X-ray absorption measurements of high resolving power for potassium, which is expected to show wider departure from free electrons, have been carried out by Platt.[16] The K edge investigated shows quite close agreement with his theoretically predicted absorption which was based on the assumption that the electrons are free. No evidence existed to show an energy gap. This, of course, is at best supporting evidence of the non-existence of a gap in potassium since gaps may exist which could be completely masked by the eigenvalue dependence upon wave vector direction.

[16] J. B. Platt, Phys. Rev. 69, 337 (1946).

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. A. Bowers for permission to publish his results on the five additional states shown in Table IV and also wish to thank Dr. Bowers for continuing the application of the method when the war interrupted the work.

PHYSICAL REVIEW VOLUME 71, NUMBER 9 MAY 1, 1947

The Band Theory of Graphite

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(Received December 19, 1946)

The structure of the electronic energy bands and Brillouin zones for graphite is developed using the "tight binding" approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for fields across the layers. The volume optical absorption is accounted for.

1. INTRODUCTION

THE purpose of this paper is to develop a basis for the explanation of some of the physical properties of graphite through the band theory of solids. We shall be concerned primarily with a discussion of its electrical conductivity, but the treatment given makes possible the explanation not only of the electrical conductivity and its anisotropy but also the thermal conductivity, diamagnetic susceptibility, and optical absorption.

The electrical resistivity of single crystals of graphite is about 4 to 6×10^{-5} ohm-cm.[1] This corresponds to a conductivity of the order of that of a poor metal. The temperature coefficient of the conductivity is negative, as in the case of a metal. Polycrystalline graphite, on the other hand, has a much higher resistivity which varies very strongly according to the type of graphite used, and has a *positive* temperature coefficient of conductivity[2] to about 1400°C, and negative thereafter. Since the crystals of commercial graphites tend to be of the order of 10^{-6} cm, and it is quite porous (density ~1.6 as against 2.25 for single crystals), it seems reasonable to attribute the high resistivity of polycrystalline graphite to the crystal boundaries, on which may be lodged impurity atoms. The latter would tend to be driven off on heating, thus accounting for the observed temperature dependence. We shall show, however, that the band theory would seem to make possible the explanation of the conductivity properties of single crystals.

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[1] Given by E. Ryschewitsch, Zeits. f. Elektrochem. ang. physik. Chemie 29, 474 (1923), as $3.9–6\times10^{-5}$ ohm-cm.

[2] C. A. Hansen, Trans. Am. Electrochem. Soc. 16, 329 (1909) gives 137.5×10^{-5} at 0°C 82.5×10^{-5} at 1400°C.

2. ZONE STRUCTURE OF A SINGLE HEXAGONAL LAYER

Since the spacing of the lattice planes of graphite is large (3.37A) compared with the hexagonal spacing in the layer (1.42A), a first approximation in the treatment of graphite may be obtained by neglecting the interactions between planes, and supposing that conduction takes place only in layers.

Graphite possesses four valence electrons. Three of these form tight bonds with neighboring atoms in the plane. Their wave functions are of the form

$$\frac{1}{\sqrt{3}}(\psi_c(2s)+\sqrt{2}\psi_c(\sigma_i 2p)) \quad (i=1, 2, 3),$$

where $\psi_c(2s)$ is the $(2s)$ wave function for carbon and $\psi_c(\sigma_i 2p)$ are the $(2p)$ wave functions whose axes are in the directions σ_i joining the graphite atom to its three neighbors in the plane. The fourth electron is considered to be in the $2p_z$ state, its nodal plane being the lattice plane and its axis of symmetry perpendicular to it. The three electrons forming co-planar bonds will not play a part in the conductivity; we shall therefore treat graphite as having one conduction electron, in the $2p_z$ state.

For the hexagonal layer the unit cell, which is designated by $WXYZ$ in Fig. 1, contains two atoms, A and B. The fundamental lattice displacements are $a_1=\mathbf{AA'}$ and $a_2=\mathbf{AA''}$; their magnitude is $1.42\times\sqrt{3}=2.46\text{A}=a$. The reciprocal lattice vectors have magnitude $2/\sqrt{3}a$, and are in the direction AB and AZ, respectively. From this it follows that the first Brillouin zone is a

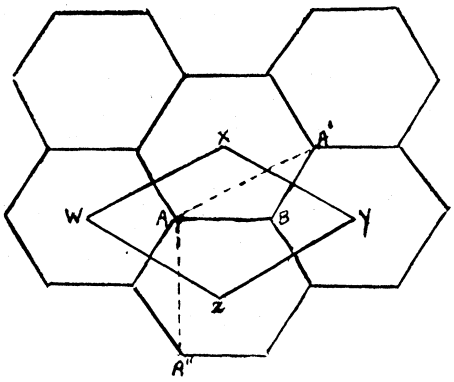

FIG. 1.

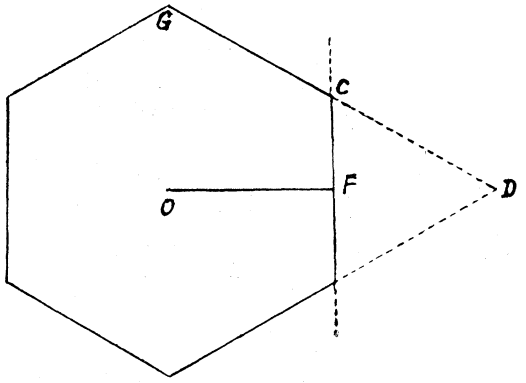

FIG. 2.

hexagon (Fig. 2) whose sides are distant $1/\sqrt{3}a$ from its center. It is easily shown that this zone contains one electron per atom, for the density of electron states in k-space is $2A$, where A is the area of the crystal. The zone in question therefore contains $2A\times 2/(\sqrt{3}a^2)$ electron states. But the atomic area (area per atom in the layer) is $\sqrt{3}a^2/4$, and the number of atoms is $4A/\sqrt{3}a^2$, which is exactly equal to the number of electrons in the zone.

The zone containing two states per atom is obtained by extending the sides of the hexagon to form a six pointed star.

Let us now consider the problem from the viewpoint of the "tight binding approximation." If $X(r)$ is the normalized orbital $2p_z$ wave function for an isolated atom, then the wave function in the tight binding approximation has the form:

$$\psi=\varphi_1+\lambda\varphi_2 \tag{2.1}$$

where

$$\left.\begin{aligned}\varphi_1&=\textstyle\sum_A \exp[2\pi i\mathbf{k}\cdot\mathbf{r}_A]X(\mathbf{r}-\mathbf{r}_A)\\ \text{and}\quad \varphi_2&=\textstyle\sum_B \exp[2\pi i\mathbf{k}\cdot\mathbf{r}_B]X(\mathbf{r}-\mathbf{r}_B)\end{aligned}\right\}. \tag{2.2}$$

The first sum is taken over A and all the lattice points generated from it by primitive lattice translations; the second sum is similarly over the points generated from B.

