec{k}) = (2\pi) \int e^{-i\vec{k}\cdot\vec{r}} \mathcal{U}(\vec{r}) d^{3}r$$

it is easily shown that the generalization of equation (1.5) becomes:

$$H^{o}_{u}(\vec{k})d_{i}(\vec{k}) + H^{o}_{i2}(\vec{k})d_{2}(\vec{k}) + \int \mathcal{U}(\vec{k}-\vec{k}')d_{i}(\vec{k}')d^{3}k' = Ed_{i}(\vec{k}) (1.10a)$$

$$H^{o}_{2i}(\vec{k})d_{i}(\vec{k}) + H^{o}_{22}(\vec{k})d_{2}(\vec{k}) + \int \mathcal{U}(\vec{k}-\vec{k}')d_{2}(\vec{k}')d^{3}k' = Ed_{2}(\vec{k}) (1.10b)$$

In this form our results are easily compared with a tight binding calculation such as the one in A. Suppose that the perturbation $U(\mathbf{r}) \rightarrow 0$. Then equations (1.18a) and (1.18b) reduce to a set of algebraic equations. The condition for a non-trivial solution (d_1, d_2) is then simply:

$$\begin{array}{ccc} H_{11}^{O} & E & H_{12}^{O} \\ H_{21}^{O} & H_{22}^{O} & E \end{array} = 0$$

This is exactly the secular equation which determines the E(k) relation in the absence of a perturbation.

We now turn to the case of an external magnetic field. We shall follow the derivation given by Luttinger (18). However, as in the previous case, we shall generalize this derivation by taking into account two bands. Wherever it is possible, we shall use the notation employed in reference (18).

In the previous derivation we chose:

$$\Psi = \sum_{R_{j}} c_{1}(\vec{R}_{j}) \varphi_{1j} + \sum_{R_{j}} c_{2}(\vec{R}_{j}) \varphi_{2j} \qquad (1.14)$$

This form of ψ is no longer suitable for the magnetic field case, because of the $\overrightarrow{A \cdot p}$ term in the Mamiltonian operator. We shall see that we can approximately remove this term from the Mamiltonian by replacing (1.14) by

$$\psi = \sum_{R_j} c_i(\vec{R}_j) \exp\left[\frac{ie}{\hbar c} G_{ij}\right] \varphi_{ij} + \sum_{R_j} c_2(\vec{R}_j) \exp\left[\frac{ie}{\hbar c} G_{2j}\right] \varphi_{2j} \quad (1.19)$$
where:

$$\vec{T} = \left(\vec{A}(\vec{r}') d\vec{r}'\right)$$

Here,
$$R_{\prec j}$$
 is the position vector of the \prec th atom in the jth
unit cell, and the integral is taken along the straight line
path from $R_{\prec j}$ to \tilde{r} . The exponential terms essentially re-
center the magnetic potential for each atom, so that this
potential never becomes infinitely large at any atomic site.
The factors $G_{\prec j}$ can be represented parametrically:

$$G_{\alpha j} = \int_{0}^{1} (\vec{r} - \vec{R}_{j}) \cdot \vec{A} [\vec{R}_{j} + \lambda(\vec{r} - \vec{R}_{\alpha j})] d\lambda \qquad (1.20)$$

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We now proceed to evaluate $\mathbb{H} \bigvee$. The Hamiltonian operator \mathbb{H} has the form:

$$H = \frac{1}{2m} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^{2} + V(\vec{r})$$
 (1.21)

where V(r) is the periodic lattice potential. Thus:

$$\begin{aligned} H\psi &= \sum_{\mathbf{R}_{j}} c_{i}(\vec{\mathbf{R}}_{j}) H \exp\left[\frac{i\mathbf{e}}{\hbar c} \mathbf{G}_{ij}\right] \varphi_{ij} + \sum_{\mathbf{R}_{j}} c_{2}(\vec{\mathbf{R}}_{j}) H \exp\left[\frac{i\mathbf{e}}{\hbar c} \mathbf{G}_{2j}\right] \varphi_{2j} \\ &= \sum_{\mathbf{R}_{j}} c_{i}(\vec{\mathbf{R}}_{j}) \exp\left[\frac{i\mathbf{e}}{\hbar c} \mathbf{G}_{ij}\right] \left\{ \frac{1}{2m} \left[\vec{\mathbf{p}} - \frac{\mathbf{e}}{\mathbf{c}} \left(\vec{\mathbf{A}} - \vec{\nabla} \mathbf{G}_{ij}\right)\right]^{2} + V \right\} \varphi_{ij} \\ &+ \sum_{\mathbf{R}_{j}} c_{2}(\vec{\mathbf{R}}_{j}) \exp\left[\frac{i\mathbf{e}}{\hbar c} \mathbf{G}_{2j}\right] \cdot \left\{ \frac{1}{2m} \left[\vec{\mathbf{p}} - \frac{\mathbf{e}}{\mathbf{c}} \left(\vec{\mathbf{A}} - \vec{\nabla} \mathbf{G}_{2j}\right)\right]^{2} + V \right\} \varphi_{2j} \end{aligned}$$
(1.22)

In Appendix 1 of reference (18), ∇G_j is computed. For a constant magnetic field one finds:

$$\vec{\nabla} \mathbf{G}_{\alpha j} = \vec{A}(\vec{r}) + \frac{1}{2} (\vec{r} - \vec{R}_{\alpha j}) \times \vec{H}$$
(1.23)

Substituting (1.23) into (1.22), we see that we have accomplished our aim of removing the $A \cdot p$ term. Hence:

$$\begin{aligned} H\psi &= \sum_{R_j} c_1(\vec{R_j}) \exp\left[\frac{ie}{\hbar c} G_{ij}\right] \cdot \left\{ \frac{1}{2m} \left[\vec{P} + \frac{e}{c}(\vec{r} - \vec{R_{ij}}) \times \frac{\vec{H}}{2}\right]^2 + V \right\} \psi_{1j} \\ &+ \sum_{R_j} c_2(\vec{R_j}) \exp\left[\frac{ie}{\hbar c} G_{2j}\right] \cdot \left\{ \frac{1}{2m} \left[\vec{P} + \frac{e}{c}(\vec{r} - \vec{R_{2j}}) \times \frac{\vec{H}}{2}\right]^2 + V \right\} \psi_{2j} \end{aligned}$$
(1.24)

The localization of φ_{ij} and φ_{2j} allows us to put $\vec{r} \sim R_{1j}$ and $\vec{r} \sim R_{2j}$ in the operators which act on φ_{ij} and φ_{2j} respectively, provided H is not too rapidly varying. We then find:

$$H \psi = \sum_{R_j} c_1(\vec{R_j}) \exp\left[\frac{ie}{\hbar c} G_{1j}\right] H_o \varphi_{1j}$$

+
$$\sum_{R_j} c_2(\vec{R_j}) \exp\left[\frac{ie}{\hbar c} G_{2j}\right] H_o \varphi_{2j}$$

This procedure still leaves us with an expression which involves two different phases, due to the terms G_{1j} and G_{2j} . Although it is possible to carry the calculation through in this case, a considerable simplification results under certain conditions.

Suppose that we ignored the phase changes between the two atoms in a unit cell and replaced them by an average phase. That is, suppose that we put $G_{1j} = G_{2j} = G_j$. Then, since our Lowdin functions Ψ_{ij} and Ψ_{2j} are centered at different points in the jth cell, the localization of these functions would no longer cause the $\overline{\nabla} G_{\alpha j}$ terms to vanish in (1.24). Instead, these terms are now

$\frac{e}{2c}(\vec{r}-\vec{R}_j)\times\vec{H}$

and we are replacing \vec{r} by $\vec{R_{1j}}$ or $\vec{R_{2j}}$, depending on whether the operator acts on φ_{ij} or φ_{2j} . Let us choose the origin of the jth unit cell (given by $\vec{R_{j}}$) to be halfway between the two atoms. In this case, our equation becomes:

$$\begin{split} H\psi &= \sum_{R_j} c_i(\vec{R_j}) \exp\left[\frac{ie}{\pi c} G_j\right] \left\{ \frac{1}{2m} \left[\vec{p} + \frac{e}{4c} \vec{r_{12}} \times \vec{H}\right]^2 + V \right\} \psi_{1j} \\ &+ \sum_{R_j} c_2(\vec{R_j}) \exp\left[\frac{ie}{\pi c} G_j\right] \left\{ \frac{1}{2m} \left[\vec{p} - \frac{e}{4c} \vec{r_{12}} \times \vec{H}\right]^2 + V \right\} \psi_{2j} \\ \text{where } \vec{r_{12}} = \vec{R_{1j}} - \vec{R_{2j}}. \text{ In graphite, for example, } r_{12} \text{ is } 1.42\text{A}^{0}. \end{split}$$

We would like to neglect the $r_{12} \times H$ terms in the above operators. Let us estimate the error involved in this approximation. Since we are primarily interested in a calculation of the susceptibility, we see that we are neglecting H^2 terms in the energy which are of the order of

$$\sim \frac{\mathrm{e}^2}{\mathrm{8mc}^2} \left[\overline{\mathrm{H}} \times \frac{\overline{\mathrm{r}_{12}}}{2} \right]^2$$

These terms thus lead to a contribution to the susceptibility which is of the order of the ion core susceptibility. Whenever the electronic susceptibility is much larger than the ion core contribution, one may neglect the variation of the phase terms within one unit cell and write:

$$H\psi = \sum_{R_j} c_1(\vec{R}_j) \exp\left[\frac{ie}{\hbar c} G_j\right] H_0 \varphi_{1j}$$

+
$$\sum_{R_j} c_2(\vec{R}_j) \exp\left[\frac{ie}{\hbar c} G_j\right] H_0 \varphi_{2j} \qquad (1.25)$$

Substituting (1.13a) and (1.13b) into (1.25) we find:

$$H \psi = \sum_{\substack{R_{j}, R_{L}}} c_{i}(\vec{R}_{j}) \exp\left[\frac{ie}{\hbar c}G_{j}\right] \left\{ \delta_{ii}(\vec{R}_{j} - \vec{R}_{L}) \varphi_{1\ell} + \delta_{2i}(\vec{R}_{j} - \vec{R}_{L}) \varphi_{2\ell} \right\} \\ + \sum_{\substack{R_{j}, R_{L}}} c_{2}(\vec{R}_{j}) \exp\left[\frac{ie}{\hbar c}G_{j}\right] \left\{ \delta_{i2}(\vec{R}_{j} - \vec{R}_{L}) \varphi_{1\ell} + \delta_{22}(\vec{R}_{j} - \vec{R}_{L}) \varphi_{2\ell} \right\}$$
(1.26)

The resulting equations for c₁ and c₂ are derived in Appendix II. These equations may be written:

$$H_{12}^{\circ}(-i\vec{\nabla}-e\vec{A})c_{1}(\vec{r}) + H_{12}^{\circ}(-i\vec{\nabla}-e\vec{A})c_{2}(\vec{r}) = Ec_{1}(\vec{r})$$
 (1.27a)

$$H_{21}^{\circ}(-i\vec{\nabla}-\underline{e}\vec{A})c_{1}(\vec{r})+H_{22}^{\circ}(-i\vec{\nabla}-\underline{e}\vec{A})c_{2}(\vec{r}) = Ec_{2}(\vec{r}) (1.27b)$$

Defining

$$c_{m}(\vec{r}) = \int e^{i\vec{k}\cdot\vec{r}} B_{m}(\vec{k}) d^{3}k \qquad (m = 1,2)$$

the Fourier transforms of equations (1.27a) and (1.27b) become (for the special case of the Landau gauge):

$$H^{\nu}_{\mu}(k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z})B_{1}+H^{\nu}_{12}(k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z})B_{2} = EB_{1} \qquad (1.20a)$$

$$H_{21}^{\circ}(k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z})B_{1}+H_{22}^{\circ}(k_{x}-is\frac{\partial}{\partial k_{y}},k_{y},k_{z})B_{2} = EB_{2} \qquad (1.28b)$$

These equations form the basis of our calculation of the susceptibility. Note, that as $s = \frac{eH}{\hbar c} \longrightarrow 0$, the equations again become algebraic, and the condition for a non-trivial solution is the same as that given earlier.

The generalization of these results to the case of an m-fold degeneracy is straightforward. In that case one will obtain a set of m coupled equations of the same type as the equations we have considered here.

II. THE ENERGY SPECTRUM IN THE PRESENCE OF A MAGNETIC FIELD.

In this section, we shall be interested in the solution of equations (1.20a) and (1.20b) in the case of two-dimensional graphite. We shall also extend the treatment of section I, so that the theory may be applied to three-dimensional graphite. In both cases, we shall be interested in calculating the magnetic susceptibility of graphite when the magnetic field \overrightarrow{H} is applied along the crystallographic c-axis; that is, perpendicular to the graphite layers. In this case the observed susceptibility is much larger than the ion core contribution, so that our approximations will be valid. The susceptibility perpendicular to the c-axis turns out to be of the order of the ion core contribution, so that the quantity we shall be calculating is essentially the difference between these two susceptibilities, $\chi_{\mu} - \chi_{\mu} \simeq \chi_{\mu}$.

Section I resulted in a simple prescription, which tells one how the set of coupled equations, which yield the energy spectrum in the presence of a magnetic field, are to be written down. One simply takes the secular determinant which determines the E(k) relation in the absence of the magnetic field, and makes the elements of this determinant operators by replacing k_x by k_x -is $\frac{\partial}{\partial k_y}$ (s = $\frac{eH}{\hbar c}$). The elements of the resulting matrix operator are to be taken in the sense of an expansion, and the operator acts on a column vector $B_1(k)$, whose dimensionality is the multiplicity of the degeneracy in question.

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Let us first consider the case of two-dimensional graphite. The secular equation in the two-dimensional approximation is given in A as:

$$\begin{array}{cccc} H_{11}^{i} - E & H_{12}^{i} \\ H_{21}^{i} & H_{22}^{i} - E \end{array} = 0$$

where:

$$H'_{12} = H'_{21} = -\delta_{o} \left[e_{xp} \left(-\frac{i k'_{xa}}{\sqrt{3}} \right) + 2 \cos \left(\frac{k'_{ya}}{2} \right) e_{xp} \left(\frac{i k'_{xa}}{2\sqrt{3}} \right) \right]$$

$$H'_{11} = H'_{22} = E_{o} - 2\delta_{o} \left[\cos \left(k'_{ya} \right) + 2 \cos \left(\frac{k'_{xa}}{2} \right) \cos \left(\frac{k'_{ya}}{2} \right) \right]$$

The notation here is the same as that used in A except that our \vec{k} 's are defined differently by a factor of 2π .

We now expand these elements to lowest order about the degeneracy corner. Introducing:

$$k_{x}^{'} = k_{x}^{C} + k_{x} \qquad k_{x}^{C} = \frac{2\pi}{\sqrt{3} a}$$

$$k_{y}^{c} = k_{y}^{C} + k_{y} \qquad k_{y}^{C} = \frac{2\pi}{3 a}$$

we find:

$$H'_{11} = H'_{22} \cong B_0 + 3\%'$$

$$H'_{12} = \frac{\sqrt{3}}{2}\% a e^{\frac{1}{3}} [k_y - ik_x] = \hbar v e^{\frac{1}{3}} [k_y - ik_x]$$

The notation $\pi_{V} = \frac{\sqrt{3}}{2} \delta_{0} a$ was first introduced by McClure (3) and will be used throughout this thesis. Furthermore, we shall from here on measure energy from the degeneracy corner; that is, we shall put $H'_{11} = H'_{22} = 0$.

