PHYSICAL REVIEW VOLUME 123, NUMBER 5 SEPTEMBER 1, 1961

Carrier Densities and Mobilities in Pyrolytic Graphite

CLAUDE A. KLEIN AND W. DETER STRAUB
Research Division, Raytheon Company, Waltham, Massachusetts

(Received March 22, 1961)

Based on conductivity, Hall effect, and magnetoresistance measurements an attempt is made to describe the behavior of current carriers in the layer planes of well-ordered pyrolytic graphite. The total carrier concentration decreases from approximately 11×10^{18} cm^{-3} at room temperature to less than 4×10^{18} cm^{-3} at very low temperatures, in good agreement with single-crystal results. The average mobility, which is strongly dependent upon the crystallite size, was found to exceed 3000 cm^2/v-sec at liquid nitrogen temperature in specimens deposited at 2500°C; the mobility ratio (μ_e/μ_h) appears to remain temperature independent and equal to 1.08 ± 0.01.

I. INTRODUCTION

FACTORS such as macroporosity, lack of purity, and random orientation of the crystallites preclude a straightforward interpretation of electrical measurements performed on materials commonly referred to as "synthetic graphites."[1] Massive compact deposits of carbon can now be produced by cracking methane on a heated substrate.[2] These deposits are made up of well-aligned packets of hexagonal carbon atom networks, or layer planes, all lying essentially parallel to each other. Furthermore, at deposition temperatures of the order of 2500°C an appreciable fraction of the layer planes exhibits the three-dimensional lattice arrangement typical of graphite; we shall restrict the denomination of "pyrolytic graphite" (PG) to carbon deposits of this nature. As expected, thermal and electrical conductivity measurements along and across the basal planes of PG reveal a remarkable anisotropy,[3] which confers much technical importance to these materials. On the other hand, structural features such as high density and preferred orientation make PG very desirable in the framework of an investigation of the transport mechanisms in polycrystalline graphite.

The main purpose of this note is to report on a study of the low-temperature behavior of current carriers in the basal planes of pyrolytic graphite, and to correlate this behavior with available indications on natural single-crystal as well as conventional synthetic graphite. Accordingly, we have measured the galvanomagnetic coefficients of selected PG specimens at temperatures ranging down to 4.2°K, applying magnetic fields of up to 25 kgauss across the deposit in order to confine the current path to the carbon layers. Since regular bridge-shaped samples can be prepared, our data are presumed quite accurate in spite of temperature-independent geometric errors, which entail some difficulty in obtaining strictly reproducible results.

II. DATA AND RESULTS

The two-band model and other concepts evolving from the electron-band theory have been successfully used to evaluate graphite single-crystal measurements.[1] Soule[4] and McClure,[5] in particular, have analyzed a considerable body of galvanomagnetic data and arrived at reasonable estimates of the carrier densities and mobilities in near-ideal crystals. Thus, if we assume that in PG the individual crystallites are highly developed and do not give rise to contact resistance effects, an interpretation of the basal plane phenomena in terms of a mixed conduction by free electrons and holes belonging to slightly overlapping bands appears to be justified and suggests the following treatment:

(1) The transverse magnetoresistance measured as a function of the magnetic field strength exhibits a quadratic dependence if $H\lesssim3$ kgauss. In the low-field region the magnetoresistive coefficient should therefore be proportional to an average mobility squared; for graphite it is actually a good approximation to write

$$(\mu_e\mu_h)^{\frac{1}{2}}=(\Delta\rho/\rho_0)^{\frac{1}{2}}\times10^8/H, \tag{1}$$

in laboratory units.[4] The average carrier mobilities that this expression yields from data taken at 2520 gauss on two PG specimens are plotted against temperature in Fig. 1. We infer that the carrier mobility is a slowly-varying function of temperature down to about 20°K. At still lower temperatures, $(\mu_e\mu_h)^{\frac{1}{2}}$ drops rather fast and apparently according to a $T^{\frac{3}{2}}$ law, which implies that ionized impurity scattering predominates in the liquid helium temperature range. Above 77°K, the general trend of the mobility behavior indicates that lattice scattering processes contribute to the transport mechanism, and it is indeed feasible to fit the shape simply by adding the reciprocal thermal mean free path to the reciprocal crystallite diameter perpendicular to the c axis.[3]

(2) Soule has pointed out that, in graphite, an adequate evaluation of the total carrier concentration can

---

[1] For references see A. R. Ubbelohde and F. A. Lewis, *Graphite and Its Crystal Compounds* (Oxford University Press, New York, 1960), pp. 94–108. In our terminology synthetic graphite designates an extruded or molded coke-binder mixture graphitized at $T_0\geqslant2500$°C.

[2] A. R. G. Brown and W. Watt, *Industrial Carbon and Graphite* (Society of Chemical Industry, London, 1958), p. 86.

[3] C. A. Klein, *Proceedings of the Inter-Industry Conference on Organic Semiconductors, Chicago, 1961* [The Macmillan Company, New York (to be published)]; also available as Raytheon Technical Report R-58.