From variational principles it is known that to get the best value of E for this approximation we substitute in the wave equation from (2.1), multiply by φ_1 and φ_2, respectively, integrate, and then eliminate λ from the resulting two equations.

Let us neglect the overlap of the p_z wave functions centered on different atoms, i.e., let us

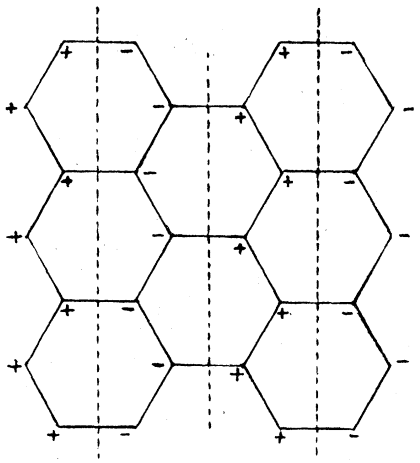

FIG. 3.

assume

$$\int X(\mathbf{r}-\mathbf{r}_A)X(\mathbf{r}-\mathbf{r}_B)d\tau=0. \tag{2.3}$$

Then, substituting (2.1) in

$$H\psi=E\psi \tag{2.4}$$

and proceeding as outlined, we get

$$H_{11}+\lambda H_{12}=ES,$$
$$H_{21}+\lambda H_{22}=\lambda ES,$$

where

$$H_{11}=\int \phi_1^* H\phi_1 d\tau, \quad H_{12}=H_{21}^*=\int \phi_1^* H\phi_2 d\tau,$$

$$H_{22}=\int \phi_2^* H\phi_2 d\tau$$

and

$$S=\int \phi_1^*\phi_1 d\tau=\int \phi_2^*\phi_2 d\tau.$$

Eliminating λ we obtain the secular equation

$$\begin{vmatrix} H_{11}-ES & H_{12} \\ H_{21} & H_{22}-ES \end{vmatrix}=0,$$

from which it is found that

$$E=\frac{1}{2S}\{H_{11}+H_{22} \pm((H_{11}-H_{22})^2+4|H_{12}|^2)^{\frac{1}{2}}\}. \tag{2.5}$$

Now by virtue of the neglect of the overlap integrals, $S=N$, the number of unit cells in the crystal, and by symmetry $H_{11}=H_{22}$. Introducing

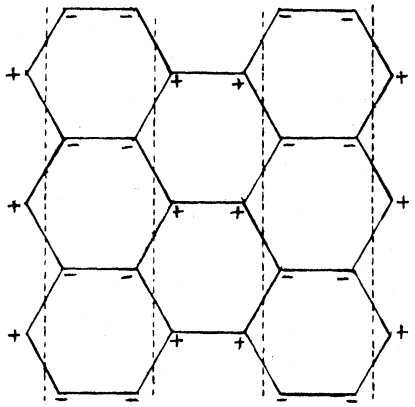

FIG. 4.

$$H_{11}'=H_{22}'=\frac{1}{N}H_{11}=\frac{1}{N}H_{22}, \tag{2.6}$$

$$H_{12}'=\frac{1}{N}H_{12}$$

we have, finally

$$E=H_{11}'\pm|H_{12}'|. \tag{2.7}$$

The positive sign will apply to the outside of the hexagonal zone, the negative sign to the inside. The discontinuity of energy across the zone boundary is then

$$\Delta E=2|H_{12}'|. \tag{2.8}$$

Let us now calculate $H_{11}'=H_{22}'$ and H_{12}'.

$$H_{11}'=\frac{1}{N}\sum_{A,A'}\exp[-2\pi i\mathbf{k}\cdot(\mathbf{r}_A-\mathbf{r}_{A'})] \times\int X^*(\mathbf{r}-\mathbf{r}_A)HX(\mathbf{r}-\mathbf{r}_{A'})d\tau.$$

Omitting the exchange integrals over atoms more distant than nearest neighbors amongst the atoms A, and writing

$$E_0=\int X^*(\mathbf{r})HX(\mathbf{r})d\tau,$$

$$\gamma_0'=-\int X^*(\mathbf{r}-\boldsymbol{\varrho}')HX(\mathbf{r})d\tau,$$

where $\boldsymbol{\varrho}'=\mathbf{a}_1$ (say) is a vector joining nearest

neighbors among the atoms A, we get

$$H_{11}'=E_0-2\gamma_0'(\cos 2\pi k_y a+2\cos\pi k_x a\sqrt{3}\cos\pi k_y a).$$

If we write

$$H=H_0+(H-H_0),$$

where H_0 is the Hamiltonian for an isolated carbon atom, and put

$$H-H_0=V-U<0,$$

where V is the periodic potential of the lattice and U is the potential field for an isolated atom, we may write, since $H_0X=E_0X$,

$$E_0=\bar{E}-\int X^*(\mathbf{r})(U-V)X(\mathbf{r})d\tau, \quad (2.9)$$

and

$$\gamma_0'=\int X^*(\mathbf{r}-\boldsymbol{\varrho}')(U-V)X(\mathbf{r})d\tau>0. \quad (2.10)$$

E_0 is the energy of an electron on the $2p_z$ state in carbon.

Let us next calculate H_{12}. For this, we shall consider only interactions between nearest neighbors in the lattice, the nearest neighbors of atoms of type A being always atoms of type B and *vice versa*. Writing

$$\gamma_0=\int X^*(\mathbf{r}-\boldsymbol{\varrho})(U-V)X(\mathbf{r})d\tau>0, \quad (2.11)$$

where $\boldsymbol{\varrho}=\mathbf{AB}$, we obtain

$$H_{12}'=-\gamma_0(\exp[-2\pi i k_x(a/\sqrt{3})]+2\cos\pi k_y a\cdot\exp[2\pi i k_x(a/2\sqrt{3})]),$$

so that

$$|H_{12}|^2=\gamma_0^2(1+4\cos^2\pi k_y a+4\cos\pi k_y a\cos\pi k_x\sqrt{3}a).$$

The energies at various points may now be written down:

at O: $E=E_0-3\gamma_0-6\gamma_0'$,
at D: $E=E_0+3\gamma_0-6\gamma_0'$,
at C: $E=E_0+3\gamma_0'$;
at F, inside: $E=E_0-\gamma_0+2\gamma_0'$,
outside: $E=E_0+\gamma_0+2\gamma_0'$.

Over a side of the zone there is across the boundary at any point a discontinuity of energy of amount

$$2\gamma_0(2\cos\pi k_y a-1) \quad (2.12)$$

which is greatest at the center and decreases to zero at the corners.

The degeneracy at C and similar points, and the zero-energy gap at these points, are presumably consequences of the symmetry of the lattice, and are independent of the approximations considered.

It is easy to determine the form of the wave functions corresponding to different k. Consider, for example, the point F. Inside the zone boundary $\lambda=-1$, and consequently the nodes of the wave functions bisect the lines joining A and B atoms: the sign of the wave function at lattice points is designated by $+$ or $-$ signs in Fig. 3. It is readily seen how the expression for the energy arises. Since an atom has two nearest neighbors of the same sign, and one opposite, and since $(V-U)$ is negative, there will be a contribution to the energy from exchange between nearest neighbors of $-2\gamma_0+\gamma_0=-\gamma_0$. Of second neighbors, we have two of the same sign and four opposite, giving us $2\gamma_0'$.