Thus, in the absence of a magnetic field H along the c-axis, the energy spectrum in the vicinity of the degeneracy point is:

$E(\vec{k}) = \pm \hbar v [k_x^2 + k_y^2]^2 = \pm \hbar v K$

Let us now apply a magnetic field along the z-direction (the c-axis in graphite). Following our prescription, our set of coupled equations is:

$$\begin{pmatrix} -E & f_{V}e^{\frac{i\pi}{3}}[k_{y}-ik_{x}-s\frac{\partial}{\partial k_{y}}] \\ f_{V}e^{\frac{i\pi}{3}}[k_{y}+ik_{x}+s\frac{\partial}{\partial k_{y}}] & -E \end{pmatrix} \begin{pmatrix} B_{i} \\ B_{2} \end{pmatrix} = 0$$

or:

$$\hbar v e^{\frac{i\pi}{3}} \left[k_y - ik_x - s \frac{\partial}{\partial k_y} \right] B_2 = EB_1$$

$$\hbar v e^{\frac{i\pi}{3}} \left[k_y + ik_x + s \frac{\partial}{\partial k_y} \right] B_1 = EB_2$$

These equations are completely equivalent to McClure's equations (2.7a) and (2.7b). The solution for B_1 , B_2 and the allowed energies E is given by Ecclure (3). The predicted energy spectrum near the degeneracy point is:

$E = \pm \pi v (2ns)^{\frac{1}{2}} = \pm y (ns)^{\frac{1}{2}}$

It should be pointed out that the secular determinant used here neglects overlap. This is clearly equivalent to assuming that the Löwdin functions are simply atomic orbitals and not combinations of atomic orbitals centered on different atoms. Coulson and Taylor (11) have estimated the various overlap integrals for p_z -orbitals in graphite, and have shown that only nearest neighbor overlaps are important. If this overlap, which we shall call σ , is considered, it is easily shown that the above energy spectrum is replaced by:

$$\frac{E}{1-\frac{E\sigma}{2}} = \pm y(ns)^{\frac{1}{2}}$$

Coulson and Taylor (11) estimate that $\sigma \simeq .25$. Since we are interested in energies near the degeneracy corner, $0 \le E \le \zeta_0$, and since $\chi_0 \simeq 2.6$ ev, it is clear that overlap contributions are completely unimportant. It may similarly be verified that inclusion of second-neighbor exchange integrals has no appreciable effect in the region of k-space which is of interest, namely, near the corners of the Brillouin zone.

Let us now extend this treatment to three dimensions. We shall consider only nearest neighbor exchange integrals in the plane and nearest out-of-plane exchange integrals. Second-nearest in-plane exchange integrals again turn out to be unimportant. The introduction of the out-of-plane interaction, on the other nand, changes the energy spectrum completely, since it is this term which introduces the k_z -dependence into the problem. This k_z -dependence will have the effect of spreading the sharp energy levels of the twodimensional calculation.

Under these assumptions, the secular equation for threedimensional graphite is (cf. reference A):

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The notation here is again the same as that in A, except for the slightly different definition of \vec{k} . We shall measure the energy from the point where both S and Γ are zero; that is, from the corner of the Brillouin zone at the points $k_z = \pm \frac{\pi}{c}$. Again, we shall expand S about the corner of the zone and replace k_x by k_x -is $\frac{\delta}{\delta k_y}$. The resulting set of coupled equations is:

$$\beta D^{-}B_{2} + \alpha B_{3} = \epsilon B_{1} \qquad (2.2a)$$

$$\beta^{-}D^{+}B_{1} = \epsilon B_{2} \qquad (2.2b)$$

$$\propto B_1 + \beta' D^+ B_4 = \epsilon B_3$$
 (2.2c)

$$\beta \overline{D} B_3 = \epsilon B_4$$
 (2.2d)

where:

$$\alpha = \frac{x_{1}\Gamma}{\pi_{V}} = \frac{2x_{1}}{\pi_{V}}\cos\left(\frac{k_{z}c}{2}\right)$$

$$\epsilon = \frac{E}{\pi_{V}}; \quad \beta = e^{\frac{i\pi}{3}}$$

$$D^{+} = k_{y} + i\left[k_{x} - is\frac{\partial}{\partial k_{y}}\right]$$

$$D^{-} = k_{y} - i\left[k_{x} - is\frac{\partial}{\partial k_{y}}\right]$$

The substitution $B_m = b_m \cdot \exp(\frac{-ik_x k_x}{s})$, (m = 1, 2, 3, 4), results in a considerable simplification. The set of equations satisfied by the b_m 's is:

$$\beta \Omega b_2 + \alpha b_3 = \epsilon b_1 \qquad (2.3a)$$

$$\beta' \Omega' b_1 = \epsilon b_2$$
 (2.3b)

- $\alpha b_1 + \beta \Delta b_4 = \epsilon b_3 \qquad (2.3c)$
- $\beta \Omega b_3 = \epsilon b_4$ (2.3d)

In equations (2.3a) to (2.3d), the following notation has been used:

$$\Omega^{+} = k_{y} + s \frac{\partial}{\partial k_{y}}$$
$$\Omega^{-} = k_{y} - s \frac{\partial}{\partial k_{y}}$$

Eliminating b_2 , b_3 , and b_4 , the equation for b_1 becomes:

$$\left[\left(\Omega^{\dagger}\Omega^{-}-\epsilon^{2}\right)\left(\Omega^{-}\Omega^{\dagger}-\epsilon^{2}\right)-\epsilon^{2}\alpha^{2}\right]b_{i}=0$$
(2.4)

But

$$\Omega^{\dagger}\Omega^{-} = -s^{2}\frac{\partial^{2}}{\partial k_{y}^{2}} + k_{y}^{2} + s$$

and

$$\Omega_{\Omega}^{-}\Omega^{+} = -S_{\frac{\lambda^2}{\lambda k_y^2}}^2 + k_y^2 - S$$

Putting $L = -s\frac{2\delta^2}{\delta k_y^2} + k_y^2 - \epsilon^2$, (2.4) becomes: $\left(L^2 - \lambda^2 \right) b_1 = 0$ (2.5)

where:

$$\lambda^2 = \mathbf{S}^2 + \epsilon^2 \boldsymbol{\alpha}^2$$

Consider now:

$$(L+\lambda)\chi = 0$$
 and $(L-\lambda)\psi = 0$

Both of these equations can be put into standard harmonic oscillator form. Clearly, since $b_1 = \chi + \varphi$ is a solution of equation (2.5), and since $b_1 = \chi + \varphi$ involves four arbitrary constants, this is in fact the general solution of equation (2.5). Care must be taken, however, when the boundary conditions are applied. We want the b_m 's to satisfy regularity boundary conditions. Clearly b_1 will be regular if we choose both χ and φ to be regular; that is, if we build up b_1 from the Hermite polynomials (times an exponential factor). The question now arises whether it is possible to construct a regular set of b_m 's by choosing χ and φ to be separately irregular. That this is impossible can be shown by writing the solutions as linear combinations of confluent hypergeometric functions and expanding these about the point at infinity. One finds that the irregularities of χ and

 φ cannot cancel.

Hence we conclude that the most general \mathtt{b}_1 satisfying the regularity boundary conditions is \mathtt{b}_1 = $\chi+\phi$, where

 χ and ψ are independently regular functions.

Now, $(L - \lambda) \phi = 0$ leads to:

 $e^{2} + [s^{2} + \alpha^{2} e^{2}]^{\frac{1}{2}} = (2p+1)s$

(because of the regularity of φ , p = 0,1,2,3...)

while $(L + \lambda) X = 0$ leads to:

 $\epsilon^{2} - \left[5^{2} + \alpha^{2} \epsilon^{2}\right]^{\frac{1}{2}} = (2m+i)S \qquad (because of the regularity of \chi, m = 0, 1, 2, 3...)$

It is easily checked that these two energy spectra are mutually exclusive when $\propto \neq 0$. Solving each of the above relations for the energy E, we find:

$$b_{1} = \chi : \quad \epsilon^{2} = \frac{\alpha^{2}}{2} + s(2m+i) + \left[\left(\frac{\alpha^{2}}{2} \right)^{2} + \alpha^{2} s(2m+i) + s^{2} \right]^{\frac{1}{2}}$$

$$b_{1} = \psi : \quad \epsilon^{2} = \frac{\alpha^{2}}{2} + s(2p+i) - \left[\left(\frac{\alpha^{2}}{2} \right)^{2} + \alpha^{2} s(2p+i) + s^{2} \right]^{\frac{1}{2}}$$

Thus, we find that the general, regular, non-trivial B_1 can be written:

$$B_{1} \sim \exp\left[\frac{-ik_{x}k_{y}}{s}\right] \exp\left[\frac{k_{y}^{2}}{2s}\right] H_{n}\left(\frac{k_{y}}{\sqrt{s}}\right) \cdot \delta\left(k_{x}-k_{x}'\right) \cdot \delta\left(k_{z}-k_{z}'\right)$$

The corresponding energy is:

$$E = \pm \hbar v \left[\frac{\alpha^2}{2} + s(2n+i) \pm \left(\frac{\alpha^4}{4} + \alpha^2 s(2n+i) + s^2 \right)^{1/2} \right]^{1/2}$$
(2.6)

In order to determine whether or not we have missed any solutions, we must go back to the original set of equations (2.2a, 2.2b, 2.2c, 2.2d). Making use of the fact that the various operators involved in these equations are the raising and lowering operators, we find that the general solution is: $B_1 \sim H_n$; $B_2 \sim H_{n-1}$; $B_3 \sim H_n$; $B_4 \sim H_{n+1}$

(with the convention that $H_{-1} = 0$).

The solution corresponding to the energy eigenvalue zero is: $B_1 \sim H_0; B_2 = 0; B_3 = 0; B_4 \sim H_1$

However, it is also possible to find another solution with energy eigenvalue zero, not included in the above set, because in this case $B_1 = 0$. The solution is:

 $B_1 = 0; B_2 = 0; B_3 = 0; B_4 \sim H_0$

Let us now consider the limiting case of $\propto = 0$. In this case, equation (2.6) yields:

$$E = \pm \hbar v (2ns)^{\frac{1}{2}}$$
 (2.7a)

or:

$$E = \pm \hbar v [2(n+i)s]^{\frac{1}{2}}$$
 (2.7b)

In addition to the E = 0 solution coming from n = 0 in (2.7a) above, we have seen that there is an extra E = 0 solution not included in the above relations (2.7a) and (2.7b).

We shall see that the degeneracy of each level (characterized by n and \pm 1) is $\frac{2Vs}{\pi c} = \frac{qs}{2}$. Clearly, the energies arising from (2.7a) with n \geq 1 can be grouped with those from (2.7b) with n \geq 0. The result can then be written:

$$E = \pm \hbar v (2ns)^{\frac{1}{2}}$$
(2.7c)

If the extra E = 0 level is included in (2.7c), the degeneracy of each level is just qs, in agreement with McClure's result.

We shall see later that we must choose a very small value of the inter-layer exchange integral X_1 , if we wish to explain the experimentally observed susceptibility. The energy relation (2.6) is much too complicated for a calculation of the susceptibility, so that we want to expand equation (2.6) for small X_1 . Unfortunately, this cannot be done for magnetic fields of arbitrary magnitude, since the condition for the validity of the expansion is:

$$\propto^2 << \frac{S}{2n+1}$$

Our results will be meaningful only if we restrict ourselves to magnetic fields which satisfy this condition. Fortunately, we shall never have to consider very large values of n, since only levels with small n lie near the degeneracy point and hence near the Fermi level. We shall never be able to extrapolate our expansion to the zero field case, but since measurements of the susceptibility usually involve a torsional technique, fields of several thousand gauss are generally employed in these measurements. In this region of magnetic fields, our expansion will be valid over the entire range of k_z . This can easily be checked by substituting the previously quoted numerical values for the various parameters into the above condition for the validity of our expansion.

The resulting energy spectrum for small values of δ_1 may be expressed in the following form:

$$E = \pm \hbar_{V} (2ns)^{\frac{1}{2}} \{ 1 \pm \frac{\alpha^{2}}{4s} \}$$
 (2.8)

We have again grouped the levels and included the extra E = 0 level, so that the degeneracy of each level (characterized by n and the external \pm sign) is just qs.

Note that the inter-planar interaction has spread each level into a narrow band of width $\frac{\hbar v \alpha^2}{2s} (2ns)^2$. Thus the levels become wider with increasing n values. The n = 0 level, however, has remained sharp. This result is independent of our approximation and follows directly from equation (2.6). Note also, that the level width depends upon the magnetic field and that all the levels become sharp as the magnetic field becomes very large. This fact has an interesting consequence in the de Haas-Van Alphen effect, and will be discussed further in a later section.

Eventually, the levels corresponding to the higher n values will overlap each other even when δ_i is assumed small. However, the levels near the degeneracy point are discrete

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when the inter-layer interaction is small. For example, in a field of 10^{4} gauss, with $\chi_{1} = .005$ ev, the levels do not overlap until one reaches an energy of .07 ev. This occurs between the n = 5 and n = 6 levels.

III. APPROXIMATE CALCULATION OF THE SUSCEPTIBILITY AT HIGH TEMPERATURES.

We shall now estimate the susceptibility of graphite at high temperatures in a manner analogous to the estimate made by McClure (3) for the two-dimensional case. Such a calculation shows very clearly why the inter-layer interaction must necessarily be very weak.

Let us now calculate the energy gain of our system when the magnetic field is turned on. For this purpose we need only the general features of our energy spectrum as predicted by equation (2.6). In particular, we note that the n = 0level is sharp and that the spacing between this level and the two n = 1 levels is larger than the spacing between any other two levels. Furthermore, it will be shown later that at high temperatures the Fermi level is very near the n = 0level. It follows that most of the energy gain of the system is due to the electrons, which in the presence of the field, occupy the n = 0 level.

When a magnetic field H is applied, there is room for qs electrons in the n=0 level. The number of electrons in the n = 0 level is thus qsf(0), where f(0) is the value of the Fermi distribution function at energy zero. The total energy of these qsf(0) electrons is clearly zero. Before the field was applied, these electrons had energies between $-\Delta$ and $+\Delta$, the negative energy states being preferentially occupied, because of the Fermi distribution function. The total energy of these electrons in the absence of the field was thus:

$$E = \int_{-\Delta}^{+\Delta} N(E)f(E)EdE \qquad (3.1)$$

where N(E) is the density of states in the absence of a field, and is given by:

$$V(E) = \frac{2V}{\pi^{2}c(\hbar_{V})^{2}} \left[(4\chi_{i}^{2} - E^{2})^{\frac{1}{2}} + \pi |E| + 2E\sin^{2}\left(\frac{E}{2\chi_{i}}\right) \right] \quad E < 2\chi_{i} \quad (3.2a)$$
$$= \frac{4V}{\pi c(\hbar_{V})^{2}} |E| \quad (3.2b)$$

The relation (3.2a) is given in A; (3.2b) is easily calculated in a manner analogous to the calculation in A.

