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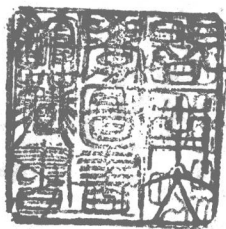
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PROCEEDINGS OF THE
Fifth
Conference on Carbon

VOLUME 2

Held at the
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FOREWORD

THE Fifth Carbon Conference, co-sponsored by the American Carbon Committee and the Pennsylvania State University, was held at the Pennsylvania State University, University Park, Pennsylvania, June 19-23, 1961. This Conference was so successful that the *Proceedings* could not be contained in a single volume. This second volume contains the 57 papers which were submitted for publication in the *Proceedings* of the Fifth Carbon Conference and could not be accommodated in the first volume.

This is the fifth and last volume of the series, and the fourth one published by Pergamon Press. The cooperation of all authors and of Pergamon Press in the preparation of this volume is greatly appreciated.

The spectacular growth of these Conferences resulting from greatly increasing interest and expanding research in the carbon field as well as from the growing prestige of these Conferences themselves, led to a situation where it became very difficult, if not impossible, to publish the *Proceedings* in a reasonable time, the publication time of such volumes being determined by the processing time of the slowest papers. It was felt that there is a growing need of a truly international medium of exchange of information in this field which would be available all the time and not only sporadically at the time of various conferences. Consequently, the American Carbon Committee decided to discontinue publication of the *Proceedings* and to sponsor the formation of an international journal entitled *CARBON* to which, in addition to others, papers presented at our American Conferences will be acceptable for publication. Thus, submission deadlines will no longer limit the authors; the speed of publication being dependent on each individual case. Although the new journal will not completely replace the *Proceedings* of the American Conferences, those who will attend future conferences will find the majority of presented papers appearing in the journal. An announcement concerning this new journal and its organization is presented on the following pages.

To those of us who participated in the Carbon Conferences since their inception, the termination of the *Proceedings* brings to a close an unforgettable pioneering period. Glancing through the volumes one name comes to mind which did not appear anywhere in the *Proceedings*—J. Fred White, then of the U.S. Atomic Energy Commission. Although not a carbon man, he was one of the first to realize the potential of the field; his enthusiastic support was instrumental in the establishment of the *Proceedings*. With the growth of the Conferences and inevitable breakup into parallel sessions, the direct value of putting all papers into a single volume was diminished; publication of multiple volumes becoming really a transitory stage to a journal. This is only the beginning of a new period and let us enter it with anticipation.

S. MROZOWSKI

M. L. STUDEBAKER

P. L. WALKER, Jr.

Buffalo, New York

September 18, 1962

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The spectacular growth of the interest and the expansion of research in the field of carbons in the last decade have shown the need of a truly international medium for distribution and exchange of information. The new journal *Carbon* will be devoted to the physics and chemistry as well as to the scientific aspects of technology of a class of materials ranging from organic

crystals and polymers through chars and carbons to graphite. This is a class of solids forming a group by itself. To unravel its secrets, physicists, chemists, and technologists have to pool all their techniques and resources; only by collaboration and exchange of information can progress be achieved. The aim of the journal is to supply a source where the majority of information concerning research on these materials will be found in the form of reports on original research and, from time to time, in reviews on limited problems. Also included will be a special reference section (by title) of carbon work published elsewhere.

From the vast variety of organic substances only those which in some way are either related to aromatic or tetrahedrally bonded carbonaceous solids, or which can be transformed into such by heat treatment or other means, are of interest to the journal. Papers on natural organic substances will be published if the research has some relation to resulting carbon materials.

The journal will publish papers in English, French, or German. An English abstract will accompany each paper.