In Fig. 4 are represented the nodes of the wave function corresponding to a point *outside* the zone boundary at A. Since here $\lambda=1$, the maxima and minima correspond to the nodes of the previous case. The expression for the energy can be verified in the same way. Similar arguments may be carried out for other points in k-space.

Consider next the energy contours. Near the bottom of the band they are circular:

$$E=E_0-3\gamma_0-6\gamma_0'+\pi^2(\gamma_0+6\gamma_0')(k_x^2+k_y^2)a^2. \quad (2.13)$$

The hexagon whose sides are distant $1/2a$ from the center of the Brillouin zone is a surface of constant energy. (This conclusion is, of course, true only in the approximation which we are

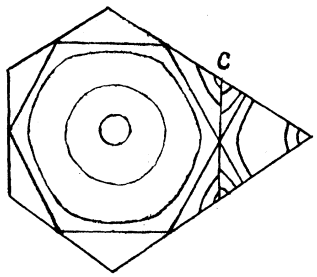

FIG. 5.

here considering.) Curves of constant energy are indicated in Fig. 5. Near the corner C

$$E=E_0+3\gamma_0'\pm\sqrt{3}\pi\gamma_0|\mathbf{k}-\mathbf{k}_c|a-3\pi^2\gamma_0'|\mathbf{k}-\mathbf{k}_c|^2a^2, \tag{2.14}$$

and the surfaces of constant energy are again circular.

It should be noted that, when the reduced zone scheme is used, the energy contours have the same shape for the second zone as for the first.

3. NUMBER OF FREE ELECTRONS AND CONDUCTIVITY OF A SINGLE HEXAGONAL LAYER

In this section we shall neglect γ_0' relative to γ_0. We then have

$$|E-E_c|\approx\sqrt{3}\pi\gamma_0 a|\mathbf{k}-\mathbf{k}_c| \tag{3.1}$$

near the corners of the Brillouin zone. At the absolute zero of temperature, the hexagonal zone will be completely filled, and the next zone will be completely empty. At higher temperatures, there will be some thermal "overflow" into the outer zone. The extent of this overflow will be (in energy) of amount comparable to kT. The energy contour $E=E_c+kT$ is approximately circular with radius $kT/(\pi\sqrt{3}\gamma_0 a)$ provided $kT\gg\gamma_0$, which is certainly the case at ordinary temperatures.

Now if $N(E)dE$ is the number of electronic energy states in the energy interval dE,

$$N(E)=2A\int\frac{d\sigma}{|\mathrm{grad}_k E|}, \tag{3.2}$$

where A is the area of the lattice, and the integral is taken over the curve on which the energy is E. This gives, since $|\mathrm{grad}_k E|$ is constant,

$$N(E)=\frac{4A|E-E_c|}{3\pi\gamma_0^2a^2}, \tag{3.3}$$

or, since the area per atom is $\sqrt{3}a^2/4$,

$$N(E)/N_a=\frac{1}{\pi\sqrt{3}\gamma_0^2}|E-E_c|=\frac{|\epsilon|}{\pi\sqrt{3}\gamma_0^2}, \tag{3.4}$$

where N_a is the number of atoms in the lattice. The form of $N(E)$ near E_c is illustrated in Fig. 6.

Conduction will take place through the electrons excited into the upper band, and through the positive holes (equal in number) created in the lower band.

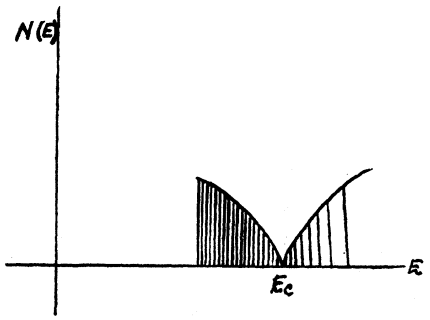

FIG. 6.

To calculate the number of these, we must know the Fermi distribution. For moderate temperatures, $N(E)$ is even in $\epsilon=|E-E_c|$ over the whole range in which the Fermi distribution is different from its value at absolute zero. Therefore, in the Fermi distribution function

$$f(E)=\frac{1}{\exp[(E-\zeta)/kT]+1},$$

we shall have $\zeta=E_c$; in other words, we may write

$$f(E)=f(\epsilon)=1/(e^{\epsilon/kT}+1). \tag{3.5}$$

It follows that the number of free electrons plus positive holes per atom is

$$2\int_0^\infty\frac{N(E)}{N_a}f(E)dE=\frac{\pi}{6\sqrt{3}}\left(\frac{kT}{\gamma_0}\right)^2. \tag{3.6}$$

Now C. A. Coulson[3] has estimated that γ_0 is about 20 kcal./mole, or about 0.9 ev. At room temperature $kT=0.025$ ev. Therefore the "effective number of free electrons" n_{eff}, per atom, is

$$n_{\mathrm{eff}}=2.3\times10^{-4}.$$

To determine the conductivity of our graphite layer, let us calculate directly the current in the presence of a given external field. Explicitly, this is given by

$$\mathbf{j}=2\int e\mathbf{v}f(\mathbf{k})d\tau_k\cdot(2/c), \tag{3.7}$$

where $f(\mathbf{k})$ is the Fermi distribution in the presence of the field, and $\frac{1}{2}c=3.37$A is the dis-

[3] Private communication to the author.

tance between graphite layers. $f(\mathbf{k})$ is given by

$$f(\mathbf{k})=f_0\left(\mathbf{k}-\frac{e\tau}{h}\mathbf{F}\right), \tag{3.8}$$

where f_0 is the undisturbed Fermi function (3.5), and τ is the inverse of the probability of scattering per unit time. For moderate fields we may expand this

$$f(\mathbf{k})=f_0(\mathbf{k})+g(\mathbf{k}) \tag{3.9}$$

where

$$g(\mathbf{k})=-\frac{e\tau}{h}\mathbf{F}\cdot\mathrm{grad}f_0. \tag{3.10}$$

Writing

$$\mathbf{v}=\frac{1}{h}\mathrm{grad}_k E,\quad \mathrm{grad}f_0=\frac{df_0}{dE}\mathrm{grad}_k E,$$

$$d\tau_k=d\sigma_k\frac{dE}{|\mathrm{grad}E|},$$

$d\sigma_k$ being element of length on the curve $E=$constant, we have

$$\mathbf{j}=-\frac{4e^2\tau}{h^2c}\int\frac{df_0}{dE}\left[\int(\mathbf{F}\cdot\mathrm{grad}E)\frac{\mathrm{grad}E}{|\mathrm{grad}E|}d\sigma_k\right]dE,$$

where the inner integral is over the surface of constant energy E. The component of current $\mathbf{j}_F$ in the direction of the field is

$$\mathbf{j}_F=-\frac{4e^2\tau}{h^2c}\int\frac{df_0}{dE}\left[\frac{1}{F}\int\frac{(F\cdot\mathrm{grad}E)^2}{|\mathrm{grad}E|}d\sigma_k\right]dE.$$