Furthermore, Δ is determined by the condition:

$$\int_{-\Delta} N(E)f(E)dE = qsf(0) \qquad (3.3a)$$

At high temperatures, this condition simply becomes:

$$\int_{\Delta} N(E) dE = qs \qquad (3.3b)$$

since we can replace f(E) by f(O) and factor it outside the integral. Specifically, we are assuming that the integration range in (3.3b), which is of the order of the magnetic level spacing, is much smaller than the thermal energy.

We now consider two separate cases. First, let us choose a high value for the inter-layer exchange integral \aleph_1 , say $\aleph_1 \simeq .1$ ev. Since the integrations in (3.1) and (3.3b) extend over a range of the order of the magnetic level spacing, all energies involved in the integrals will then satisfy the condition: $\frac{\mathbf{E}}{\mathbf{v}_i} \ll 1$. Hence the N(E) in question is given by (3.2a). In fact, we only require this relation for small E and hence we may expand in powers of $\frac{\mathbf{E}}{\mathbf{v}_i}$. We find:

$$N(E) \simeq \frac{4V_{\lambda_1}}{\pi^2 c(\hbar\nu)^2} + \frac{2V}{\pi c(\hbar\nu)^2} |E| \qquad (3.4)$$

It is easily checked that under these circumstances

$$\Delta \simeq \frac{\pi (\pi v)^2 s}{v_i} \tag{3.5}$$

and that the increase in energy contains no term proportional to s^2 . This result has a simple physical interpretation. We note that in the three-dimensional case the density of states in the absence of a field does not approach zero as the energy approaches zero (cf. equation 3.4). Instead, it approaches a value proportional to \aleph_1 . Hence there are already some electrons whose energies are zero before the field is applied. In fact, there are too many of them. The result is that the energy of the system cannot be raised much through the application of the field, since Δ becomes very small and advantage cannot be taken of the preferential occupation of the lower energy states.

It is clear what one has to do in order to retain a susceptibility in the three-dimensional case. We need to reduce the number of electrons whose energies are zero before the field is applied; that is, we need to reduce X_1 . It is easily shown that if $X_1 \ll h \sqrt{\frac{1}{2}}$, the susceptibility is just equal to that predicted by McClure in the two-dimensional case.

This simple argument does not depend on the detailed structure of the energy spectrum and is independent of any approximations. We are thus led to the conclusion that graphite is essentially two-dimensional in structure. We shall see that $\aleph_1 \simeq .005$ ev is consistent with all the observed properties of graphite. An upper limit of about .01 ev can be put on \aleph_1 in this way. Our value of \aleph_1 is about twenty times smaller than that used in A. A theoretical estimate of \aleph_1 was made by Godin (19). His value for \aleph_1 is .007 ev, but no other estimate of this order of magnitude seems to have appeared in the literature. IV. CALCULATION OF THE FREE ENERGY.

In order to be able to carry through a proper calculation of the susceptibility, we need to obtain an expression for the free energy of our system in the presence of an applied magnetic field. An evaluation of this free energy function involves a knowledge of the density of states in the presence of the magnetic field. We shall write:

$$g(E) = \sum_{n} g(E_{n}) \tag{11.1}$$

where g(E) is the density of states in question; $g(E_n)$ is the density of states within the nth level, and the sum extends over all levels n which contribute at the energy E. For a general n, $g(E_n)$ is simply:

$$g(E_n) = \frac{8Vs}{4\pi^2} \cdot \frac{dk_z}{dE_n}$$
(4.2)

The factor of 6 accounts for the various degeneracies in graphite: spin degeneracy (a factor of 2) and site degeneracy (a factor of 4). The total number of states for each value of n and choice of sign is just:

$$\frac{8Vs}{4\pi^2} \times \frac{2\pi}{c} = \frac{4Vs}{\pi c} = qs \qquad (4.3)$$

For the n = 0 level, which we have seen is always sharp, (4.2) is simply replaced by a δ -function. This level also contains qs states, exactly as in the two-dimensional case.

The above arguments are completely analogous to those

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made in the counting of states in the free electron case. This is a direct consequence of the form of our solutions $\beta_{m}(\vec{k})$. We note that k_{x} and k_{z} enter these solutions only parametrically. Thus the $\delta(k_{x} - k_{x}')$ and $\delta(k_{z} - k_{z}')$ factors lead to $\exp(ik_{x}'\cdot x)$ and $\exp(ik_{z}'\cdot z)$ in the spatial functions. Furthermore, the complex exponential factor $\exp(\frac{-ik_{x}k_{y}}{s})$ centers these functions at $y - \frac{k_{x}'}{s}$. Thus we can apply cyclic boundary conditions in the x and z directions. Limiting y to lie within the crystal then limits k_{x} and hence equation (3.2) follows.

Following equation (2.8), we take E_n to be:

$$E_{n} = \mathcal{V}(ns)^{\frac{1}{2}} \left[1 \pm \frac{2\gamma_{1}^{2} \cos^{2}\left(\frac{kzc}{2}\right)}{\mathcal{V}^{2}s} \right]$$
^(4.4)

Evaluating $\frac{dk_{x}}{dE_{n}}$, it becomes convenient to introduce three new symbols. Let:

Minimum energy of nth level = $A_n = \mathcal{V}(ns)^{\frac{1}{2}} \left[1 - \frac{2\aleph_1^2}{\nu^2 s} \right]$ Average energy of nth level = $C_n = \mathcal{V}(ns)^{\frac{1}{2}}$ Maximum energy of nth level = $B_n = \mathcal{V}(ns)^{\frac{1}{2}} \left[1 + \frac{2\aleph_1^2}{\nu^2 s} \right]$

The resulting $g(E_n)$ may then be written:

$$g(E_n) = \frac{q_5}{2\pi} \left[(E - A_n)(C_n - E) \right]^2 \qquad A_n \le E \le C_n \qquad (4.5a)$$

$$= \frac{95}{2\pi} \left[(B_n - E)(E - C_n) \right]^{\frac{7}{2}} \qquad C_n \le E \le B_n \qquad (4.5b)$$

We are now ready to evaluate the expression for the free energy of our system. Following McClure (3), we write:

$$F = NG + E_{o} + \int_{-\infty}^{+\infty} dE \phi(E) \left(-\frac{\delta f}{\delta E}\right)$$
(4.6)

where:

$$N = N_{\text{total}} - \int_{E(0)}^{0} g(x) dx \qquad (4.7)$$

$$E_{o} = \int_{E(o)}^{o} x \cdot g(x) dx \qquad (1+.0)$$

$$\phi(E) = \int_{0}^{E} (x - E) g(x) dx \qquad (4.9)$$

In these expressions, energy is measured from the degeneracy point, and E(o) is the energy of the lowest state in the valence band. It has been assumed that $\zeta - E(o) \gg kT$. We shall be primarily interested in $\phi(E)$ for $E \leq \zeta_o \simeq .06$ ev. Since (4.4) involves the assumption that $\frac{2\xi_1^2}{\nu^2 s} \ll 1$, it is easy to see that the magnetic energy levels corresponding to the first few n values do not overlap at all. Thus, for $E < \zeta_o$, the integration in (4.9) never involves a sum over various n. Carrying out the integrals in $\phi(E)$, we find:

$$\phi(E) = qs \left\{ -(m+\frac{1}{2})E + \frac{1}{4} \sum_{\substack{n=1 \\ n < i}}^{m} (A_n + B_n + 2c_n) + \delta \right\}$$

$$= qs \left\{ -(m+\frac{1}{2})E + \frac{1}{4} \sum_{\substack{n=1 \\ n < i}}^{m} 4c_n + \delta \right\}$$

$$= qs \left\{ -(m+\frac{1}{2})E + \sum_{\substack{n=1 \\ n < i}}^{m} \mathcal{V}(ns)^{\frac{1}{2}} + \delta \right\}$$

$$(4.10)$$

where: $m = \langle r^2 \rangle = maximum integer \leq r^2 = \frac{E^2}{y^2 s}$

The term § indicates the departure from the two-dimensional model. In general this term will involve contributions from several levels, but as long as the levels do not overlap

§ will involve at most a fractional contribution from one level.

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Our expression (4.10) is in agreement with McClure's result when S = 0. We shall see that S is an unimportant correction term for the high temperature susceptibility and for the average low temperature susceptibility. However, this term does play a role in the fluctuations of the susceptibility at low temperatures, where it serves to reduce the amplitudes of the oscillations and introduces an aperiodicity when the results are plotted against the reciprocal of the magnetic field.

V. THE SHIFT OF THE FERMI LEVEL WITH TEMPERATURE.

Before we go on to calculate the susceptibility at various temperatures, we will need to know the position of the Fermi surface at these temperatures. We shall now calculate the shift of the Fermi level with temperature. The calculation will be based on a two-dimensional model. The error made in such a calculation is very small, since it is caused solely by the use of an approximate N(E) relation in the region $0 \le E \le 2\chi_1$. In general, we can have confidence in our result, provided $\zeta(T) > 2\chi_1$. As we shall see, this condition is satisfied up to a temperature of about 800° K.

The total number of electrons, N_0 , is given by:

$$N_{o} = \int_{-\infty}^{+\infty} N(E)f(E)dE = \int_{-\infty}^{\xi_{o}} N(E)dE \qquad (5.1)$$

where:

$$N(E) = \frac{4V}{\pi c (\hbar v)^2} \cdot |E|$$

Using the above density of states, one can rewrite equation (5.1) as:

$$\int_{\infty}^{\infty} E[1-f(E)] dE + \int_{\infty}^{\infty} Ef(E) dE = \frac{G_0^2}{2}$$

The integrals on the left-hand side of the above equation can be evaluated by standard methods. Here, we are interested in transforming this condition in such a way that it will be suitable for numerical evaluation.

If we make the substitution $E = (kT) \cdot x + \zeta$, our condition may be written:

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Fig. 1. The Variation of the Fermi Level with Temperature. The upper and lower curve corresponds to ς_{\bullet} .06 ev and ς_{\bullet} .055 ev respectively.

$$\frac{\zeta_{co}^{2}}{2} = kTC_{i} \left[\int_{-\infty}^{-\frac{C}{kT}} \frac{e^{-x} dx}{1+e^{-x}} + \int_{0}^{0} \frac{e^{-x} dx}{1+e^{-x}} + \int_{0}^{\infty} \frac{e^{-x} dx}{1+e^{-x}} \right] \\ + (kT)^{2} \left[\int_{-\infty}^{-\frac{C}{kT}} \frac{xe^{x} dx}{1+e^{-x}} + \int_{0}^{\infty} \frac{xe^{-x} dx}{1+e^{-x}} \right] \\ The individual integrals can now be done by expanding the integrands in a power series of exponential factors. Writing
$$\Theta = \frac{\zeta}{kT} \text{ and } \Theta_{c} = \frac{\zeta_{c}}{kT}, \text{ one finds:} \\ \Theta_{c}^{2} = 2\Theta \log \left[\frac{1+e^{\Theta}}{1+e^{-\Theta}} \right] - 3\Theta^{2} + 4 \int_{0}^{0} \log (1+e^{x}) dx$$
(5.2)$$

This expression can be approximated for large and small $oldsymbol{\Theta}$.

$$\Theta_o^2 \simeq \Theta \log 16 \qquad \Theta << 1 \quad (5.2a)$$

$$\Theta_{o}^{2} \simeq \Theta^{2} + \frac{\pi^{2}}{3} \qquad \qquad \Theta >> 1 \qquad (5.2b)$$

By choosing a value of ζ_c , one can plot ζ_c as a function of temperature using equation (5.2). This is done by giving Θ a value and solving the equation for Θ_c . If ζ_c is assumed known, this procedure yields ζ_c and the corresponding temperature T.

The results are plotted in Fig. 1 for two different values of ζ_c . The shift of the Fermi level plays an important role in the susceptibility of graphite. Without this variation of the Fermi surface one could not reconcile the high and low temperature results. It is also this shift with temperature which is primarily responsible for the observed variation of the Hall coefficient with temperature. Thus at high temperatures, one finds that the Hall coefficient approaches zero, since the Fermi level is approaching the degeneracy point and the ratio of electrons to holes is approaching unity.

The variation of the Fermi surface with temperature is often neglected in theoretical treatments of this kind. The case of graphite shows that one may not always be justified in making this approximation, and that it is precisely this variation which in graphite accounts for some of the general features of the experimental results.

VI. CALCULATION OF THE SUSCEPTIBILITY AND THE DE HAAS-VAN ALPHEN EFFECT.

The magnetic moment and the susceptibility are defined in terms of the free energy by the following relations:

$$M = -\frac{\partial F}{\partial H} \tag{6.1}$$

$$\chi = -\frac{1}{H} \frac{\partial F}{\partial H} = \frac{M}{H}$$
(6.2)

Our calculation of these quantities will thus be based on equation (1, 6) and the additional relation (3.10). The correction term δ , which is a measure of the departure from the two-dimensional model, is given by (4.11). However, this relation is far too complicated to be treated exactly. At high temperatures, this term need not be considered at all, since it does not contribute appreciably to the susceptibility. This can be seen as follows: At high temperatures the Fermi level is very near the n = 0 level (see Fig. 1). In this region the energy levels are very nearly sharp and the spacing between these levels is large. It follows that the correction term δ is defined primarily by equation (4.11b) and can thus be ignored completely. Therefore, at high temperatures the susceptibility is just equal to that calculated by McClure on the basis of a twodimensional model and is given by (cf. reference 3):

$$\chi = -.044 q v^2 \left(\frac{e}{hc}\right)^2 \frac{1}{kT} \operatorname{sech}^2 \left(\frac{\zeta}{2kT}\right)$$
(6.3)



Fig. 2. The Variation of the Susceptibility with Temperature. The dashed curve is taken from Ganguli and Krishnan. The two solid curves represent the theoretical variation of the susceptibility corresponding to ς_{\circ} =.06 ev and ς_{\circ} =.055 ev. The latter value results in slightly better agreement with experiment.

Converted to emu/gm, (6.3) becomes:

$$\chi = -\frac{010}{T} \operatorname{sech}^{2}\left(\frac{G}{2kT}\right) \quad \operatorname{emu}/\operatorname{gm} \qquad (6.4)$$

We have used 2.22 gm/cm³ for the density of graphite and we have put: $a = 2.46 A^{\circ}$; $c = 6.74 A^{\circ}$ and $\delta_{\circ} = -2.6 ev$.

The condition for the validity of this result is that the level splitting be small compared to the thermal energy; that is, $kT > > 5^{\frac{1}{2}}$. In a field of $10^{\frac{1}{4}}$ gauss, $> 5^{\frac{1}{2}} \sim .03$ ev, so that the relation (6.4) is valid at temperatures higher than about 400° K.

McClure (3) did not consider the variation of the Fermi level with temperature and simply replaced the $\operatorname{sech}^2(\frac{\zeta}{2k\tau})$ factor by one. Using the results of section V, we can now obtain the deviation of the high temperature susceptibility from an inverse T law (for temperatures higher than about 400° K). This is done simply by obtaining the value of $\frac{\zeta}{2k\tau}$ for various temperatures from Fig. 1, and substituting the result into equation (6.4). The theoretical and experimental susceptibilities are illustrated in Fig. 2.