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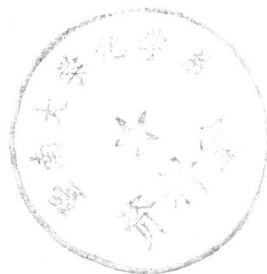
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PART I

ELECTRONIC PROPERTIES



THEORY OF THE ELECTRON TRANSPORT PROPERTIES OF SINGLE-CRYSTALLINE GRAPHITE*

J. W. McCLURE and L. B. SMITH

Parma Research Laboratory, Union Carbide Corporation, Parma, Ohio

(Manuscript received September 23, 1961)

Theoretical calculations have been performed of the electrical resistivity, magnetoresistivity, Hall effect, and thermoelectric power of graphite single crystals, as functions of the temperature and impurity content. The calculations are based upon the three-dimensional model of the electronic band structure and upon a simple scattering law. The scattering law, which may be justified by the deformation-potential theory, is that the scattering rate is proportional to the density of electronic states multiplied by the phonon density. The integrals which appear in the calculation were performed numerically, using an electronic computer. The results for the electrical resistivity of pure graphite agree with experiment to better than 5% for all temperatures between 50°K and 700°K (the highest temperature of measurement for a single crystal). The magnetoresistivity results agree with experiment to within 30% from 50°K to 300°K, which is a considerable improvement over the simple two-band theory. The Hall effect and thermoelectric power results are in rough agreement with experiment (about 50% error). However, the latter quantities are more sensitive to the details of the band structure and scattering law. Calculations for various values of the parameters entering into the band structure and scattering law are being performed, and it is expected that agreement with experiment will be improved.

I. INTRODUCTION

The electronic transport properties of a solid are determined by its electronic energy band structure and by the scattering of the free electrons and/or holes. Most previous theoretical work¹⁻³ on the electronic transport properties of graphite used the two-dimensional band model of Wallace¹. A calculation of the Hall coefficient has been made by Johnston⁴, using his three-dimensional band structure results. In this paper the three-dimensional band model of Slonczewski and Weiss⁵ is used. This latter model has given good agreement with the results of

several different types of experiments⁶. In treating the scattering, we assume that a relaxation time exists and that it is inversely proportional to the product of the density of electronic states and the density of phonons. This assumption is similar to that commonly made in treating semiconductors⁷ and was indicated by previous work on graphite⁸.

A description of the calculation is given in Section II. Theoretical results and comparison with experiment are given in Section III. Discussion and conclusions are given in Section IV.

II. THEORETICAL MODEL

The electrical conductivity due to a single type of carrier can be expressed as⁹

$$\sigma_{xx} = [2e^2/(2\pi)^3] \int d^3k \tau v_x^2 (-\partial f / \partial E) \quad (1)$$

* Work partially supported by U.S. Navy Bureau of Ships, Contract No. NObs-77066.

¹ P. R. Wallace, *Phys. Rev.* **71**, 622 (1947).

² W. P. Eatherly, AEC Research and Development Report NAA-SR-146 (1951). See also J. E. Hove, *Proc. First and Second Carbon Conf.*, University of Buffalo (1956), p. 125.

³ I. B. Mason, *Industrial Carbon and Graphite*, Society of the Chemical Industry, London (1958), p. 60.

⁴ D. F. Johnston, *Proc. Roy. Soc. A* **227**, 359 (1955).

⁵ J. C. Slonczewski and P. R. Weiss, *Phys. Rev.* **109**, 272 (1958).

⁶ J. W. McClure, *Proc. Fourth Carbon Conf.*, Pergamon Press (1960), p. 177.

⁷ See, for example, F. J. Blatt, *Solid State Physics*, Academic Press, vol. 4 (1957), p. 200.

⁸ D. E. Soule and J. W. McClure, *J. Phys. Chem. Solids* **8**, 29 (1959).