Averaging over all directions of the field in the plane of the layer we get

$$\sigma_{||}=-\frac{2e^2\tau}{h^2c}\int\frac{df_0}{dE}\left[\int|\mathrm{grad}E|\,d\sigma_k\right]dE. \tag{3.11}$$

By virtue of (3.1) this is

$$\sigma_{||}=-\frac{8\pi e^2\tau}{h^2c}\int|\epsilon|\frac{\partial f_0}{\partial\epsilon}d\epsilon$$
$$=\frac{16\pi e^2\tau}{h^2c}kT\log 2. \tag{3.12}$$

To get a numerical value of the conductivity it is necessary to know something about τ, or alternatively about the mean free path $l=v\tau$. We will not attempt to calculate this quantity in the present paper. Let us note, however, that experimental evidence requires that the mean free path decrease with temperature faster than T^{-1}. In this connection, one might call attention to the sharply increased mobility found in polar salts at low temperatures for thermal electrons. The mean free path has the form

$$l=C\left(\frac{T}{\theta}\right)^{\frac{1}{2}}(e^{\theta/T}-1),^4 \tag{3.13}$$

where θ is the Debye temperature and C is a constant of the order of one atomic distance. The conductivity electrons in graphite are also essentially thermal. If the mean free path is assumed to be of the same order of magnitude as given by (3.13), with $C=2\times10^{-8}$ cm and θ estimated from specific heat evidence as about 2000°C we will get

$$l\approx3\times10^{-6}\text{ cm}. \tag{3.14}$$

This gives rise to a resistivity

$$\rho\approx5\times10^{-5}\text{ ohm-cm}.$$

It seems therefore, that (3.14) gives at least the right order of magnitude for l. This point, and the temperature dependence of l, seem worth further investigation.

From the formula

$$\sigma=N_{\mathrm{eff}}e^2\tau/m_{\mathrm{eff}}, \tag{3.15}$$

we can calculate the "mean effective mass," m_{eff}, of our conductivity electrons. This is found to be

$$m_{\mathrm{eff}}=\frac{h^2kT}{36\log 2\cdot a^2\gamma_0^2} \tag{3.16}$$

which yields, on numerical evaluation, at room temperature

$$m_{\mathrm{eff}}=1/18\text{ electron mass}. \tag{3.17}$$

4. THE BRILLOUIN ZONES OF GRAPHITE

The graphite lattice is built up of hexagonal layers whose relation to each other is indicated in Fig. 7. Dotted lines indicate one layer, and

[4] N. F. Mott and R. A. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1940), p. 107. Note also the increase of mobility with decreasing temperature in the semiconductor Cu_2O shown in Fig. 66, p. 168.

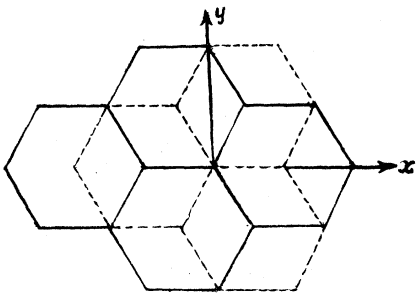

FIG. 7.

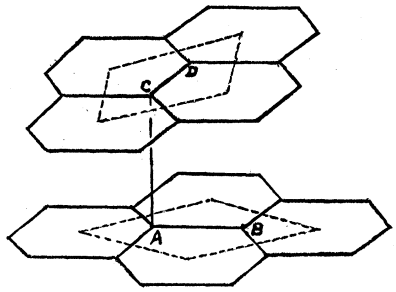

FIG. 8.

the full lines the one immediately above it. A set of basic displacement vectors of the lattice is

$$\mathbf{a}_1=[\tfrac{1}{2}\sqrt{3}a,\ -\tfrac{1}{2}a,\ 0],\quad \mathbf{a}_2=[0,\ a,\ 0],\quad \mathbf{a}_3=[0,\ 0,\ c],\qquad (4.1)$$

c being twice the distance between layers of the lattice. In Fig. 8 the relation between the layers is shown in perspective. The points A, B, C, D are the four atoms of a unit cell.

The volume of the unit cell is

$$V_{\text{cell}}=\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)=\frac{\sqrt{3}}{2}a^2c,$$

so that the atomic volume is

$$V_{\text{atomic}}=\frac{\sqrt{3}a^2c}{8}.\qquad (4.2)$$

The intercepts of a possible unit cell on adjacent planes are shown in Fig. 8. The cell would extend beyond these two planes on each side halfway to the next planes, which are not shown.

Reciprocal lattice vectors corresponding to (4.1) are

$$\mathbf{b}_1=\left[\frac{2}{\sqrt{3}a},\ 0,\ 0\right],$$

$$\mathbf{b}_2=\left[\frac{1}{\sqrt{3}a},\ \frac{1}{a},\ 0\right],$$

$$\mathbf{b}_3=\left[0,\ 0,\ \frac{1}{c}\right].$$

It follows that the lowest Brillouin zone is bounded by six vertical planes forming a right hexagonal cylinder whose sides are distant $1/\sqrt{3}a$ from its axis. It appears at first that the height of the lowest zone is $1/c$. This is, however, not the case, for the plane at height $1/2c$ corresponds to Bragg reflection of waves whose wave-length is $2c$. Thus reflections from successive planes (distance $c/2$) differ in phase by π, and therefore destroy each other. The structure factor therefore vanishes on the planes $k_z=\pm(1/2c)$, and there is no energy discontinuity over them. The horizontal boundaries of the first zone are therefore at $k_z=\pm(1/c)$. The lowest Brillouin zone so described has the volume $4/\sqrt{3}a^2c$. But the density of states is twice the volume of the crystal, that is,

$$2\times(\text{number } N \text{ of cells})\times(\text{volume of cell})=\sqrt{3}a^2cN.$$

Thus there are 4 N electron states in the lowest Brillouin zone, or one per atom. Since as in the case of a single layer, there is just one "conductivity" electron per atom, the lowest Brillouin zone will be just filled at the absolute zero of temperature.

In Fig. 9 we indicate the *upper half* of the zone in question.

Let us now consider the problem from the viewpoint of the "tight binding approximation." As in the case of a single layer, let $X(r)$ be the $2p_z$ wave function of an isolated C atom. Then we assume for the collective wave function of the crystal

$$\Psi=\sum_{i=1\cdots4}\lambda_i\Psi_i$$

$$=\sum_{i=1\cdots4}\lambda_i(\textstyle\sum_\alpha \exp[2\pi i\mathbf{k}\cdot\mathbf{r}_i^\alpha]X(\mathbf{r}-\mathbf{r}_i^\alpha)),\qquad (4.3)$$

where $i=1, 2, 3, 4$ correspond to atoms of the type A, B, C, D, respectively, and α enumerates the different atoms of a given type in the crystal.