At low temperatures there is no a priori reason why one can neglect the correction term δ . However, it will be seen that even at low temperatures the average value of the susceptibility is not affected by this term. On the other hand, the fluctuations of the susceptibility are affected. Let us for the present deal with the two-dimensional model and consider the correction later. We thus choose for $\phi(E)$:

$$\varphi(\mathbf{E}) = qs \left\{ \sum_{h=0}^{m} \mathcal{V}(ns)^{\frac{1}{2}} - (m+\frac{1}{2})\mathbf{E} \right\}$$
Here m is the maximum integer $\leq \frac{\mathbf{E}^2}{\sqrt{2}}$. The notation (6.5)

$$\frac{E^2}{\mathcal{V}^2 s} = r^2 \qquad m = \langle r^2 \rangle$$

will be convenient. We shall now evaluate the sum involved in (6.5) by the Poisson summation formula (20).

One form of this formula is:

$$\sum_{n=0}^{\infty} f(n) = \sum_{m=-\infty}^{+\infty} \int_{0}^{\infty} f(x) e^{2\pi i m x} dx$$

where: 1. f(x) is of bounded variation in the interval $(0, \infty)$

and
$$f(x) = 0$$
 for $x < 0$.
2. $\int_{f(x)dx}^{\infty} exists$

3. f(x) is continuous at least near the points where x is an integer; i.e. $\frac{1}{2} \left[f(n_+) + f(n_-) \right] = f(n)$

We see how we have to define f(x) in our case. Let us introduce the step function P(x) defined by:

> $P(x) = 1 x \le 0$ P(x) = 0 x > 0

Then we may define f(x) to be the function:

$$f(x) = x^{\frac{1}{2}} \cdot P(-x) \cdot P(x-r^2)$$
 (6.6)

With this definition one clearly has:

$$\sum_{n=0}^{m} n^{\frac{1}{2}} = \sum_{n=0}^{\infty} f(n)$$
 (6.7)

Just exactly where we "chop" the function between $\langle r^2 \rangle$ and $\langle r^2 \rangle$ +1 is immaterial. By choosing the point to be r^2 we know that our result is exact provided r^2 is not an integer.

In that case the continuity condition is not satisfied, but this clearly does not matter since these points coincide with the points of discontinuity of our original sum.

In this way we find:

$$\sum_{h=0}^{m} n^{\frac{1}{2}} = \sum_{m=-\infty}^{+\infty} \int_{0}^{n^{2}} x^{\frac{1}{2}} e^{2\pi i m x} dx$$

= $\frac{2}{3}r^{3} + r \sum_{m=1}^{\infty} \frac{\sin(2\pi m r^{2})}{\pi m} - \frac{1}{2\pi} \sum_{m=1}^{\infty} m^{\frac{3}{2}} S(2rm^{\frac{1}{2}})$ (6.8)

where:

$$S(\varphi) = \int_{2}^{1} \sin\left(\frac{\pi}{2}t^{2}\right) dt$$

We can now substitute (6.8) into (6.5). The result is:

$$\Phi(E) = q v_{S}^{3/2} \left\{ -\frac{1}{3}r^{3} - \frac{1}{2\pi} \sum_{m=1}^{\infty} m^{3/2} S(2rm^{1/2}) \right\}$$
(6.9)

In the above substitution, we have made use of the relation

$$\sum_{m=1}^{\infty} \frac{\sin\left(2\pi m r^2\right)}{\pi m} = \langle r^2 \rangle + \frac{1}{2} - r^2 \quad ; \quad \langle r^2 \rangle < r^2 < \langle r^2 \rangle + 1$$

Equation (6.9) is exact. For large energies $r \rightarrow \infty$, and

$$S(2rm^{k_2}) \longrightarrow S(\infty) = \frac{1}{2}$$

Thus in the limit of large energies, (6.9) becomes:

$$\phi(\epsilon) \simeq q v s^{\frac{3}{2}} \left[-\frac{1}{3} r^{3} - \frac{1}{4\pi} \zeta(\frac{3}{2}) \right]$$

$$\simeq q v s^{\frac{3}{2}} \left[-\frac{1}{3} r^{3} - .208 \right] \qquad (6.10)$$

Here ζ is the Riemann Zeta-function.

The above result agrees with McClure's equation (3.9). We note that of the two terms in equation (6.10), the first is independent of the magnetic field and the second is independent of the energy. Hence the first term does not contribute to the susceptibility. One can easily verify that the term independent of the energy just cancels that part of E_0 which depends upon the magnetic field when this term is integrated in (4.6) Again following McClure, we write:

$$\psi(E) = \phi(E) + \frac{1}{3}q \frac{E^3}{y^2} + .208qys^{\frac{3}{2}}$$
(6.11)

Neglecting the field dependence of ${\boldsymbol{\varsigma}}$, the susceptibility is then given by:

$$\chi = \frac{-1}{H} \frac{\partial F}{\partial H} = \frac{-1}{H} \frac{\partial}{\partial H} (F - N\zeta) = \frac{-1}{H} \frac{\partial}{\partial H} \int_{-\infty}^{+\infty} \psi(E) \left(-\frac{\partial F}{\partial E}\right) dE \quad (6.12)$$

Since we are interested only in very low temperatures for the present, (6.12) simply becomes:

$$\chi = -\frac{1}{H} \frac{\partial}{\partial H} \psi(\zeta_{c})$$
(6.13)

Here, $\psi(\mathbf{E})$ is given by equation (6.11). We now anticipate where the Fermi surface will lie at low temperatures. This information can be obtained for instance, from the Hall effect. Thus our A, the zero field Hall coefficient, will show that $\zeta_{\circ} \simeq .06$ ev. Another independent estimate can be obtained from the period of the de Haas-Van Alphen effect fluctuations (cf. reference 3). Again we find $\zeta_{\circ} \simeq .06$ ev. Thus in fields of the order of 10^{14} gauss, $\mathbf{r} \simeq 2$. We shall now expand $\psi(\mathbf{E})$ asymptotically for large r. This asymptotic form of $\psi(\mathbf{E})$ will be completely adequate at $\mathbf{E} = \zeta_{\circ}$. We now proceed to expand $S(2r\sqrt{m})$ asymptotically using the method of integration by parts. Thus:

$$S(2rm^{\frac{1}{2}}) = \int_{0}^{2rm^{\frac{1}{2}}} \sin(\frac{\pi}{2}z^{2}) dz$$

= $\frac{1}{2} - \int_{0}^{\infty} \sin(\frac{\pi}{2}z^{2}) dz$
 $2rm^{\frac{1}{2}}$
 $\simeq \frac{1}{2} - \frac{1}{2\pi} \cdot \frac{\cos(2\pi mr^{2})}{(2\pi mr^{2})^{\frac{1}{2}}}$

When this result is substituted into (6.11) one finds:

$$\psi(E) \simeq q v s^{3/2} \left[\frac{1}{4\pi^2 r} \sum_{m=1}^{\infty} \frac{\cos(2\pi m r^2)}{m^2} \right]$$
 (6.14)

It may be verified by actual numerical computation that $\Psi(E)$ as given by (6.14) differs from the exact $\Psi(E)$ defined by (6.11) and (6.5) by less than one percent when $r \gtrsim \frac{1}{2}$. Hence we are completely justified in using (6.14) at low temperatures, even in very large magnetic fields.

The magnetic moment and the susceptibility are now easily evaluated at low temperatures. Making use of the relation

 $\sum_{m=1}^{\infty} \frac{\cos(2\pi mr^2)}{\pi^2 m^2} = \frac{1}{6} + \left[r^2 \langle r^2 \rangle \right] \left[r^2 - \langle r^2 \rangle - 1\right]; \quad \langle r^2 \rangle < r^2 < \langle r^2 \rangle + 1$ we find, using equations (6.1), (6.13) and (6.14):

$$M = -\frac{q\zeta_{o}}{12} \left(\frac{e}{\hbar c}\right) r_{o}^{-2} - \frac{q\zeta_{o}}{2} \left(\frac{e}{\hbar c}\right) \left[\frac{\langle r_{o}^{2} \rangle}{r_{o}^{2}} \left(1 + \langle r_{o}^{2} \rangle\right) - \langle r_{o}^{2} \rangle - \frac{1}{2}\right] \quad (6.15)$$

The first factor in this relation is proportional to the magnetic field and yields the average value of the magnetic moment. The second factor, when plotted against the magnetic



Fig. 3. Plot of the Oscillatory Part of the Magnetic Moment as a function of the Magnetic Field. The curve is based on a two-dimensional model.



field, oscillates about zero. The oscillatory part of the magnetic moment is plotted against $r_0^{-2} = \frac{y^2 s}{\zeta_0^2}$ in Fig. 3. The observed behaviour is characteristic of a two-dimensional calculation and should be compared with the results of Seitz (21) for free electrons. The susceptibility resulting from (6.15) is thus:

$$\chi = -\frac{q\nu^2}{i2\zeta_c} \left(\frac{e}{\hbar c}\right)^2 - \frac{q\nu^2}{2\zeta_c} \left(\frac{e}{\hbar c}\right)^2 \left\{ \langle r_c^2 \rangle \left[i + \langle r_c^2 \rangle \right] - r_c^2 \left[\frac{1}{2} + \langle r_c^2 \rangle \right] \right\}$$
(6.16)

The first factor is independent of the magnetic field and yields the average value of the susceptibility at low temperatures. The second factor in (6.16) is periodic in H^{-1} with period $\frac{e}{h_c} \cdot \frac{y^2}{\zeta_c^2}$. A plot of the oscillatory part of (6.16) is given in Fig. 4. Converting the quantities in (6.16) to emu/gm, we find that the first factor leads to:

$$\chi_{av} = \frac{-qv^2}{12\zeta_o} \left(\frac{e}{h_c}\right)^2 \simeq -27.2 \times 10^{-6} \, \text{emu/gm} \tag{6.17}$$

We have chosen $\zeta_{e} = .06$ ev. In order that the period of our oscillations agree with the experimental period of 2.15×10^{-5} gauss⁻¹ we require $\zeta_{e} \simeq .065$ ev. On the other hand, the theoretical amplitude of the susceptibility oscillations is approximately 300 x 10^{-6} emu/gm in a field of 10^{4} gauss. The experimentally observed amplitude is only 2 - 3 x 10^{-6} emu/gm. This discrepancy between theory and experiment will be discussed later.

The average value of the low temperature susceptibility is in good agreement with the experimental value of -30 x 10⁻⁶ emu/gm (1). The experimental value tends to vary from crystal to crystal, the range being about -28 x 10⁻⁶ emu/gm to -34 x 10⁻⁶ emu/gm. Such a variation is easily interpreted within our model, since the exact position of the Fermi level is determined by impurities and the size of the crystal. Equation (6.17) allows one to predict qualitatively, the dependence of the susceptibility on crystal size. Because large crystals have a smaller number of excess electrons per atom, ζ_{c} will be somewhat smaller for these crystals and hence large crystals will have a larger susceptibility than smaller crystals.

Lifschitz and Kosevich (12) have developed a semiclassical theory of susceptibility. If their results are applied to graphite, one finds a period for the susceptibility oscillations which is in agreement with our result. The oscillation amplitudes, however, are infinite in their approximation. We shall return to their treatment when we consider the introduction of the third dimension into our problem.

Before we go on to consider these three-dimensional effects, we shall calculate the temperature variation of the average susceptibility at low temperatures. We have already seen that at high temperatures the susceptibility is given by (6.4). In calculating the temperature dependence of the susceptibility at low temperatures, we shall not be interested in the oscillatory part of the susceptibility, since these

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oscillations are observable only at very low temperatures $(T \sim 4^{\circ}K)$, because of temperature damping (cf. reference 12). Hence we shall retain only that part of $\Psi(E)$ which gives rise to the part of the magnetic moment which is proportional to H. In this case $\Psi(E)$ simply becomes:

$$\psi(E) = \frac{1}{24} \frac{q \nu^2 s^2}{E}$$
(6.18)

Actually $\psi(E)$ is a symmetric function of E, so that E should be replaced by |E| (cf. reference 3). However, at low temperatures the contribution to χ from the E < 0 region is completely negligible because of the position of the Fermi level at these temperatures. Using (6.18) the expression (6.12) for the susceptibility becomes:

$$\begin{aligned} \chi &= \frac{-1}{48} \frac{qy^2}{kT} \left(\frac{e}{\pi c}\right)^2 \int_{-\infty}^{\infty} \frac{dE}{lEl} \operatorname{Sech}^2 \left(\frac{\zeta - E}{2kT}\right) \\
&\simeq \frac{-1}{48} \frac{qy^2}{kT} \left(\frac{e}{\pi c}\right)^2 \int_{-\infty}^{\infty} \frac{dE}{E} \operatorname{Sech}^2 \left(\frac{\zeta - E}{2kT}\right)
\end{aligned}$$
(6.19)

The integral in (6.19) is easily evaluated approximately in terms of a power series in kT. The method is the same as that used for evaluating the integrals in equation (5.1) of section V. Upon evaluation one finds:

$$\chi \simeq \frac{-1}{12} q r^2 \left(\frac{e}{hc}\right)^2 \frac{1}{G} \left[1 - \frac{kT}{G} \log 2\right]$$
(6.20)

Converted to emu/gm, equation (6.20) becomes:

$$\chi \simeq \frac{-1.63 \times 10^{-6}}{\zeta} \left[1 - \frac{kT}{\zeta} \log 2 \right] \text{ emu/gm} \qquad (6.21)$$

where ζ and kT must be measured in ev. The result, together

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with the variation at high temperatures, is plotted in Fig. 2. Because of the method of evaluation, the expressions (6.20) and (6.21) are valid only if kT $\langle \zeta \rangle$. In Fig. 2, these expressions have been used to obtain the theoretical curves at temperatures below 200°K. Above 400°K the curves are based on equations (6.3) and (6.4), and between 200°K and 400°K the high and low temperature curves have been joined by the best-fitting smooth curve. Fig. 2 shows that $\zeta_{\circ} \propto .055$ ev results in a slightly better fit to the experimental curve. However, the uncertainties of the measurements are such that the curve with $\zeta_{\circ} \propto .06$ ev cannot be excluded. Thus the experimental measurements determine ζ_{\circ} to within about 10%.

We have seen that a two-dimensional model of graphite is capable of explaining all the features of the susceptibility except the amplitude of the oscillations at very low temperatures, which turn out to be 100-150 times too large. There are three main factors which serve to reduce this amplitude. These are:

- Introduction of k_Z-dependence by a three-dimensional model. This has the effect of broadening the energy levels in the presence of a magnetic field and hence reduces the amplitude of the susceptibility fluctuations.
- 2. Temperature damping of the oscillations at temperatures for which the thermal energy becomes of the order of or greater than the mean level spacing.

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3. Collision damping of the oscillations. The effect of collisions is also to broaden the energy levels by an amount $\sim \frac{\pi}{2}$, where τ is the relaxation time for electrons whose energies lie near the Fermi energy.