⁹ F. J. Blatt, *op. cit.*, p. 217.

where σ_{xx} is the conductivity in the x -direction, e is the electronic charge, k is the wave number ($2\pi/\lambda$), τ is the relaxation time, v_x is the velocity in the x -direction, f is the Fermi-Dirac distribution function, and E is the energy. The integral is taken over the Brillouin zone, spin degeneracy is included explicitly, and the result is in esu units. The velocity can be found from a knowledge of the energy band structure $E(k)$,

$$v_x = \frac{1}{\hbar} \frac{\partial}{\partial k_x} E(k) \quad (2)$$

In working out (1) and (2) we shall use the same coordinate scheme as in previous work^{10,11}. The z -axis is taken parallel to the c -axis of the crystal. Displacements in this direction are measured by $\xi = k_z c_0$ (where $c_0 = 6.72 \text{ \AA}$). The distance from one of the vertical edges of the Brillouin zone is* $\sigma = \sqrt{3} \cdot a \kappa / 2$, where κ is the actual distance in the k space (and $a = 2.46 \text{ \AA}$). We shall use the approximation that the surfaces of constant energy are figures of rotation about the vertical zone edge, so that the azimuthal angle α will not enter the calculation. Because of this rotational symmetry, we may replace v_x^2 in the integral by $v^2/2$, where

$$v = \frac{1}{\hbar} \frac{\partial E}{\partial \kappa} = \frac{\sqrt{3} \cdot a}{2\hbar} \frac{\partial E}{\partial \sigma} = \frac{\sqrt{3} \cdot a \sigma}{\hbar} \frac{\partial E}{\partial \sigma^2} \quad (3)$$

We change the integral on k to

$$\begin{aligned} \int d^3k &= \frac{4\pi}{3a^2c_0} \int d\xi \int d\sigma^2 \\ &= \frac{4\pi}{3a^2c_0} \int d\xi \int dE \left| \frac{d\sigma^2}{dE} \right| \end{aligned} \quad (4)$$

In the above we have anticipated the fact that E depends upon σ^2 . We now combine the results to obtain

$$\sigma_{xx} = \frac{e^2}{\hbar^2 \pi^2 c_0} \int d\xi \int dE \tau \sigma^2 \left| \frac{\partial E}{\partial \sigma^2} \right| \left(-\frac{\partial f}{\partial E} \right) \quad (5)$$

In obtaining the above, we have used the fact that there are two vertical edges in the Brillouin zone which are independent. The integral is to be taken from $\xi = -\pi$ to π and for E values for which $(-\partial f/\partial E)$ is not negligible. The approximations are not valid for very high temperatures or very high concentrations of impurities such that $(-\partial f/\partial E)$ would be finite for states far from the zone edge. The above formula then gives the contribution to the conductivity from a single band, and the total conductivity will be a sum of such contributions. The band model which we shall use^{10,11} is characterized by

$$\sigma^2 = (E - E_2)(E - E_3)/[\gamma_0(1 - \nu)]^2 \quad (6a)$$

where

$$E_2 = -2\gamma_1 \cos(\xi/2) + 2\gamma_5 \cos^2(\xi/2) + \Delta \quad (6b)$$

$$E_3 = 2\gamma_2 \cos^2(\xi/2) \quad (6c)$$

$$\nu = 2\gamma_4 \cos(\xi/2)/\gamma_0 \quad (6d)$$

If we let ξ range from $-\pi$ to $+\pi$, we shall obtain both valence and conduction bands. Equation (6a) is actually the secular equation for the energy band structure, but it is sufficient for this calculation. Note that our assumption of rotational symmetry amounts to neglecting the parameter γ_3 . We find

$$d\sigma^2/dE = (2E - E_2 - E_3)/[\gamma_0(1 - \nu)]^2 \quad (7)$$

so that

$$\begin{aligned} \sigma_{xx} &= \frac{e^2}{\hbar^2 \pi^2 c_0} \int d\xi \int dE \tau \times \\ &\times \frac{(E - E_2)(E - E_3)}{|2E - E_2 - E_3|} \left(-\frac{\partial f}{\partial E} \right) \end{aligned} \quad (8)$$

Note that γ_0 and γ_4 have cancelled out this equation, though they will appear later in τ . In the two-dimensional approximation $E_2 = E_3 = 0$, and the integral on ξ yields a factor 4π . The result is then

$$\sigma_{xx} = \frac{2e^2}{\hbar^2 \pi c_0} \int dE \tau |E| \left(-\frac{\partial f}{\partial E} \right) \quad (9)$$

in agreement with Wallace¹.

¹⁰ J. W. McClure, *Phys. Rev.* **108**, 612 (1957).