Proceeding exactly as in the case of the hexagonal layer, we are led to a secular equation for the energy

$$\|H_{ij}'-E\delta_{ij}\|=0. \tag{4.4}$$

Now the diagonal elements are

$$H_{11}'=H_{22}'=H_{33}'=H_{44}'=E_0'-2\gamma_0'(\cos 2\pi k_y a + 2\cos\pi\sqrt{3}k_y a\cos\pi k_y a)=H_0. \tag{4.5}$$

E_0' is not quite the same as the E_0 in the previous section, due to a difference in the potential; we shall, however, subsequently drop the prime for convenience.

In calculating the non-diagonal terms, we shall at first consider first and second neighbors *in* the planes, and also first and second neighbors *between* planes.

The elements may now be calculated:

H_{12}. This is equal to

$$-\gamma_0(\exp[-2\pi ik_x(a/\sqrt{3})]+2\cos\pi k_y a\cdot\exp[\pi ik_x(a/\sqrt{3})])$$

where

$$\gamma_0=\int X^*(\mathbf{r}-\varrho_{AB})(U-V)X(\mathbf{r})d\tau>0.$$

H_{13}. This is equal to

$$2\gamma_1\cos\pi k_z c$$

where

$$\gamma_1=\int X^*(\mathbf{r}-\varrho_{AC})(V-U)X(\mathbf{r})d\tau.$$

$\gamma_1>0$ because $(V-U)$ is negative, and

$$X^*(\mathbf{r}-\varrho_{AC}),$$

$X(\mathbf{r})$ have opposite signs between the planes, where the contribution to the integral is greatest.

H_{14}. This is equal to

$$2\gamma_1'\cos\pi k_z c(\exp[2\pi ik_x(a/\sqrt{3})]+2\cos\pi k_y a\cdot\exp[-\pi ik_x(a/\sqrt{3})]),$$

where

$$\gamma_1'=\int X^*(\mathbf{r}-\varrho_{AD})(V-U)X(\mathbf{r})d\tau,$$

and is almost certainly positive, though it has not been evaluated.

The other elements may be written in terms of the above. It may easily be verified that

$$H_{23}=H_{14},\quad H_{24}=H_{23}^*,\quad H_{34}=H_{12}^*.$$

If we put the diagonal elements equal to H_0, $2\cos\pi k_z c=\Gamma$ and

$$\exp[-2\pi ik_x(a/\sqrt{3})]+2\cos\pi k_y a\cdot\exp[\pi ik_x(a/\sqrt{3})]=S, \tag{4.5}$$

the secular equation becomes

$$\begin{vmatrix} E-H_0 & -\gamma_0 S & \gamma_1\Gamma & \gamma_1'\Gamma S \\ -\gamma_0 S^* & E-H_0 & \gamma_1'\Gamma S & \gamma_1'\Gamma S \\ \gamma_1\Gamma & \gamma_1'\Gamma S & E-H_0 & -\gamma_0 S^* \\ \gamma_1'\Gamma S^* & \gamma_1'\Gamma S & -\gamma_0 S & E-H_0 \end{vmatrix}=0. \tag{4.6}$$

The exact solution of this equation presents some difficulty. We shall neglect γ_1' at first, and later treat it as a perturbation. In the lowest approximation, then, we get on solving,

$$E=H_0\pm\tfrac{1}{2}\gamma_1\Gamma\pm[\tfrac{1}{4}\gamma_1^2\Gamma^2+\gamma_0^2|S|^2]^{\frac{1}{2}}.$$

With regard to the sign in front of the $\frac{1}{2}\gamma_1\Gamma$ term, the choice here is immaterial, a change of sign merely corresponding to reflection in the plane $k_z=1/2c$ of the two halves of the upper half-zone, and similarly in the lower half-zone. By choosing the negative sign, we adhere to the convention that the bottom of the zone (point of lowest energy) should be at the center.

The signs $\pm$ in front of the square root correspond to the outside and inside of the lowest zone, respectively, i.e. inside

$$E=H_0-\tfrac{1}{2}\gamma_1\Gamma-[\tfrac{1}{4}\gamma_1^2\Gamma^2+\gamma_0^2|S|^2]^{\frac{1}{2}}, \tag{4.7a}$$

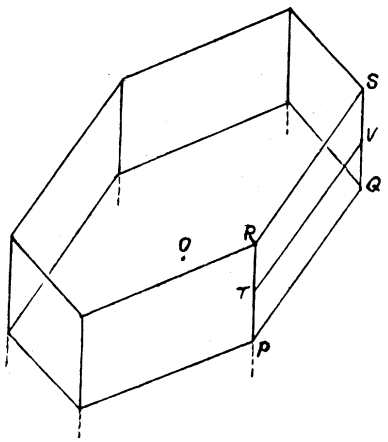

FIG. 9.

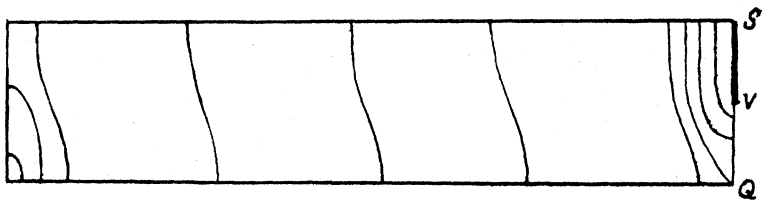

FIG. 10. Energy contours on the inside of the zone.

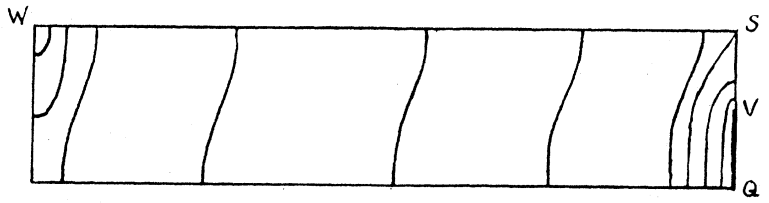

FIG. 11. Energy contours on the outside of the zone.

and outside

$$E=H_0-\tfrac{1}{2}\gamma_1\Gamma+[\tfrac{1}{4}\gamma_1^2\Gamma^2+\gamma_0^2|S|^2]^{\frac{1}{2}}. \quad (4.7b)$$

The energy inside is always $\leqslant H_0=E_0$; it has the latter value for $|S|^2=0$ and $\Gamma<0$ (i.e., $k_z\geqslant 1/2c$). Now

$$|S|^2=(1-2\cos\pi k_y a)^2 \quad (4.8)$$

on the sides of the zone, and is zero at the vertical edges. Thus the maximum energy inside (E_0) is attained on the upper (and lower) quarter of the vertical edges of the zone.

By a similar argument, the energy outside has its *minimum* value, (which is also E_0) on the middle half of the vertical edges of the zone. The energy gap is therefore zero only at twelve points; two on each vertical edge.

In Fig. 10 we indicate the form of the sections of surfaces of constant energy by a plane such as that through $OSVQ$ in Fig. 9.