The last two of these factors are unimportant at very low temperatures. We shall see later that the relaxation time in graphite at such temperatures is of the order of 10^{-11} seconds. If one uses this value for \sim , and estimates the collision damping factor in the manner of Dingle (22), one finds that the amplitudes are only reduced by about 5% through the collision process. Similarly, temperature damping can be made arbitrarily unimportant by going to sufficiently low temperatures. We shall now study the three-dimensional model of graphite, in order to attempt to find an explanation of the discrepancy between the observed and the previously calculated amplitudes of the susceptibility fluctuations.

It is interesting to apply the theory of Onsager (23) and of Lifschitz and Kosevich (12) to graphite. As we shall see, their theory, together with the usually assumed band structure, affords a very nice picture for the origin of the two periodicities in the de Haas-Van Alphen effect of graphite. Unfortunately, since their approach is based on Bohr-Sommerfeld quantization, one cannot have faith in their results when the theory is applied to graphite. Such an approach can in general only be trusted when the E(k)relationship is quadratic, as in the case of free electrons.

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Fig. 5. The Nature of the Energy Surfaces in Graphite. Two Brillouin Zones are shown. Actually 1/3 of the surfaces shown lies at each corner of the zone, resulting in a two-fold degeneracy of the illustrated surfaces, which have been pieced together for clarity. We shall find important differences between such a semiclassical treatment and a treatment based on the results of sections I and II of this thesis. Let us first outline the semi-classical approach.

The $E(\vec{k})$ relation near the corner of the Brillouin zone is given in A as:

$$E(\vec{k}) = -\aleph_{1}\cos(\frac{k_{z}c}{2}) \pm \left[\aleph_{1}^{2}\cos^{2}(\frac{k_{z}c}{2}) + (\hbar \vee K)^{2}\right]^{\frac{1}{2}}$$
(6.22)

As before, $K = (k_X^2 + k_y^2)^{\frac{1}{2}}$ is measured from the corner of the zone, while k_z is measured from the half-way point on the vertical edge. The surfaces of constant energy described by (6.22) are illustrated in Fig. 5. When $E < 2X_i$ the surfaces are closed and capsule-shaped with the long axis of the capsule parallel to the vertical edge of the zone. However, for $E > 2X_i$ the surfaces are open at the upper and lower ends of the zone, so that if all zones are considered, the surfaces become endless tubes of variable cross-section.

Now consider a magnetic field applied along the c-axis in graphite. In the actual graphite crystal, the electrons will then move in helical orbits, the axis of the helix being along the direction of the magnetic field. It follows from the Lorentz equation that k_z is a constant of the motion for an electron in one of these orbits. Such an electron thus moves in an orbit in k-space which is the intersection of a constant energy surface with the plane $k_z = \text{constant}$. In the theory of Lifschitz and Kosevich (12), the periods of the susceptibility oscillations are then determined by the extreme cross-sectional areas of the planes $k_z = \text{constant}$ with the surface of constant energy for $E = \zeta_{\circ}$. It is clear that two different periodicities can result only if $\zeta_{\circ} > 2\chi_{1}$, since otherwise the minimum cross-sectional area is zero and gives no periodicity. The extremal areas in question are the shaded areas in Fig. 5.

Applying the theory of Lifschitz and Kosevich (12) to equation (6.22) we find:

$$S(E, k_z) = \frac{\pi E\left[E + 2\aleph_1 \cos \frac{\kappa_z c}{2}\right]}{(\pi_v)^2} = 2\pi (n+\varkappa) S ; E > 2\aleph_1 (6.23)$$

Here $S(E,k_Z)$ is the cross-sectional area of the plane k_Z = constant with the surface of constant energy corresponding to energy E. The maximum and minimum areas in question are thus:

$$S_{ext}(\zeta_{c}) = \frac{\pi \zeta_{c} [\zeta_{c} [\zeta_{o} \pm 2\aleph_{i}]}{(\hbar \nu)^{2}} ; \zeta_{o} > 2\aleph_{i} \qquad (6.24)$$

It is interesting to note that (6.23) predicts the energy spectrum in the presence of a magnetic field. Solving (6.23) for $E(n,H,k_z)$ we find:

$$E(n, H, k_z) = -\delta_1 \cos(\frac{k_z c}{2}) \pm \left[\lambda_1^2 \cos^2(\frac{k_z c}{2}) + y^2 \sin(n+y) \right]^{1/2}$$
(6.25)

When $X_1 = 0$ this relation agrees with our result for the two-dimensional spectrum, provided the parameter X is chosen to be zero. However, if $X_1 \neq 0$, the above energy spectrum

is radically different from that found in section II (cf. equation 2.8). When \aleph_i is small, (6.25) predicts a width of $\sim 2\aleph_i$ for the higher n levels, independently of the magnetic field, while in our treatment the level width increases with n and depends on the magnetic field. We shall see later how this difference affects the de Haas-Van Alphen effect.

Since in the semi-classical treatment the periods of the susceptibility oscillations are completely determined by the two values of $S_{ext}(\zeta_o)$, a knowledge of the two periods completely determines ζ_c and χ_i in this approximation. Using the formulae of Lifschitz and Kosevich (12) and the experimental periods (9,10) one finds:

 $\zeta_{\circ} \simeq .065 \text{ ev}$ and $\frac{\zeta_{\circ}}{\gamma_{1}} \simeq 14$

The amplitudes of the oscillations may also be determined by an application of the results of reference (12). At $T = 1.37^{\circ}K$ an evaluation yields approximately 20 x 10^{-6} emu/gm for the amplitudes in a field of 10^{4} gauss. This is a factor of about 10 larger than the observed amplitudes (9,10).

An exact calculation of the three-dimensional de Haas-Van Alphen effect is impractical because of the complex nature of the correction term δ in equation (4.10). We can however construct a simplified model by noting how the density of states varies within the nth level. Note that this density function is highly peaked at the extremes and at the center of the nth level. We shall replace $g(E_n)$ defined by (4.5a) and (4.5b) by the simpler relation:

$$g(E_n) = qs \left\{ \frac{1}{4} \delta(E - A_n) + \frac{1}{4} \delta(E - B_n) + \frac{1}{2} \delta(E - C_n) \right\} \quad (6.26)$$

It is easily checked that this expression gives the correct degeneracy for the nth level, namely qs.

If (6.26) is used in place of (4.5a) and (4.5b), the correction term δ can be shown to be:

$$\delta = \frac{95}{4} \left[(2m - m' - m'') + \sum_{m}^{m'} A_{n} + \sum_{m''}^{m} B_{n} \right]$$
(6.27)

where: $m = \langle r^2 \rangle$

$$m' = \left\langle r^{2} (1 - \Delta)^{-2} \right\rangle \qquad \Delta = \frac{2 \chi_{1}^{2}}{\nu^{2} S}$$
$$m'' = \left\langle r^{2} (1 + \Delta)^{-2} \right\rangle$$

It is a straightforward matter to calculate the contribution of (6.27) to the low temperature susceptibility. The calculation is completely analogous to the two-dimensional model calculation carried out earlier. In calculating the derivative with respect to H, it is not necessary to differentiate the various $(1 \pm \Delta)$ factors, since these vary very slowly with H. The result is that to the oscillatory part of χ from (6.16) one must add the following term:

$$-\frac{q_{\nu}^{2}}{8\zeta_{o}}\left(\frac{e}{\hbar_{c}}\right)^{2}\left\{r_{o}^{2}\left[2\langle r_{o}^{2}\rangle-\left\langle\frac{r_{o}^{2}}{(1+\Delta)^{2}}\right\rangle-\left\langle\frac{r_{o}^{2}}{(1-\Delta)^{2}}\right\rangle\right]-2\langle r_{o}^{2}\rangle^{2}+(1+\Delta)^{2}\left\langle\frac{r_{o}^{2}}{(1+\Delta)^{2}}\right\rangle^{2}\right\}$$
$$+(1-\Delta)^{2}\left\langle\frac{r_{o}^{2}}{(1-\Delta)^{2}}\right\rangle^{2}-2\langle r_{o}^{2}\rangle+(1+\Delta)^{2}\left\langle\frac{r_{o}^{2}}{(1+\Delta)^{2}}\right\rangle+(1-\Delta)^{2}\left\langle\frac{r_{o}^{2}}{(1-\Delta)^{2}}\right\rangle\right\} \quad (6.26)$$



Fig. 6. The De Haas-Van Alphen Effect in three-dimensional Graphite.

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effect in graphite, as calculated from this simplified threedimensional model. In the plot of Fig. 6, Δ has been chosen to be .014 r_0^2 , which corresponds to $Y_1 \simeq .005$ ev and $\zeta_2 \simeq .06$ ev. It can be seen that the simple periodicity in H-1 has been destroyed. Semi-classically this pattern was interpreted in terms of two slightly different periods, both however, strictly periodic in H⁻¹. Note that the amplitudes have been reduced by a factor of about two in a field of 10⁴ gauss (which corresponds to $r_0^2 \simeq 4$). They are, however, still far too large to be in agreement with experiment.

The detailed features of Fig. 6 are not to be interpreted too closely, since they are partly due to our simplifying assumption about $g(E_n)$. Furthermore, we have completely neglected temperature and collision damping effects, which would tend to smear out the features of Fig. 6. Thus in comparison with experiment one would need to replace the discontinuous plot of Fig. 6 by some sort of average smooth curve. It is mainly intended to be shown here that an interference effect of roughly the right periodicity is obtained, even from a crudely oversimplified three-dimensional model.

Perhaps the most significant thing in the three-dimensional calculation is the behaviour of the oscillations in very large magnetic fields $(r_0^2 < 1)$. Our calculation indicates that in these fields graphite will not display what looks like two different periods. Instead, the oscillations will

be strictly periodic in H⁻¹ the period being just that predicted by the two-dimensional model. The semi-classical treatment on the other hand, predicts two periods regardless of the magnitude of the magnetic field. This result is independent of our simplifying assumptions and follows directly from the fact that the energy levels become sharp in very large magnetic fields (cf. equation 2.8).

It seems possible that this difference could be investigated experimentally by the recently developed pulsed field technique. A careful analysis of the oscillations may be required, since the difference between these two predictions is not apparent on every half-cycle. VII. THE ELECTRICAL CONDUCTIVITIES OF GRAPHITE.

Let us now evaluate the electrical conductivity of graphite parallel and perpendicular to the graphite planes. We shall assume that the relaxation time \mathcal{T} does not depend significantly on \vec{k} .

Following the theory in A, we write for the conductivity in the direction of the unit vector \vec{u} :

$$\sigma(\vec{u}) = \frac{-2e^2\tau}{h^2} \int \frac{df_o}{dE} \left[\int (\vec{u} \cdot \vec{n})^2 \cdot |g_{rad_k}E| \cdot dS_k \right] dE \qquad (7.1)$$

The inner integral in (7.1) is taken over a surface of constant energy, and $\vec{n} \cdot dS_k$ is the vector element of area on this surface.

For our $\vec{E(k)}$ relation we shall use equation (6.22), which is valid provided $\vec{E} \ll \delta_0 = 2.6$ ev. (cf. reference A).

The integral in (7.1) is easily transformed intó an integral over K and an integral over E, by projecting the surface of constant energy onto the plane $k_z = 0$. A factor of 4 is introduced because of the equivalence of the six corners of the Brillouin zone, and because of the two projections onto the plane $k_z = 0$ coming from above and below this plane.

When \overline{u} is chosen in the graphite plane and perpendicular to it, we find respectively:

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$$\sigma_{\rm L} = \frac{-2e^2\tau}{2\pi h^2} \int \frac{df_o}{dE} \left[\int \left| \frac{\partial E}{\partial k_z} \right| \cdot 6\pi \, \text{KdK} \right] dE \qquad (7.3)$$

Before the inner integrals can be evaluated, we must evaluate $\frac{\partial E}{\partial k}$ and $\left|\frac{\partial E}{\partial k_z}\right|$ from equation (6.22) in such a way that k_z is eliminated from these expressions. One finds:

$$\frac{\partial E}{\partial K} = \pm \frac{2(\hbar v)^2 E \cdot K}{E^2 + (\hbar v K)^2}$$
(7.4)

$$\frac{\partial E}{\partial k_z} = \pm \frac{cE}{2} \cdot \frac{\left[4E^2 \chi_1^2 - (E^2 - [\pi \vee K]^2)^2\right]^2}{E^2 + (\pi \vee K)^2}$$
(7.5)

Let us now look at the range of the inner integrals in (7.2) and (7.3). As long as we are dealing with low temperatures, $\frac{df_{c}}{dE}$ will be a sharply peaked function at $E = \zeta_{c}$, and we know that $\zeta_{c} \gg 2\aleph_{1}$. From (6.22) it follows that the surfaces of constant energy for $E > 2\aleph_{1}$ are open, endless tubes of variable cross-section. Hence the range of K is:

$$\frac{1}{\pi \sqrt{1}} \left[E^2 - 2x_i E \right]^{\frac{1}{2}} \leq K \leq \frac{1}{\pi \sqrt{1}} \left[E^2 + 2x_i E \right]^{\frac{1}{2}} ; E > 2x_i$$

However, for higher temperatures $\frac{df_c}{dE}$ is not sufficiently peaked to exclude contributions to the conductivity from $E < 2 \aleph_1$. We then write:

$$-\frac{2\pi h^{2}\sigma_{1}}{e^{2}\tau} = \int_{\infty}^{-2\varkappa_{1}} f_{0}^{\prime}C_{1} dE + \int_{0}^{0} f_{0}^{\prime}C_{2} dE + \int_{0}^{2\varkappa_{1}} f_{0}^{\prime}C_{3} dE + \int_{0}^{0} f_{0}^{\prime}C_{4} dE$$
(7.6)

$$\frac{-2\pi h^2 \sigma_1}{2e^2 c} = \int_{-\infty}^{-2\delta_1} f_c' D_i dE + \int_{-2\delta_1}^{0} f_c' D_2 dE + \int_{0}^{2\delta_1} f_c' D_3 dE + \int_{0}^{\infty} f_c' D_4 dE \qquad (7.7)$$

where $C_{\kappa}(E)$ and $D_{\kappa}(E)$ stand for the inner integrals in (7.2) and (7.3) respectively, with the proper range of integration

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substituted in each case. Thus in $C_1(E)$, $C_4(E)$, $D_1(E)$ and $D_4(E)$ the range of K is the same as that used at very low temperatures, while in $C_2(E)$, $C_3(E)$, $D_2(E)$ and $D_3(E)$ the range of K is:

$$0 \leq K \leq \frac{i}{\hbar v} \left[E^2 + 2 \varepsilon_i E \right]^{1/2}; \quad E < 2 \varepsilon_i$$

Because of the simplification of (7.6) and (7.7) at very low temperatures, the zero temperatures conductivities are easily evaluated. Using equations (7.4), (7.5) and the defining relations (7.2) and (7.3) one finds at zero temperature:

$$\sigma_{ii}(0) = \frac{8\pi e^2 \tau}{h^2 c} \cdot \zeta_0 \qquad (7.8)$$

$$\sigma_{\perp}(0) = \frac{2\pi e^2 \tau}{h^2 c} \cdot \frac{\xi_1^2 c^2}{(\pi v)^2} \cdot \zeta_0$$
(7.9)

And hence:

$$\frac{\sigma_{ii}(0)}{\sigma_{i}(0)} = \frac{4(\pi_{V})^{2}}{\chi_{i}^{2} c^{2}}$$
(7.10)

With a = 2.46 A° ; c = 6.74 A° , δ_c = 2.5 ev and δ_i = .005 ev, one finds:

$$\frac{\overline{\sigma_{1}}(0)}{\overline{\sigma_{1}}(0)} = 10^{5} \tag{7.11}$$

Krishnan and Ganguli (14) have found a ratio of about 10^5 experimentally. Dutta (15) reports a ratio of 10^4 - 10^5 , while Primak and Fuchs (16) report a considerably lower ratio. The experiment is however a difficult one, and it is easy, because of the large anisotropy, to underestimate the ratio of $\frac{\sigma_{11}}{\sigma_{1}}$, while it seems impossible to obtain too large a value in any experiment. This was pointed out by Prozowski (13).