¹¹ J. W. McClure, *Phys. Rev.* **119**, 606 (1960).

* This σ should not be confused with the conductivity.

An approximate expression for the relaxation time τ is given by the "golden rule" for transition probabilities¹²

$$\tau^{-1} = (2\pi/\hbar) |V|^2 N(E) \quad (10)$$

where V is the matrix element of the scattering potential and $N(E)$ is the density of final states. Theories of electron scattering by phonons have shown¹³ that V is independent of k and E for small changes in k . This requirement is met for changes of the k vector perpendicular to the c -axis, but may not be met for changes parallel to the c -axis. We shall assume V is constant, but must remember that the assumption may cause discrepancies. Thus we have a relaxation time which depends upon energy alone. The constant $|V|^2$ is given by deformation potential theory¹³ as

$$|V|^2 = KTD^2/Ms^2 \quad (11)$$

where K is Boltzmann's constant, T is the absolute temperature, M is the atomic mass, s is the velocity of sound, and D is the deformation potential constant (change in band edge per unit strain). The expression assumes that the energies of the phonons involved in the scattering processes are all less than KT . We believe that this is true above 50°K for the following reason: most of the scattering should be done by the in-plane lattice vibrations, the maximum change in k_x should be about 4×10^6 wave numbers, and the appropriate velocity of sound¹⁴ in the plane is 2×10^6 cm/sec which gives 0.005 eV for the phonon energy. The change in k_z could be as much as 5×10^7 wave numbers (one-half the Brillouin zone height), and the appropriate velocity of sound is about 1.5×10^5 cm/sec, which gives a phonon energy of 0.005 eV. The density of states (per atom) is given by¹⁰

$$\begin{aligned} N(E) &= \frac{1}{4\sqrt{3} \cdot \pi^2} \int d\xi \left| \frac{d\sigma^2}{dE} \right| \\ &= \frac{1}{4\sqrt{3} \cdot \pi^2} \int d\xi \frac{|2E - E_2 - E_3|}{\gamma_0^2(1 - \nu)^2} \quad (12) \end{aligned}$$

We define separate deformation potential constants for electrons and for holes (D_e and D_h). Also, in the overlap region (those energy values for which there are both electrons and holes) there is the possibility of scattering from electron to hole energy surfaces and vice versa. Thus, instead of $N(E)$ in (10) we take $N_e(E) + \mu_1 N_h(E)$ for electrons, and $N_h(E) + \mu_2 N_e(E)$ for holes. Then the scattering probability for scattering from the electron surface to the hole surface is proportional to $\mu_1 D_e^2$ and that from hole surface to electron surface to $\mu_2 D_h^2$. As the principal of detailed balance requires that the two rates be equal, we have a three-parameter model (assuming that the band-structure parameters are known) which should describe the transport properties above about 50°K and when all the scattering is due to phonons.

We now wish to discuss the transport effects in the presence of a magnetic field. For this we need an expression for the cyclotron frequency ω . We use the result¹⁵ that

$$\omega = - \frac{2\pi eH}{\hbar^2 c} \frac{dE}{dA} \quad (13)$$

where H is the magnetic field strength and A is the area of the "orbit", i.e. the intersection in k space of the surface of constant energy E and a plane perpendicular to the magnetic field. Note that in this definition ω is positive for holes and negative for electrons. In the present work, H is always parallel to the c -axis, and $A = \pi\kappa^2$. Thus, we find

$$\begin{aligned} \omega &= - \frac{3eHa^2}{2\hbar^2 c} \frac{dE}{d\sigma^2} \\ &= - \frac{3eHa^2}{2\hbar^2 c} \frac{\gamma_0^2(1 - \nu)^2}{(2E - E_2 - E_3)} \quad (14) \end{aligned}$$

¹² See, for example, L. I. Schiff, *Quantum Mechanics*, McGraw-Hill (1949), 1st edition, p. 193.

¹³ F. J. Blatt, *op. cit.*, p. 333.

¹⁴ J. C. Bowman and J. A. Krumhansl, *J. Phys. Chem. Solids* 6, 367 (1958).