In Fig. 11 we represent the cross sections of the energy contours by a plane such as the extension of $PQRS$ beyond QS. W is at a tip of the six-pointed star which forms the upper boundary of the second zone, this zone being obtained by extending the vertical sides and the top and bottom of the first zone.

The energy contours in planes $k_z=$constant will have a form similar to those shown in Fig. 5. The hexagonal lines of constant energy will appear in each plane, but will correspond to different energies in different planes. The zero energy gap will of course only appear in the planes $k_z=\pm(1/2c)$.

The strong anisotropy in some of the properties of graphite (electrical and thermal conductivity, magnetic susceptibility) is caused by the very anisotropic form of the energy surfaces near the corner of the zone. These anisotropies will become greater as the temperature is lowered, and the surfaces of energy ($E_0\pm kT$) approach segments of lines.

Let us now see how this picture is altered if we take account of γ_1', the exchange integral between atoms such as A and D in Fig. 8. If we expand (4.6) to terms of the first order in γ_1' and solve, using the relation (4.7), we find that the energy is increased by an amount

$$\epsilon=\gamma_0\gamma_1'\Gamma\frac{\gamma_0|S|^2(S+S^*)-2E_{\rm un}(S^2+S^{*2})}{2E_{\rm un}\gamma_1\Gamma\pm 4\gamma_0^2|S|^2}, \quad (4.9)$$

where $E_{\rm un}$ is the "unperturbed" energy given by (4.7). Since in the vertical edges $S=0$, $\epsilon=0$ there both inside and out, and consequently there is no overlap on these edges. Also, ϵ vanishes identically in the planes $k_z=\pm 1/2c$. Thus, at the only points at which the energy is continuous on crossing the boundary of the zone, $\epsilon=0$, and it is also identically zero in two directions at right angles through this point. This alone makes it seem likely that the addition of ϵ will not give rise to any overlapping of the zones. More detailed consideration shows that such is in fact the case.

It should be noted finally that the two energy bands corresponding to the zones considered above arise from the same energy level (corresponding to the $2p$-state for C). The "splitting" of the energy level into *two* bands when the C

atoms are brought together to form the crystal is caused by the fact that the graphite crystallizes in a form having more than one atom per unit cell. Thus, the general properties of the zones (and in particular their touching) does not depend on the details of the potential field, but rather on the geometrical form of the lattice.

5. NUMBER OF FREE ELECTRONS IN GRAPHITE

The first problem is to find $N(E)$, the distribution of energy levels. The well-known formula for this is

$$N(E)=2V\int\frac{d\sigma}{|\mathrm{grad}_k E|},$$

where V is the volume of the crystal, and the integral is taken over the surface on which the energy has the constant value E. The formula may be readily transformed to

$$N(E)=2V\int\frac{dk_x dk_y}{(\partial E/\partial k_z)_{\text{surface}}}, \tag{5.1}$$

the integral now being taken over the projection of the surface $E=$constant on the (k_x-k_y) plane.

Throughout this and the subsequent sections we shall consider only the exchange integrals γ_0 and γ_1 (nearest neighbors in and between planes).

Let us write (4.7)

$$\epsilon=E-E_0=-\gamma_1\cos\pi k_z c \pm(\gamma_1^2\cos^2\pi k_z c+\gamma_0^2|S|^2)^{\frac{1}{2}}. \tag{5.2}$$

Calculating $\partial\epsilon/\partial k_z$ and eliminating k_z we get, for $2\gamma_1>\epsilon>0$,

$$\left(\frac{\partial\epsilon}{\partial k_z}\right)_{\text{surface}}=\frac{1}{2}\frac{\epsilon c}{\gamma_0^2|S|^2+\epsilon^2}\times(4\gamma_1^2\epsilon^2-(\gamma_0^2|S|^2-\epsilon^2)^2)^{\frac{1}{2}}. \tag{5.3}$$

Now we shall be interested in $\epsilon\approx kT\ll\gamma_0$. In this case we may write

$$|S|^2=3\pi^2(k_x^2+k_y^2)a^2=u.$$

The integral (5.1) may be transformed to an integral over u:

$$N(E)=\frac{4V}{3\pi a^2 c\epsilon}\int_0^{(\epsilon^2+2\epsilon\gamma_1)/\gamma_0^2}\frac{(\gamma_0^2u+\epsilon^2)du}{(\gamma_1^2\epsilon^2-\frac{1}{4}(\gamma_0^2u-\epsilon^2)^2)^{\frac{1}{2}}}$$

which yields, on evaluation

$$N(E)=\frac{8V}{3\pi a^2 c\gamma_0^2}\left[(4\gamma_1^2-\epsilon^2)^{\frac{1}{2}}+|\epsilon|\pi+2\epsilon\sin^{-1}\frac{\epsilon}{2\gamma_1}\right]; \tag{5.4}$$

the result has been extended to the case $\epsilon<0$ by observing that it is, for $\epsilon\ll\gamma_0$, *even* in ϵ.

The result (5.4) holds only for $\epsilon<2\gamma_1$. Coulson[3] has estimated that $\gamma_1\approx\frac{1}{10}\gamma_0=0.09$ ev. This corresponds to a temperature of nearly 1000°C, so that, insofar as calculations of the properties of graphite near room temperature are concerned, the expression (5.4) will be adequate.

It should be noticed that $N(E)$ does not go to zero when $\epsilon\to0$, but approaches a finite value proportional to γ_1 (see Fig. 12). Nevertheless, as can easily be seen, at the absolute zero of temperature the number of free electrons is zero.

The number of free electrons is in fact approximately

$$N_{\text{eff}}=2\int_0^{2\gamma_1}N(E)f(E)dE,$$

where

$$f(E)=\frac{1}{e^{\epsilon/kT}+1},$$

as in the case of the plane layer. Now with small error we may expand $N(E)$:

$$N(E)=\frac{8V\gamma_1}{3\pi a^2 c\gamma_0^2}\left[2+\frac{|\epsilon|}{\gamma_1}\pi+\frac{3}{4}\frac{\epsilon^2}{\gamma_1^2}+O\left(\frac{\epsilon^4}{\gamma_1^4}\right)+\cdots\right]$$

and extend the integral from 0 to ∞. Doing

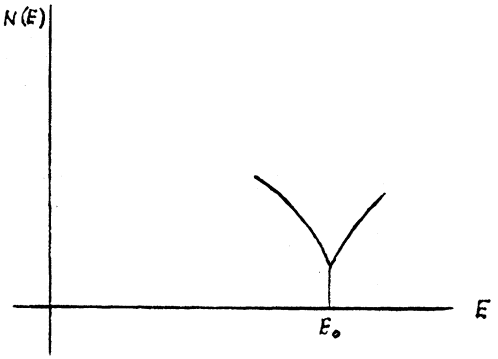

FIG. 12.

this we obtain

$$N_{\text{eff}}=\frac{32V}{3\pi a^2c}\frac{kT\gamma_1}{\gamma_0^2}\left[s_1+\frac{\pi}{2}\frac{kT}{\gamma_1}s_2+\frac{3}{4}\left(\frac{kT}{\gamma_1}\right)^2 s_3+O\left(\left(\frac{kT}{\gamma_1}\right)^3\right)+\cdots\right] \quad (5.5)$$

where

$$s_n=\sum_{m=0}(-1)^m\frac{1}{(m+1)^n}; \quad (5.6)$$

$s_1=\log 2$, $s_2=\pi^2/12$, etc., the s_n's being tabulated in Dale's *Mathematical Tables*.