We now proceed to the evaluation of the ratio of the two principal conductivities for arbitrary temperature. The inner integrals in equations (7.6) and (7.7) can all be evaluated analytically. The procedure is somewhat lengthy but completely straightforward and will not be given here. Because of the analytic form of the integrands, it is necessary to split the range of integration not only at $2\gamma_i$ but also at γ_i . The final results can be written in the following form:

$$\sigma_{\parallel}(\tau) = \frac{4e^{2}\tau}{h^{2}} \cdot \frac{\chi_{i}^{2}}{c(kT)} \int_{-\infty}^{+\infty} \operatorname{sech}^{2}\left(\frac{x-\xi/\chi_{i}}{\frac{2kT}{\chi_{i}}}\right) \cdot F(x) \, dx \qquad (7.12)$$

where:

$$= \times \left\{ \frac{\pi}{2} + \sin^{-1}(\frac{x}{2}) - \frac{x}{2[x^{2} - i]^{\frac{1}{2}}} \cdot \left[\frac{\pi}{2} - \sin^{-1}(\frac{2 - x^{2}}{x}) \right] \right\} \qquad 1 \le x \le 2$$
$$= \times \left\{ \pi - \frac{\pi}{2} \frac{x}{[x^{2} - i]^{\frac{1}{2}}} \right\} \qquad x \ge 2$$

(F(x) is symmetric about x = 0.)

$$\sigma_{\perp}(\tau) = \frac{e^2 \tau c}{2 h^2} \cdot \frac{\chi_1^4}{(kT)(\pi v)^2} \int_{-\infty}^{+\infty} \operatorname{sech}^2 \left(\frac{x - \frac{5}{5} g_1}{\frac{2kT}{y_1}} \right) \cdot G(x) dx \quad (7.13)$$

where:

$$\begin{aligned} G(x) &= x^{2} \left\{ -(4 - x^{2})^{\frac{1}{2}} + 2x \left[\frac{\pi}{2} + \sin^{-1} \left(\frac{x}{2} \right) \right] + 2(1 - x^{2})^{\frac{1}{2}} \log \left[\left(\frac{(4 - x^{2})^{\frac{1}{2}} + 2 - x^{2}}{x} \right] \right] \right\} & 0 \le x \le 1 \\ &= \frac{4\pi}{3} - \sqrt{3} & x = 1 \\ &= x^{2} \left\{ -(4 - x^{2})^{\frac{1}{2}} + 2x \left[\frac{\pi}{2} + \sin^{-1} \left(\frac{x}{2} \right) \right] - 2(x^{2} - 1)^{\frac{1}{2}} \left[\frac{\pi}{2} - \sin^{-1} \left(\frac{2 - x^{2}}{x} \right) \right] \right\} & 1 \le x \le 2 \\ &= x^{2} \left\{ 2\pi x - 2\pi (x^{2} - 1)^{\frac{1}{2}} \right\} & x \ge 2 \\ & (G(x) \text{ is symmetric about } x = 0.) \end{aligned}$$

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Equations (7.12) and (7.13) can now be evaluated numerically for any temperature. This is done as follows: F(x)and G(x) are evaluated once and for all, for the entire range of x required (this range is about: -70 < x < 70 at 600° K). Throughout, Y_1 is chosen to be .005 ev. Then T and $\zeta (T)$ are chosen (the latter from Fig. 1) and the integrals can be evaluated by any of the standard approximate methods. The numerical values for these integrals at various temperatures are tabulated in Table 1 below. The third integral tabulated here does not appear in the conductivity theory but occurs later, when we consider the Hall effect.

	100°K	200 ⁰ K	300°K	⁷⁺⁰⁰ 0 ^K	500 ⁰ К	600°K
¥	149	273	400	575	790	1110
Ĝ	304	5 55	815	1170	1610	2260
K	23.4	41.2	46.5	41.8	37.5	34.3

Table 1. Numerical values of the various integrals in the conductivity and Hall effect of Graphite.

The notation in Table 1 is as follows:

$$\mathcal{F} = \int_{-\infty}^{+\infty} \operatorname{Sech}^{2} \left(\frac{x - \frac{\zeta_{g_{1}}}{2KT}}{\frac{2KT}{y_{1}}} \right) \cdot F(x) dx$$

$$\mathcal{F} = \int_{-\infty}^{+\infty} \operatorname{Sech}^{2} \left(\frac{x - \frac{\zeta_{g_{1}}}{2KT}}{\frac{2KT}{y_{1}}} \right) \cdot G(x) dx$$

$$\mathcal{K} = \int_{-\infty}^{+\infty} \operatorname{Sech}^{2} \left(\frac{x - \frac{\zeta_{g_{1}}}{2KT}}{\frac{2KT}{y_{1}}} \right) \cdot K(x) dx$$

(The function K(x) appears in section VIII which deals with the Hall effect.)

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When the numerical values in Table 1 are substituted into equations (7.12) and (7.13) one finds that the ratio $\frac{\nabla n}{\sigma_{\perp}}$ is almost independent of temperature between 0°K and 600°K. Thus:

$$\frac{\overline{\sigma_{1}(T)}}{\overline{\sigma_{1}(T)}} \simeq \frac{\overline{\sigma_{1}(0)}}{\overline{\sigma_{1}(0)}} = 10^{5}$$
(7.14)

Experimentally, Dutta reports a variation by a factor of 2 over this temperature range (15).

Thus, our results show that $\sigma_{\overline{n}}$ and $\sigma_{\underline{1}}$ exhibit the same temperature dependence (within 1 or 2%). Agreement with experiment could of course be obtained by attributing <u>different</u> temperature dependences to the two relaxation times parallel and perpendicular to the graphite planes.

However, such an assignment implies that $\boldsymbol{\tau}$ is $\mathbf{\hat{k}}$ -dependent and thus violates our original assumption. It is reasonable to assume that in graphite, the relaxation time is indeed a markedly anisotropic function of $\mathbf{\hat{k}}$. Until more is known about this quantity it does not seem profitable to extend this simple calculation.

An approximation, which is sometimes made is the following: one assumes that the relaxation time \mathcal{T} depends on \overline{k} , but only through the energy; that is, one assumes $\mathcal{T} - \mathcal{T}(E)$. In this case, \mathcal{T} factors outside the inner integrals in equations (7.2) and (7.3), since these are integrals over surfaces of constant energy and hence of constant \mathcal{T} . Then, at low temperatures, the ratio of $\frac{\sigma_{ii}}{\sigma_{i}}$ is independent of

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 τ , since the outer integrations in equations (7.2) and (7.3) will involve a δ -function. At higher temperatures, the ratio $\frac{\sigma_{h}}{\sigma_{1}}$ will however still depend slightly on τ , even in this approximation.

We conclude that the low temperature value of $\frac{\sigma_{ii}}{\sigma_L}$ predicted by our choice of ζ_0 , ζ_1 and ζ_2 is in good agreement with experiment. It is interesting to note that the ratio

 $\frac{\sigma_{n}(o)}{\sigma_{1}(o)}$ does not depend explicitly on ζ_{o} . However, this ratio does depend on the assumption that $\zeta_{o} > 2 \mathscr{C}_{1}$, since this condition determines the range of the K-integration. At higher temperatures, our calculation becomes doubtful because of the simplifying assumptions about the relaxation time. Thus, conductivity data does not violate our choice of the parameters \mathscr{C}_{o} , \mathscr{C}_{1} and ζ_{o} .

VILL. THE HALL COEFFICIENT OF GRAPHITE.

We shall now evaluate the zero field Hall coefficient of graphite. We shall make use of the same approximation as we used in calculating the ratio of the principal conductivities, namely that the relaxation time is assumed to be independent of \vec{k} .

When a magnetic field is applied along the z-axis (the c-axis in the case of graphite), the general formula for the zero field Hall coefficient is (24):

$$A_{\mu+0} = \frac{-8\pi^{3}}{2e} \frac{\int \frac{\partial E}{\partial k_{y}} \left[\frac{\partial E}{\partial k_{y}} \left(\frac{\partial^{2} E}{\partial k_{x}^{2}} \right) - \frac{\partial E}{\partial k_{x}} \left(\frac{\partial^{2} E}{\partial k_{x} \partial k_{y}} \right) \right] \frac{df_{0}}{dE} d^{3}k}{\int \left(\frac{\partial E}{\partial k_{x}} \right)^{2} \frac{df_{0}}{dE} d^{3}k} \cdot \int \left(\frac{\partial E}{\partial k_{y}} \right)^{2} \frac{df_{0}}{dE} d^{3}k}{dE}$$
(8.1)

Using the $E(\vec{k})$ relation given by equation (6.22), one can express $\frac{\partial E}{\partial k_x}$, $\frac{\partial E}{\partial k_y}$, $\frac{\partial^2 E}{\partial k_x^2}$, $\frac{\partial^2 E}{\partial k_y^2}$ and $\frac{\partial^2 E}{\partial k_x \partial k_y}$ in terms of cylindrical coordinates K, k_z and Θ . Thus:

$$\frac{\partial E}{\partial k_x} = \frac{\partial E}{\partial K} \cos \Theta \tag{8.2a}$$

$$\frac{\partial E}{\partial k_y} = \frac{\partial E}{\partial K} \sin \Theta \tag{8.2b}$$

$$\frac{\partial^2 E}{\partial k_x^2} = \cos^2 \Theta \frac{\partial^2 E}{\partial \kappa^2} + \sin^2 \Theta \frac{1}{\kappa} \frac{\partial E}{\partial \kappa}$$
(8.2c)

$$\frac{\partial^2 E}{\partial k_x \partial k_y} = \sin \Theta \cos \Theta \left[\frac{\partial^2 E}{\partial \kappa^2} - \frac{i}{\kappa} \frac{\partial E}{\partial \kappa} \right]$$
(0.2d)

$$\frac{\partial^2 E}{\partial k_v^2} = \sin^2 \Theta \frac{\partial^2 E}{\partial K^2} + \cos^2 \Theta \frac{i}{K} \frac{\partial E}{\partial K}$$
(8.2e)

Relation (8.2e) is not required here, but will occur in section IX.

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We now replace the integral over \vec{k} in (8.1) by an integral over E and a surface integral over a surface of constant energy. As in the case of the conductivities, we will carry out the integral over the constant energy surface by projecting this surface onto the plane $k_z = 0$. Symbolically we can express this transformation as:

$$\int d^{3}k \longrightarrow 2 \int dE \int \frac{K \, dK \, d\Theta}{\left| \frac{\partial E}{\partial k} \right|}$$

Here, the angular integral extends from 0 to 4π , because the Brillouin zone has six corners and the surface extends 1/3 of the way around each of these corners. The factor of 2 is due to the two projections of the surface, coming from above and below the plane $k_z = 0$.

When the above transformation is applied to equation (0.1) using the expressions (0.2a)-(0.2d), the angular integrations are easily carried out and the result is:

$$A_{H \to 0} = \frac{-\pi^{2}}{e} \frac{\int \frac{df_{o}}{dE} \left[\int \left(\frac{\partial E}{\partial K} \right)^{3} \frac{dK}{\left| \frac{\partial E}{\partial K_{z}} \right|} \right] dE}{\left\{ \int \frac{df_{o}}{dE} \left[\int \left(\frac{\partial E}{\partial K} \right)^{2} \frac{K dK}{\left| \frac{\partial E}{\partial K_{z}} \right|} \right] dE \right\}^{2}}$$
(8.3)

As in the case of the conductivities, the integrals involved here are easily evaluated at very low temperatures, because of our assumption that $\zeta_{\infty} \sim .06 \text{ ev} \gg \xi_{1} \simeq .005 \text{ ev}$. The result for the zero field Hall coefficient at absolute zero of temperature is:

$$A_{H \to c}^{(0)} = -\frac{\pi c (\pi v)^2}{2e \zeta_o^2} \simeq -.705 \text{ cm}^3/\text{ceulomb}$$
(8.4)



Fig. 7. The Variation of the Hall Coefficient with Temperature. The dashed curve is taken from Kinchin, the dotted one from Johnston. The solid curve shows the result of the present calculation. The point at 300°K is taken from Hennig.

The numerical value is obtained if we use:

a = 2.46 A° ; c = 6.74 A° ; δ_{o} = 2.5 ev; ζ_{o} = .06 ev.

Kinchin (25) has measured the zero field Hall coefficient for a single crystal of graphite, and reports a value of $-.69 \text{ cm}^3/\text{coulomb}$ at very low temperatures, in good agreement with the value predicted by equation (5.4).

In the general case of arbitrary temperature, the integrations over energy in (8.3) must again be carried out numerically. By a process completely analogous to the conductivity calculation, one can write:

$$A(T)_{H \to 0} = \frac{-\pi_c^2 (hv)^2 kT}{2e x_i^2} \frac{\int_{-\infty}^{+\infty} sech^2 \left(\frac{x - \frac{\zeta_i}{2kT}}{Y_i}\right) K(x) dx}{\left\{ \int_{-\infty}^{+\infty} sech^2 \left(\frac{x - \frac{\zeta_i}{2kT}}{Y_i}\right) F(x) dx \right\}^2}$$
(8.5)

where:

$$K(x) = \frac{-x[4-x^2]^{\frac{1}{2}}}{1-x^2} + \frac{x(2-x^2)}{[1-x^2]^{\frac{3}{2}}} \log\left[\frac{((4-x^2)(1-x^2))^{\frac{1}{2}}+2-x^2}{x}\right] \qquad 0 \le x \le 1$$

= $\sqrt{3}$

$$= \frac{\pm x [4 - x^{2}]^{\frac{1}{2}}}{x^{2} - 1} - \frac{x (2 - x^{2})}{(x^{2} - 1)^{\frac{3}{2}}} \left[\frac{\pi}{2} - \sin^{-1} \left(\frac{2 - x^{2}}{x} \right) \right]$$

$$= \pi x (x^{2} - 2) (x^{2} - 1)^{-\frac{3}{2}}$$

($\Lambda(x)$ is anti-symmetric about x = 0.)

The integral in the denominator of (8.5) is the same as the integral which occurs in σ_{w} . The function F(x) is defined by equation (7.12).