¹⁵ P. Nozières, *Phys. Rev.* 109, 1510 (1958).

In the presence of the magnetic field we need to know the magnetoconductivity tensor σ . Because of the rotational symmetry in the band structure and because we are only treating properties in the hexagonal plane, we need to know only σ_{xx} and σ_{xy} . Let the conductivity in the absence of the magnetic field be written as

$$\sigma_{xx}^0 = \int d^3k I \quad (15a)$$

(where the integration is also meant to include summation over bands). Then in the presence of the field¹⁶

$$\sigma_{xx} = \int d^3k I / [1 + (\omega\tau)^2] \quad (15b)$$

and

$$\sigma_{xy} = \int d^3k I \omega\tau / [1 + (\omega\tau)^2] \quad (15c)$$

Note that in our model τ depends upon energy alone, but ω depends upon k . These integrals may be combined to give the Hall coefficient and magnetoresistance¹⁷,

$$R = \sigma_{xy} / [H(\sigma_{xx}^2 + \sigma_{xy}^2)] \quad (16a)$$

$$\rho = \sigma_{xx} / (\sigma_{xx}^2 + \sigma_{xy}^2) \quad (16b)$$

$\Delta\rho/\rho_0$

$$= (\sigma_{xx}^0\sigma_{xx} - \sigma_{xx}^2 - \sigma_{xy}^2) / (\sigma_{xx}^2 + \sigma_{xy}^2) \quad (16c)$$

It is usual practice to expand these formulas in powers of the magnetic field to find the low-field Hall coefficient and magnetoresistance. However, the integral

$$\int d^3k I (\omega\tau)^2$$

which is then derived from (15b) presents a difficulty in evaluation. Indeed, in the two-dimensional model (all band parameters but γ_0 put to zero) the integral diverges, a difficulty noted by Eatherly². In the three-dimensional case the integral exists, but the

integrand varies so rapidly that the numerical method used in this work was not suitable. Therefore, we have evaluated the integrals at finite fields, in which case there are no numerical difficulties. It is, of course, desirable to calculate at finite fields because of the remarkable field-dependences of R and ρ which are observed experimentally^{18,19}.

We also calculate the thermoelectric power, using the formula²⁰

$$Q = - \int d^3k I (E - \zeta) / \sigma_{xx}^0 e T \quad (17)$$

where ζ is the energy of the Fermi level. The carrier concentrations are calculated using

$$n = \frac{1}{4\sqrt{3} \cdot \pi^2} \int dE \left(- \frac{\partial f}{\partial E} \right) \int d\xi \sigma^2 \quad (18)$$

Finally, we also calculate the paramagnetic susceptibility by²¹

$$\chi_0 = \mu_B^2 \int dE N(E) (-\partial f / \partial E) \quad (19)$$

where μ_B is the Bohr magneton.

III. RESULTS AND CALCULATIONS

The double integrals have been evaluated numerically, using Simpson's rule. The LGP-30 computer has been programmed to calculate the integrals for a given set of band parameters, temperatures, and Fermi levels. It then combines the integrals for any set of μ_1 , μ_2 , D_e , and D_h to give the electrical resistivity, thermoelectric power, Hall coefficient, magnetoresistivity, the densities of electrons and holes, and the paramagnetic susceptibility. Each run takes a fairly long time, so that the model has not been thoroughly investigated. Thus, the results reported here are preliminary and subject to improvement.

¹⁸ G. H. Kinchin, *Proc. Roy. Soc. (London)* **A217**, 9 (1953).

¹⁹ D. E. Soule, *Phys. Rev.* **112**, 698 (1958).

²⁰ C. Herring, *Phys. Rev.* **96**, 1163 (1954).

²¹ C. Kittel, *Solid State Physics*, John Wiley, 2nd edition (1956), p. 261.

¹⁶ J. W. McClure, *Phys. Rev.* **101**, 1642 (1956).

¹⁷ J. M. Ziman, *Electrons and Phonons*, Oxford University Press (1960), pp. 487-94.