Now the number of free electrons per atom is $n_{\text{eff}}=N_{\text{eff}}/N_a$, N_a being the number of atoms. Since the atomic volume is $\sqrt{3}a^2c/8$,

$$N_a=8V/\sqrt{3}a^2c.$$

So

$$n_{\text{eff}}=\frac{4}{\sqrt{3}\pi}\frac{kT\gamma_1}{\gamma_0^2}\left[s_1+\frac{\pi}{2}\frac{kT}{\gamma_1}s_2+\frac{3}{2}\left(\frac{kT}{\gamma_1}\right)^2 s_3+O\left(\left(\frac{kT}{\gamma_1}\right)^3\right)+\cdots\right] \quad (5.7)$$

$$=2.25\times 10^{-3}$$

at room temperature. This is not at all in agreement with the value of 2.3×10^{-4} obtained by treating a single hexagonal layer; in fact, the dependence of n_{eff} on T is quite different in the two cases. On the other hand, as we shall see in the next section, the conductivities in the plane agree to the first order. Thus the discrepancy is merely caused by our definition of n_{eff}, and is compensated by a corresponding change in m_{eff}, the effective mass.

6. CONDUCTIVITY IN THE DIRECTION OF THE LAYERS AND PERPENDICULAR TO THEM

By a procedure closely parallelling that used in Section 3 for the single hexagonal layer, we obtain for the conductivity in the direction of the vector $\mathbf{u}$, if we assume that τ does not depend significantly on k,

$$\sigma(\mathbf{u})=-\frac{2e^2\tau}{h^2}\int\frac{df_0}{dE}\times\left[\int_{E=\text{const}}(\mathbf{u},\mathbf{n})^2|\text{grad}_k E|\,dS_k\right]dE, \quad (6.1)$$

where $\mathbf{n}$ is the normal to the surface $E=$constant and dS_k is the element of area in this surface. Averaging over-all directions in the plane and putting $dS_k=8\pi\kappa d\kappa/n_z$, where $\kappa^2=\kappa_x^2+\kappa_y^2$,

$$\sigma_{11}=-\frac{e^2\tau}{h^2}\int\frac{df_0}{dE}\left[\int_{(E)}\frac{(\partial E/\partial\kappa)^2}{\partial E/\partial k_z}8\pi\kappa d\kappa\right]dE. \quad (6.2)$$

On the other hand, the conductivity perpendicular to the layers is

$$\sigma_\perp=-\frac{2e^2\tau}{h^2}\int\frac{df_0}{dE}\left[\int_{(E)}\frac{\partial E}{\partial k_z}8\pi\kappa d\kappa\right]dE. \quad (6.3)$$

On the surface $\epsilon=$constant,

$$\frac{\partial\epsilon}{\partial\kappa}=\frac{2\epsilon\gamma_0^2(3\pi^2a^2y)^{\frac{1}{2}}}{\gamma_0^2y+\epsilon^2}, \quad (6.4)$$

where $3\pi^2(k_x^2+k_y^2)a^2=y$.

Now in the Eq. (5.2), if we remain within the limit $|\epsilon|<\gamma_1$, $|S|^2$ may be replaced by y with an error of order $(\gamma_1/\gamma_0)^2\approx 1$ percent. In terms of y, the integral in the square bracket of (6.2) may be written

$$\frac{16\epsilon\gamma_0^4}{c}\int_0^{(\epsilon^2+2\epsilon\gamma_1)/\gamma_0^2}\frac{ydy}{(\gamma_0^2y+\epsilon^2)[4\epsilon^2\gamma_1^2-(\gamma_0^2y-\epsilon^2)^2]^{\frac{1}{2}}}.$$

On evaluation this yields

$$\frac{8\epsilon}{c}\left\{\pi+2\sin^{-1}\frac{\epsilon}{2\gamma_1}-\frac{\epsilon}{[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}}\times\left[\log\frac{\epsilon+\gamma_1-[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}}{\epsilon+\gamma_1+[\gamma_1^2+\epsilon^2]^{\frac{1}{2}}}-\log\frac{[4\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-\gamma_1}{[4\gamma_1^2-\epsilon^2]^{\frac{1}{2}}+[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-\gamma_1}\right]\right\}. \quad (6.4a)$$

Let us note first that if we take only the leading term in this expression, we get

$$\sigma_{11}\doteqdot-\frac{8\pi e^2\tau}{h^2c}\int\frac{df_0}{dE}\epsilon dE=\frac{16\pi e^2\tau}{h^2c}kT\log 2 \quad (6.5)$$

which is precisely what we obtained in (3.12) for the case of a single plane layer. It follows from

this and (5.7) that to the first order the effective mass for electrons in motion parallel to the layers is independent of temperature. Taking account of the higher terms does not change the result drastically for moderate temperatures; at room temperature ($T=293°$C) we get, using the numerical values already indicated (including the value for l assumed in Section 3),

$$\sigma_{\parallel}^{-1}=\rho_{\parallel}=5.3\times10^{-5}\text{ ohm-cm.}$$

Turning now to $\sigma_{\perp}$, we get for the integral in the square bracket in (6.3)

$$\frac{8}{3}\frac{\epsilon^2\gamma_1 c}{\gamma_0^2a^2}\Big[\frac{\epsilon}{\gamma_1}\Big(\frac{\pi}{2}+\sin^{-1}\frac{\epsilon}{2\gamma_1}\Big)-\Big[1-\frac{\epsilon^2}{4\gamma_1^2}\Big]^{\frac{1}{2}}+\Big[1-\frac{\epsilon^2}{\gamma_1^2}\Big]^{\frac{1}{2}}\Big(\log\frac{\epsilon+\gamma_1-[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}}{\epsilon+\gamma_1+[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}}-\log\frac{[4\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-\gamma_1}{[4\gamma_1^2-\epsilon^2]^{\frac{1}{2}}+[\gamma_1^2-\epsilon^2]^{\frac{1}{2}}-\gamma_1}\Big)\Big] \tag{6.6}$$

valid up to $\epsilon=\gamma_1$. We shall neglect the contribution to (6.3) from beyond this point. To determine first the order of magnitude of the result, consider the leading term only under the bracket; this is $\log\gamma_1/\epsilon$. Then we get

$$\sigma_{\perp}\approx-\frac{16}{3}\frac{e^2\tau}{h^2}\frac{\gamma_1 c}{\gamma_0^2a^2}\int_{-\gamma_1}^{\gamma_1}\epsilon^2\log\frac{\gamma_1}{|\epsilon|}\frac{\partial f_0}{\partial\epsilon}d\epsilon \approx\frac{16\pi^2}{9}\frac{e^2\tau}{h^2}\frac{c}{a^2}\frac{\gamma_1(kT)^2}{\gamma_0^2}\log\frac{\gamma_1}{kT}. \tag{6.6}$$

This expression will give a good approximation only at temperatures somewhat below room temperature. We will use it, however, to indicate orders of magnitude. It gives for the anisotropy factor

$$\frac{\sigma_{\perp}}{\sigma_{\parallel}}\doteqdot\frac{\pi}{9\log2}\frac{c^2}{a^2}\frac{\gamma_1 kT}{\gamma_0^2}\log\frac{\gamma_1}{kT} \approx0.01\text{ at room temperature.} \tag{6.7}$$

Since this does not involve τ it is completely calculable without assumptions about mean free path.