A numerical evaluation of A(T) yields Fig. 7. The values of the various integrals in (0.5) are tabulated as a function of temperature in Table 1. Basically, the behaviour

of the Hall coefficient is due to the shift of the Fermi level with temperature. As the temperature is raised, the Fermi level moves towards the degeneracy point, and hence more and more positive carriers contribute. However, there will always be an excess of negative carriers, and hence the Hall coefficient approaches zero for high temperatures, but remains negative. The peculiar behaviour of the Hall coefficient between 100°K and 300°K is due to the numerator of equation (0.5). This integral has a maximum value in this temperature range (cf. Table 1), which results in a Hall coefficient slightly lower than the zero temperature value. The exact shape of the A(T) curve in Fig. 7 is a fairly sensitive function of δ_1 in this temperature range. By choosing a slightly different value for this parameter (which has been chosen to be .005 ev) it is possible to make the bump in the A(T) curve less pronounced, so that A(T) is essentially constant below room temperature and then falls off roughly in the same fashion as in Fig. 7.

Kinchin finds that the zero field Hall coefficient becomes positive between 25° K and $1/5^{\circ}$ K (cf. Fig. 7). He attributes this behaviour to the presence of acceptor impurities. However, Kinchin's curves for polycrystalline samples do not show this peak in the Hall coefficient down to a temperature of 77° K. His graphite IV sample shows no such peak down to 4.2° K, while the very low temperature range for the other samples is not discussed. It is not

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clear to the author how a single crystal sample and a polycrystalline sample can be so markedly different, since only an averaging factor is involved in the conversion. Hennig (26) has measured the Hall coefficient in graphite as a function of oxidation. For zero oxidation at room temperature, he finds A = -.65 cm³/coulomb, in good agreement with the theoretical value at this temperature. Hennig's experimental value at room temperature has been included in Fig. 7.

Perhaps the most significant feature of our crude calculation is that our value for the position of the Fermi level at very low temperatures is verified by the Hall coefficient. Previous explanations of the negative Hall coefficient have always depended on assigning different mobilities to the electrons and to the holes. There seems to be no reason why these mobilities should be different, since the bands are very nearly symmetric about the degeneracy point. While the Hall effect does not exclude an explanation based on different mobilities, we have seen that there could be no de Haas-Van Alphen effect if the Fermi surface were at the degeneracy point. Thus, a model of graphite based on excess electrons is necessary if one wishes to explain these properties simultaneously.

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IX. THE TRANSVERSE MAGNETO-RESISTANCE OF GRAPHITE.

Finally, let us evaluate the transverse magneto-resistance of graphite when the magnetic field is applied along the c-axis of the crystal. From the point of view of yielding useful information about our choice of parameters, this calculation will turn out to be not very instructive, since we shall be able to infer the correctness of our choice only indirectly. This is due to the fact that the magneto-resistance ratio, $\frac{\Delta \rho}{\rho}$, depends more radically on the relaxation time than either the ratio of the principal conductivities or the zero field Hall coefficient. We found that both of the last two expressions were essentially independent of the relaxation time, at least at low temperatures. This is not true of the magneto-resistance ratio. In fact, we shall see that $\frac{\Delta \rho}{\rho}$ is proportional to τ^2 if we make the same assumptions about the relaxation time as we made in the two previous cases.

Following Jones and Zener (24), we write for the ratio of the change in resistivity to the resistivity:

$$\frac{\Delta P}{P} = \left(\frac{eH\tau}{\hbar^2 c}\right)^2 \cdot \frac{I_3}{I_1 \cdot I_2}$$
(9.1)

where:

$$I_{i} = -\int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{x}}\right)^{2} d^{3}k \qquad ; \qquad I_{2} = -\int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{y}}\right)^{2} d^{3}k I_{3} = \int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{y}}\right) \Omega \frac{\partial E}{\partial k_{x}} d^{3}k \cdot \int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{x}}\right) \Omega \frac{\partial E}{\partial k_{y}} d^{3}k -\int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{y}}\right)^{2} d^{3}k \cdot \int \frac{df_{o}}{dE} \left(\frac{\partial E}{\partial k_{x}}\right) \Omega \frac{\partial E}{\partial k_{x}} d^{3}k \Omega = \left(\frac{\partial E}{\partial k_{y}}\right) \frac{\partial}{\partial k_{x}} - \left(\frac{\partial E}{\partial k_{x}}\right) \frac{\partial}{\partial k_{y}} d^{3}k$$

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The transformation of these integrals into integrals over E and A is straightforward but tedious. The method is completely analogous to that used in converting the integrals which enter the expression for the Hall coefficient, and will not be repeated here. At low temperatures, where the derivative of the Fermi function is sharply peaked, we find:

$$\frac{I_{3}}{I_{1} \cdot I_{2}} = \frac{-\left\{ \int \left(\frac{\partial E}{\partial K}\right)^{3} \frac{dK}{\left|\frac{\partial E}{\partial K_{2}}\right|}^{2} + \int \left(\frac{\partial E}{\partial K}\right)^{2} \frac{K dK}{\left|\frac{\partial E}{\partial K_{2}}\right|} \cdot \int \left(\frac{\partial E}{\partial K}\right)^{4} \frac{dK}{\left|\frac{\partial E}{\partial K_{2}}\right|} \right\}$$
(9.2)

Under the assumption that $\zeta_0 > 2\aleph_1$, the integrals all have the range: $\frac{1}{\hbar\nu} \left[\zeta_0^2 - 2\aleph_1 \zeta_0 \right]^{\frac{1}{2}} \leq \kappa \leq \frac{1}{\hbar\nu} \left[\zeta_0^2 + 2\aleph_1 \zeta_0 \right]^{\frac{1}{2}}$ These integrals are easily evaluated in terms of a power series in $\frac{\aleph_1^2}{\zeta_0^2}$. To the lowest non-zero order we find:

$$\frac{\Delta P}{P} = \left(\frac{eH\tau}{\hbar^2 c}\right)^2 \cdot \frac{(\hbar v)^4 \gamma_i^2}{2 \zeta_0^4}$$
(9.3)

This result may now be compared with the experiments of Kinchin (25). Using the various values of $\frac{\Delta P}{P}$ and H given in Kinchin's paper, and our previous choice of the parameters \mathcal{X}_{o} , \mathcal{X}_{i} , and \mathcal{Z}_{o} , equation (9.3) predicts a relaxation time:

$\tau \simeq$ 4-6 x 10⁻¹¹ seconds (T = 4.2°K)

Galt et al. (27) report a relaxation time of approximately 10⁻¹¹ seconds, using the cyclotron resonance technique. Thus, agreement is again satisfactory. We shall discuss the results of cyclotron resonance a little more fully in the conclusions. SUMMARY AND CONCLUSIONS.

The basis of our model of graphite is a small interplanar interaction plus a certain number of excess electrons. Perhaps the most striking feature of this model is its simplicity. Only three parameters are incorporated in it (Σ_{o} , δ_{i} and ζ_{o}), yet it explains the basic features of most of the properties of graphite in external fields. The most unsatisfactory result is obtained for the amplitudes of the de Haas-Van Alphen effect fluctuations, which turn out to be far too large, even when estimated from a simplified threedimensional model. It may be argued that if the density of states within the nth level had not been replaced by the sum of three δ -functions, the amplitudes would have been further reduced. Although some reduction of the amplitudes would occur, the major source of the trouble lies elsewhere. As long as the magnetic energy levels are narrow compared to their mutual spacing, large fluctuations (and discontinuities) will occur in the de Haas-Van Alphen effect. We must conclude that there is some other source of level broadening, which we have not considered.

The fact that the observed oscillations are smaller than the theoretically predicted ones is in line with what has been found to be the case in many other substances. In Li, Na, Cu, Ag and Au for example, no oscillations have yet been observed, although one has reason to expect them on

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theoretical grounds. These and other difficulties with the present theory have been discussed in a review article by Chambers (20).

The form of the energy relations used in this thesis were derived within the tight binding formalism. However, Slonczewski (29) has shown that the same form for these relations can be obtained by group theoretical methods using perturbation theory. It therefore seems improbable that the difficulties with the susceptibility oscillations have their origin in this approximation. It may be that electronelectron correlations are important if one wishes to explain these finer features, and one may have to abandon the oneelectron approximation altogether in order to find an explanation.

The experimental results on the Hall effect are difficult to interpret. In view of the completely different results obtained by Kinchin (25) and Hennig(26) at 300° K, the author feels that the theoretical curve cannot be excluded. It is true that Hennig (26) measured his Hall coefficient in rather large fields (14,000 gauss). However, kinchin's curves for the Hall coefficient as a function of magnetic field indicate that at 300° K this coefficient displays virtually no field variation. Johnston (30) has also calculated the Hall coefficient. His curve is included in Fig. 7. Although his calculation is restricted to temperatures between 150° K and 350 K, his result is markedly different from ours in

(4)

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this range. Further experiments seem necessary before one can decide which curve best fits the results.

We have calculated the magneto-resistance to order H^2 only. An exact calculation, which leads to a saturation factor, is possible for graphite. However, since such a calculation is based on the Boltzmann equation, one can have no confidence in the results when the magnetic fields become large enough so that quantum effects are important. (The derivation of the saturation term is outlined in Appendix III.) In graphite, the condition for the validity of the Boltzmann equation is: $\frac{S y^2 x}{2 \hbar \zeta} \ll 1$. At low temperatures, this condition breaks down in fields between 10^3 and 10^4 gauss. This condition agrees well with the experimental fact, that one can observe quantum effects such as the de Haas-Van Alphen effect in fields of the order of 5000 gauss (9,10).

Finally, we have stated that our magneto-resistance result corresponds to a relaxation time which is in good agreement with the value found by Galt et al. (27) by cyclotron resonance. Cyclotron resonance results also seem to indicate the presence of positive carriers in graphite. In their publication, Galt et al. (27) state that the presence of these carriers is uncertain, since a similar effect can under certain circumstances be due to extremely eccentric energy surfaces. In a recent private communication with Professor P.R. Wallace, Galt expressed the view that the latter explanation is not applicable to graphite and that positive carriers are almost certainly present. Furthermore, Galt now believes that the relaxation time may be as long as 10^{-9} seconds at low temperatures. If these more recent findings are correct, they are difficult to reconcile with our model of graphite. Because of our position of the Fermi surface, we would certainly not expect positive carriers at very low temperatures. If no positive carriers are present, how then is one to explain the symmetric dip in the absorption curve at H = 0, which is obtained by cyclotron resonance?

It may be that this reduction in absorption near H = Ois a magneto-resistance effect, and not a true cyclotron resonance. Chambers (32) has proposed that such an effect exists in Bismuth. His argument is the following: In poor metals, such as Bismuth, there are in general too many carriers present to attain the classical condition of cyclotron reso-The skin depth is simply not large enough in such nance. substances. However, Chambers has shown that the skin depth is proportional to the surface impedance. If for some reason the impedance is considerably larger in a magnetic field than it is when the magnetic field is zero or very small, then the skin depth will also be a function of the magnetic field. This case is realized if the sample has a large magneto-resistance. In such a case a symmetric dip in the absorption curve is to be expected near H = 0. Now if our

model of graphite is correct, then Bismuth and graphite should behave quite similarly; that is, graphite should behave more like a poor metal than like a semi-conductor, and hence Chamber's explanation may also apply to graphite. Further investigation seems necessary before these differences can be understood. In this connection, the previously mentioned measurement of the de Haas-Van Alphen effect would be of interest, since such an experiment would test one of the general features of our model. APPENDIX 1

Derivation of the coupled equations in the case of a non-magnetic perturbation.

We start with the Schrödinger equation in the presence of the perturbation.

$$H\psi = [H_o + U]\psi = E\psi \qquad (1.15)$$

Substituting the relations (1.14) into this equation, we shall first consider only the $\rm H_{O}$ part of H.

$$H_{o}\psi = \sum_{R_{j}} c_{i}(\vec{R_{j}})H_{o}\varphi_{ij} + \sum_{R_{j}} c_{2}(\vec{R_{j}})H_{o}\varphi_{2j}$$

Now we make use of the equations (1.13a) and (1.13b). Then

$$H_{o}\psi = \sum_{R_{j},R_{\ell}} c_{1}(\vec{R}_{\ell}) \chi_{i1}(\vec{R}_{j}-\vec{R}_{\ell}) \psi_{1\ell} + \sum_{R_{j},R_{\ell}} c_{1}(\vec{R}_{j}) \chi_{21}(\vec{R}_{j}-\vec{R}_{\ell}) \psi_{2\ell} + \sum_{R_{j},R_{\ell}} c_{2}(\vec{R}_{\ell}) \chi_{12}(\vec{R}_{j}-\vec{R}_{\ell}) \psi_{1\ell} + \sum_{R_{j},R_{\ell}} c_{2}(\vec{R}_{j}) \chi_{22}(\vec{R}_{j}-\vec{R}_{\ell}) \psi_{2\ell}$$

We now rename the lattice vectors. Let $\vec{R_j} - \vec{R_l} = \vec{R_s}$, and replace the sums over $\vec{R_j}$ and $\vec{R_l}$ by sums over $\vec{R_l}$ and $\vec{R_s}$. Thus

$$H_{0}\psi = \sum_{R_{1},R_{5}} \varphi_{i\ell} \chi_{il}(\vec{R}_{5}) c_{i}(\vec{R}_{\ell}+\vec{R}_{5}) + \sum_{R_{2},R_{5}} \varphi_{2\ell} \chi_{2i}(\vec{R}_{5}) c_{i}(\vec{R}_{\ell}+\vec{R}_{5})$$

Let us now make use of the operator identity

$$c(\vec{R}_{l} + \vec{R}_{s}) = e \cdot c(\vec{R}_{l})$$

where the gradient operator operates on the position vector \overrightarrow{R}_1 . Therefore, we can write:

$$\begin{split} H_{o}\psi &= \sum_{R_{\ell}} \varphi_{1\ell} \left[\sum_{R_{s}} \chi_{11}(\vec{R}_{s}) e^{\vec{R}_{s} \cdot \vec{\nabla}}(\vec{R}_{\ell}) \right] + \sum_{R_{\ell}} \varphi_{2\ell} \left[\sum_{R_{s}} \chi_{21}(\vec{R}_{s}) e^{\vec{R}_{s} \cdot \vec{\nabla}}(\vec{R}_{\ell}) \right] \\ &+ \sum_{R_{\ell}} \varphi_{1\ell} \left[\sum_{R_{s}} \chi_{12}(\vec{R}_{s}) e^{\vec{R}_{s} \cdot \vec{\nabla}}(\vec{R}_{\ell}) \right] + \sum_{R_{\ell}} \varphi_{2\ell} \left[\sum_{R_{s}} \chi_{22}(\vec{R}_{s}) e^{\vec{R}_{s} \cdot \vec{\nabla}}(\vec{R}_{\ell}) \right] \end{split}$$

Using the relation (1.17), this equation becomes:

$$\begin{split} H_{o}\psi &= \sum_{R_{g}} \varphi_{1\varrho} H_{ii}^{o}(-i\vec{\nabla}) c_{1}(\vec{R}_{g}) + \sum_{R_{g}} \varphi_{2\varrho} H_{2i}^{o}(-i\vec{\nabla}) c_{1}(\vec{R}_{g}) \\ &+ \sum_{R_{g}} \varphi_{1\varrho} H_{i2}^{o}(-i\vec{\nabla}) c_{2}(\vec{R}_{g}) + \sum_{R_{g}} \varphi_{2\varrho} H_{2i}^{o}(-i\vec{\nabla}) c_{2}(\vec{R}_{g}) \end{split}$$

We now add the terms coming from $\cup\psi$ to ${\rm H}_{0}\psi$ and equate the result to E ψ . We find:

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$$\begin{split} &\sum_{R_{\ell}} \varphi_{1\ell} \left[H_{11}^{\circ}(-i\vec{\nabla}) c_{1}(\vec{R}_{\ell}) + H_{12}^{\circ}(-i\vec{\nabla}) c_{2}(\vec{R}_{\ell}) + U(\vec{r}) c_{1}(\vec{R}_{\ell}) \right] \\ &+ \sum_{R_{\ell}} \varphi_{2\ell} \left[H_{21}^{\circ}(-i\vec{\nabla}) c_{1}(\vec{R}_{\ell}) + H_{22}^{\circ}(-i\vec{\nabla}) c_{2}(\vec{R}_{\ell}) + U(\vec{r}) c_{2}(\vec{R}_{\ell}) \right] \\ &= E \left[\sum_{R_{\ell}} c_{1}(\vec{R}_{\ell}) \varphi_{1\ell} + \sum_{R_{\ell}} c_{2}(\vec{R}_{\ell}) \varphi_{2\ell} \right] \end{split}$$

At this stage, we make the assumption that $U(\vec{r})$ is a slowly varying potential. We assume that within the jth unit cell the potential differs little from the value $U(\vec{R}_j)$. If this is the case, we can replace $U(\vec{r})$ by $U(\vec{R}_l)$ in the coefficient of $\varphi_{\prec \ell}$, since this function is peaked in the lth cell.

Next, we shall make use of the orthogonality of the $\varphi_{\alpha j}$. This allows us to equate coefficients of $\varphi_{\alpha \ell}$ on the two sides of the equation. Therefore:

 $H_{11}^{\circ}(-i\vec{\nabla})c_{1}(\vec{R}_{1}) + H_{12}^{\circ}(-i\vec{\nabla})c_{2}(\vec{R}_{2}) + U(\vec{R}_{1})c_{1}(\vec{R}_{1}) = Ec_{1}(\vec{R}_{1})$ $H_{21}^{\circ}(-i\vec{\nabla})c_{1}(\vec{R}_{2}) + H_{22}^{\circ}(-i\vec{\nabla})c_{2}(\vec{R}_{1}) + U(\vec{R}_{1})c_{2}(\vec{R}_{2}) = Ec_{2}(\vec{R}_{2})$

This completes the proof of equations (1.16a) and (1.16b) and shows that the approximate allowed energies in the presence of a slowly varying, non-magnetic perturbation are obtained from the solution of this set of coupled equations.

APPENDIX II

Derivation of the coupled equations in the case of a magnetic perturbation.

Starting with equation (1.26), we rename the lattice vectors. Let $\vec{R_j} - \vec{R_l} = \vec{R_s}$ and replace the sums over $\vec{R_j}$ and $\vec{R_l}$ by sums over $\vec{R_l}$ and $\vec{R_s}$. Hence:

$$\begin{split} H\psi &= \sum_{R_{L_{i}}R_{s}} \varphi_{i\ell} \exp\left[\frac{ie}{\pi_{c}}G_{\ell+s}\right] Y_{ii}(\vec{R}_{s}) C_{i}(\vec{R}_{L}+\vec{R}_{s}) \\ &+ \sum_{R_{\ell_{i}}R_{s}} \varphi_{2\ell} \exp\left[\frac{ie}{\pi_{c}}G_{L+s}\right] Y_{2i}(\vec{R}_{s}) C_{i}(\vec{R}_{L}+\vec{R}_{s}) \\ &+ \sum_{R_{\ell_{i}}R_{s}} \varphi_{i\ell} \exp\left[\frac{ie}{\pi_{c}}G_{L+s}\right] Y_{12}(\vec{R}_{s}) C_{2}(\vec{R}_{1}+\vec{R}_{s}) \\ &+ \sum_{R_{\ell_{i}}R_{s}} \varphi_{i\ell} \exp\left[\frac{ie}{\pi_{c}}G_{L+s}\right] Y_{12}(\vec{R}_{s}) C_{2}(\vec{R}_{1}+\vec{R}_{s}) \\ &+ \sum_{R_{\ell_{i}}R_{s}} \varphi_{2\ell} \exp\left[\frac{ie}{\pi_{c}}G_{L+s}\right] Y_{22}(\vec{R}_{s}) C_{2}(\vec{R}_{\ell}+\vec{R}_{s}) \end{split}$$

Let us again use the operator identity

$$c(\vec{R}_{\ell} + \vec{R}_{s}) = e^{\vec{R}_{s} \cdot \vec{\nabla}} c(\vec{R}_{\ell})$$

Furthermore, we shall again invoke the localization of φ_{u} and φ_{2l} to simplify the G_{1+s} factors.

$$G_{l+s} = \int_{0}^{1} d\lambda \left[\vec{r} - \vec{R}_{l} - \vec{R}_{s} \right] \cdot \vec{A} \left(\vec{R}_{l} + \vec{R}_{s} + \lambda (\vec{r} - \vec{R}_{s} - \vec{R}_{s}) \right)$$

When such a term is multiplied by $\varphi_{1\ell}$ or $\varphi_{2\ell}$ we replace \vec{r} by \vec{R}_{11} or \vec{R}_{21} respectively. But we have previously ignored phase changes between the two atoms in the same unit cell. This is equivalent to putting \vec{r} equal to \vec{R}_1 in both cases, and involves an error of the order of the ion core susceptibility. Hence we find:

$$G_{l+s}(\vec{r} = \vec{R}_{l}) = -\int d\lambda \, \vec{R}_{s} \cdot \vec{A} \left(\vec{R}_{l} + (1-\lambda)\vec{R}_{s}\right)$$

Let $\lambda' = 1 - \lambda$; then

$$G_{l+s}(\vec{r}=\vec{R}_{l})=-\int_{0}^{1}d\lambda'\vec{R}_{s}\cdot\vec{A}(\vec{R}_{l}+\lambda'\vec{R}_{s})$$

Substituting this relation into H ψ , we get:

$$\begin{split} H\psi &= \sum_{R_{\ell}} \varphi_{1\ell} \left[\sum_{R_{s}} \gamma_{11}(\vec{R}_{s}) e^{Q} \cdot e^{-\vec{R}_{s} \cdot \vec{\nabla}} c_{1}(\vec{R}_{\ell}) \right] \\ &+ \sum_{R_{\ell}} \varphi_{2\ell} \left[\sum_{R_{s}} \gamma_{21}(\vec{R}_{s}) e^{Q} \cdot e^{-\vec{R}_{s} \cdot \vec{\nabla}} c_{1}(\vec{R}_{\ell}) \right] \\ &+ \sum_{R_{\ell}} \varphi_{1\ell} \left[\sum_{R_{s}} \gamma_{12}(\vec{R}_{s}) e^{Q} \cdot e^{-\vec{R}_{s} \cdot \vec{\nabla}} c_{2}(\vec{R}_{\ell}) \right] \\ &+ \sum_{R_{\ell}} \varphi_{2\ell} \left[\sum_{R_{s}} \gamma_{22}(\vec{R}_{s}) e^{Q} \cdot e^{-\vec{R}_{s} \cdot \vec{\nabla}} c_{2}(\vec{R}_{\ell}) \right] \end{split}$$

where:

$$Q = \frac{-ie}{\hbar c} \int d\lambda \, \vec{R}_s \cdot \vec{A} (\vec{R}_1 + \lambda \vec{R}_s)$$

It is shown in Appendix II of reference (10) that: $e^{\hat{R}_{s}\cdot\vec{\nabla}} = \exp\{i\vec{R}_{s}\cdot[-i\vec{\nabla}_{s}-\vec{e}\vec{A}(\vec{R}_{s})]\}$

Using this relation and equation (1.17) we find:

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$$\begin{split} H\psi &= \sum_{R_{g}} \varphi_{1g} H_{11}^{\circ} (-i\vec{\nabla}_{g} - \vec{e}\vec{A}_{g}) c_{1}(\vec{R}_{g}) \\ &+ \sum_{R_{g}} \varphi_{2g} H_{21}^{\circ} (-i\vec{\nabla}_{g} - \vec{e}\vec{A}_{g}) c_{1}(\vec{R}_{g}) \\ &+ \sum_{R_{g}} \varphi_{1g} H_{12}^{\circ} (-i\vec{\nabla}_{g} - \vec{e}\vec{A}_{g}) c_{2}(\vec{R}_{g}) \\ &+ \sum_{R_{g}} \varphi_{2g} H_{22}^{\circ} (-i\vec{\nabla}_{g} - \vec{e}\vec{A}_{g}) c_{2}(\vec{R}_{g}) \end{split}$$

Writing $H\Psi = E\Psi$, and making use of the orthogonality of the Ψ_{K} to equate the coefficients of these functions, one obtains equations (1.2%) and (1.2%).

APPENDIX III

Saturation Factors in Magneto-Electric Effects.

We seek a solution of the Boltzmann equation

$$-\frac{e}{\pi}\left[\vec{\varepsilon} + \frac{1}{c}\vec{\nabla} \times \vec{H}\right]\cdot\vec{\nabla}_{k}f = \frac{f_{0}-f_{0}}{\tau}$$

by putting:

$$f = f_{e} - \vec{k} \cdot \vec{c}(E) \frac{\partial f_{e}}{\partial E}$$

Now $\nabla_{\mathbf{k}} \mathbf{f}$ may be written:

 $\vec{\nabla}_{k}f = \left[\vec{\nabla}_{k}f\right]_{E=constant} + \frac{\partial f}{\partial E}\vec{\nabla}_{k}E = -\vec{c}(E)\frac{\partial f}{\partial E} + \frac{\partial f}{\partial E}\vec{\nabla}_{k}E$ Using the relation $\vec{V} = \frac{1}{h}\vec{\nabla}_{k}E$, one easily finds:

$$(\vec{v} \times \vec{H}) \cdot \vec{\nabla}_{x} f = -\frac{\partial f_{0}}{\partial E} \vec{v} \cdot [\vec{H} \times \vec{c}(E)]$$

The relation between \vec{k} and \vec{v} is determined by the $E(\vec{k})$ relationship. For free electrons one has, of course, $\vec{v} = \frac{\pi \vec{k}}{m}$. We shall now write $\vec{v} = \frac{\pi \vec{k}}{\omega}$, where ω is some constant, or function of energy, but does not depend on the direction of \vec{k} . It is not possible to use such a relation for an arbitrary $\vec{E(k)}$ relation, but one is able to do so whenever the $\vec{E(k)}$ relation depends only on the magnitude of \vec{k} . For graphite, for instance, we have (in the two-dimensional case):

$$E = \frac{1}{4} \sqrt{|K|} \qquad \vec{V} = \frac{1}{4} \sqrt{|K|} = \frac{1}{4} \sqrt{$$

Let us now use this result in the Boltzmann equation. One easily finds:

$$-\frac{e}{h}\left\{h\vec{v}\cdot\vec{\varepsilon}-\frac{1}{c}\vec{v}\cdot\left[\vec{H}\times\vec{c}(\varepsilon)\right]\right\} = \left(\frac{\omega}{hc}\right)\vec{v}\cdot\vec{c}(\varepsilon)$$

We have used the fact that it is never necessary to consider powers of $\vec{\mathcal{E}}$ higher than the first, so that one can put $f = f_0$ for these terms. We now note that the vector whose scalar product with \vec{v} occurs in our equation, does not depend on the direction of \vec{k} . This clearly allows one to write:

$$\vec{F} + \frac{e}{\kappa_c} \vec{H} \times \vec{c}(e) = \frac{\omega}{\kappa_c} \vec{c}(e) \qquad ; (\vec{F} = -e\vec{e})$$

The solution of this equation for the vector c(E) is very simple. One simply takes scalar and vector products with the vector H. Using elementary vector identities, one finds:

$$\left\{\left(\frac{\omega}{\hbar\tau}\right)^{2}+s^{2}\right\}\vec{c}(E) = \frac{\omega}{\hbar\tau}\vec{F} + \frac{e}{\hbarc}\vec{H}\times\vec{F} + \frac{e^{2}\tau}{\hbar\omega}c^{2}(\vec{H}\cdot\vec{F})\vec{H}; (s = \frac{eH}{\hbarc})$$

Let us now consider the special case where the magnetic field is applied along the z-axis, while the electric field is in the xy-plane. Then the $\overline{H} \cdot \overline{F}$ term is zero and the vector $\overline{c(E)}$ has only x and y components. The equations for these components are:

$$\frac{\omega}{\hbar\tau} c_x + sc_y = F_x$$

- Sc_x + $\frac{\omega}{\hbar\tau} c_y = F_y$

Upon solving these equations, one finds:

$$c_{x} = \frac{\left(\frac{\omega}{\hbar c}\right)F_{x} - sF_{y}}{s^{2} + \left(\frac{\omega}{\hbar \tau}\right)^{2}} \quad ; \quad c_{y} = \frac{sF_{x} + \left(\frac{\omega}{\hbar c}\right)F_{y}}{s^{2} + \left(\frac{\omega}{\hbar \tau}\right)^{2}}$$

To illustrate how the saturation factors enter the integrals for the various magneto-conductivity expressions, let us look at the electric current density vector J. Thus:

$$\vec{J} = -\frac{2e}{(2\pi)^3} \int \vec{v} f(\vec{k}) d^3 k = \frac{+2e\pi}{(2\pi)^3} \int \frac{1}{\omega} \vec{v} (\vec{v}, \vec{c}(E)) \frac{\partial f_e}{\partial E} d^3 k$$

Neglecting the Hall term, this gives for the x-component of \rightarrow J, for example:

$$J_{x} = \frac{2e\hbar}{(2\pi)^{3}} \int \frac{1}{\omega} v_{x} v_{x} c_{x} \frac{\partial f_{e}}{\partial E} d^{3}k$$

The role of the saturation factors is now clear. The usual treatment in terms of a power series in H would correspond to expanding the denominator of c_x in powers of H^2 . Similar expressions are valid for the various other integrals which are derived in this manner.

It has been shown by Wilson (33) that the condition for the validity of the Boltzmann equation for free electrons is: $\frac{eHr}{mc} \ll i$. This is simply the condition that quantum effects are unimportant; that is, no electron shall have time to complete a quantized orbit before it suffers a collision. In graphite at low temperatures this condition is: $\frac{s c (\pi_v)^2}{\pi \zeta_o} \ll 1$. It is interesting that this is just the condition for the validity of the expansion in powers of H^2 of the functions c_x and c_y , again at low temperatures. At high temperatures, in graphite, the Fermi surface is near the degeneracy point and the Boltzmann equation is certainly not valid, because of the increased possibility of band-toband transitions.

One must conclude that whenever one is justified in applying the Boltzmann equation, one is also justified in using an expansion in powers of H². This makes the saturation factors meaningless from a practical point of view. BIBLIOGRAPHY

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