A comparison of the formulas (5.5) and (6.5) gives

$$m_{\text{eff}}^{\parallel}=2h^2\gamma_1/3\pi^2a^2\gamma_0^2$$

for the "mean effective mass" of electrons moving parallel to the graphite planes. This is valid so long as $kT\ll\gamma_1$, and is equal to $\approx\frac{1}{3}$. Similarly, from (5.5) and (6.6) we obtain for the mean effective mass for motion across the graphite planes

$$m_{\text{eff}}^{\perp}=\frac{24\log2\cdot\hbar^2}{\pi c^2kT\log\gamma_1/kT}.$$

With decreasing temperature this increases as $1/T|\log T|$, becoming infinite as $T\to0$. At room temperature its value is ≈25 to 30 electron masses.

More accurate calculation of $\sigma_{\perp}$ by numerical integration at room temperature gives

$$\sigma_{\perp}^{-1}=\rho_{\perp}=4.8\times10^{-3}\text{ ohm-cm,}$$

and therefore

$$\frac{\sigma_{\perp}}{\sigma_{\parallel}}=\frac{\rho_{\parallel}}{\rho_{\perp}}=1.1\times10^{-2}.$$

It is of interest to note that the anisotropy depends on temperature, the ratio $\rho_{\perp}/\rho_{\parallel}$ becoming larger, i.e., the anisotropy becoming greater, with decreasing temperature. An attempt to confirm this prediction experimentally would be interesting; the measurement of $\sigma_{\perp}$ would, however, necessarily be difficult.

In Fig. 13 is plotted a graph of the ratio $\sigma_{\perp}/\sigma_{\parallel}$ for temperatures up to room temperature.

7. REMARKS ON OTHER PROPERTIES

Several qualitative remarks can be made about the magnetic susceptibility and the volume absorption properties of graphite. Graphite is strongly diamagnetic, and the diamagnetic susceptibility of single crystals can be expected to show marked anisotropy. For a field in the z-direction, the susceptibility depends on the value of the quantity

$$\frac{\partial^2\epsilon}{\partial k_x^2}\frac{\partial^2\epsilon}{\partial k_y^2}-\Big(\frac{\partial^2\epsilon}{\partial k_x\partial k_y}\Big)^2$$

over energy surfaces in the neighborhood of the boundary of the Fermi distribution, that is to say, near the zone boundary.[5] This is a large

[5] See Seitz, *Modern Theory of Solids*, pp. 594–595.

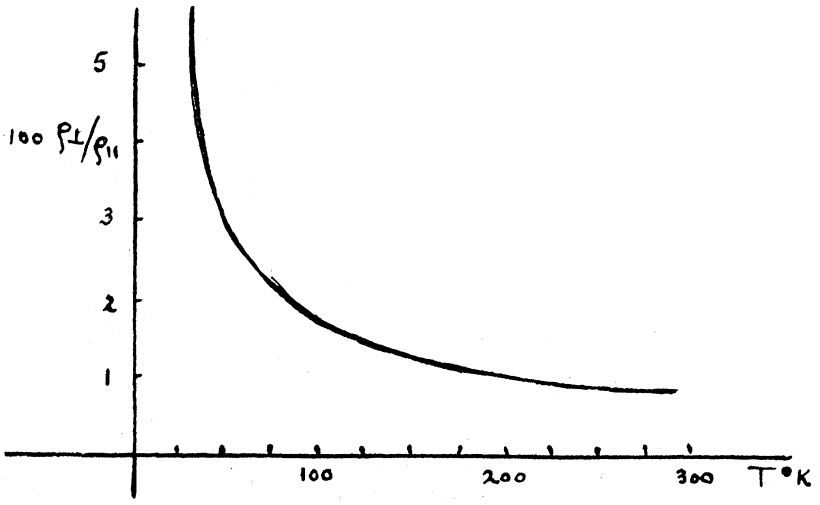

FIG. 13.

quantity, of order of magnitude $9\pi^4a^4\gamma_0^4/\gamma_1^2$, or about 6×10^4 times its value, $\hbar^4/m^2$, for free electrons. On the other hand, if the field is in the k_x-direction, say, the susceptibility depends on

$$\frac{\partial^2\epsilon}{\partial k_y^2}\frac{\partial^2\epsilon}{\partial k_z^2}-\left(\frac{\partial^2\epsilon}{\partial k_y\partial k_z}\right)^2.$$

Unlike the preceding case, this depends on T. It is, in fact, $\approx 3\pi^4a^2c^2kT\gamma_0^2/\gamma_1$, or $\approx kT\gamma_1/\gamma_0^2$ times the value for the field across the graphite planes. The difference may be ascribed to the difference in effective masses in the quantized orbits perpendicular to the field. The anisotropy is therefore of the same order of magnitude as that of the conductivity.

Our other remark concerns the "optical" absorption spectrum. It is well known[6] that electrons may under the influence of radiation make only "vertical" transitions in the reduced-zone scheme, that is, transitions in which the wave vector changes by one of the vectors of the inverse lattice. Let us then consider extreme cases. A transition from a point such as V (Fig. 9) involves zero-energy change. The greatest energy jump is from the center of the zone (O in Fig. 9) to a point at the middle of a vertical edge defining a "corner" of the star-shaped second zone. This is of amount $2[\gamma_1^2+9\gamma_0^2]^2\approx 6\gamma_0$. Transitions involving all intermediate energies are possible.

An energy jump of $6\gamma_0$ corresponds to a frequency of 1.31×10^{15} or a wave-length of about 2300A, fairly deep in the ultraviolet. Thus, there is absorption from the longest wave-lengths through the visible spectrum and a substantial part of the ultraviolet. At the extreme limits absorption will be weak, however, due to the small number of states involved. The greatest number of states will correspond to energies such as those at the mid-points of the sides of the zone, which will give rise to transitions with energy jumps of the order of $2\gamma_0$. Thus we should expect the strongest absorption to be in the neighborhood of 6900A, i.e., in the red end of the spectrum.

[6] Reference 5, Section 71, pp. 326–8.

ACKNOWLEDGMENTS

I wish to thank Professor N. F. Mott of Bristol University for valuable discussions, and Professor C. A. Coulson of Oxford University for communicating to me some preliminary results of as yet unpublished work.