[4] D. E. Soule, Phys. Rev. **112**, 698, 708 (1958).

[5] J. W. McClure, Phys. Rev. **112**, 715 (1958).

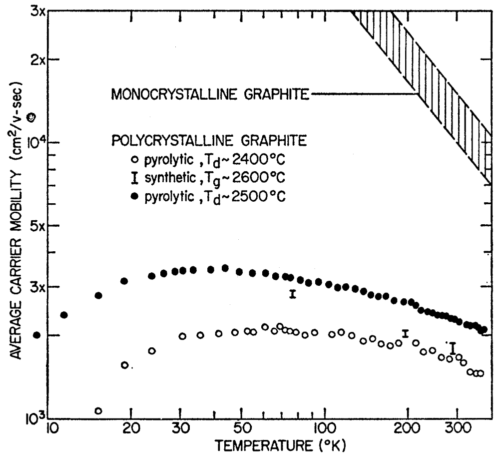

FIG. 1. Average carrier mobility in pyrolytic graphite compared with the mobilities in single-crystal (references 4 and 5) and synthetic materials. The mobility reduction experienced by specimens with smaller crystallites emphasizes the influence of boundary scattering. The synthetic graphite indications were derived by applying Eq. (1) to the magnetoresistance data recorded in reference 6 for an extruded stock with crystallites of about 1000 A.

be secured via

$$n_e+n_h=[e\rho_0(\Delta\rho/\rho_0)^{\frac{1}{2}}\times 10^8/H]^{-1}, \tag{2}$$

that is, using conductivity and low-field magnetoresistance data exclusively. Figure 2 shows our PG results, as given by Eq. (2), in confrontation with single-crystal[4,5] and synthetic graphite[6] values deduced by other methods. They agree surprisingly well; we notice that (a) in accordance with McClure's conclusions for crystal EP-14 there are less free carriers at 77°K than at 4.2°K; (b) beyond 77°K the carrier density varies linearly with temperature as suggested by Kinchin's measurements; and (c) the results confirm Soule's contention that impurities do not significantly affect (n_e+n_h).

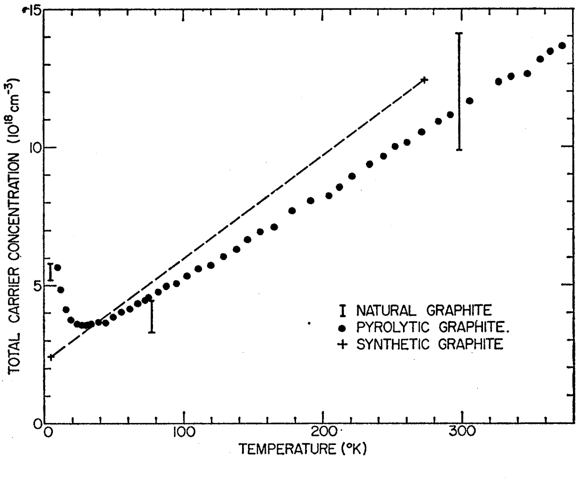

FIG. 2. Total carrier concentration in pyrolytic graphite compared with the concentrations in single-crystal (references 4 and 5) and synthetic (reference 6) materials. Deposited specimens exhibit the same general temperature dependence as Soule's graphite crystal EP-14. Kinchin's values refer to highly graphitized extruded specimens and are not well determined at low temperatures.

(3) Theoretical band-structure studies,[1] cyclotron resonance absorption curves,[7] and the magnetoconductivity analysis of galvanomagnetic data[5] reveal that in near-ideal graphite there are either equal or almost equal numbers of majority holes and electrons, throughout the temperature range. If we assume that this is also the case in pure highly-crystalline PG, the zero-field value of the Hall coefficient should be

$$R_0=\frac{1}{en}\left(\frac{1-b}{1+b}\right), \tag{3}$$

where $n=(n_e+n_h)/2$ and $b=\mu_e/\mu_h$. In harmony with Kinchin's observations on synthetic graphite, we have found the Hall coefficient of PG to be independent of the current and to remain always negative at field strengths that allow proper measurements. If our data are presumed representative of a zero-field situation—this is legitimate above 77°K—, it follows that $\mu_e>\mu_h$ at all temperatures. In conjunction with the carrier densities of Fig. 2, Eq. (3) demonstrates that the mobility ratio remains essentially constant, at least between 77°K and 370°K; more specifically, $b=1.08\pm0.01$, in fair agreement with Soule and McClure's room-temperature results as well as Uemura and Inoue's low-temperature analysis.[8] Nevertheless, in the liquid helium range the mobility ratio may well change, but this has not yet been ascertained owing to the strong field dependence of the Hall effect and the correlatively questionable applicability of Eq. (3).

III. CONCLUSION

In summary, we should like to stress that the preceding treatment yields values of n, μ_h, and b, which, after insertion into

$$1/\rho_0=en\mu_h(1+b), \tag{4}$$

reproduce the measured resistivities to within 1% over most of the considered temperature range. (See Fig. 3.) A significant feature of this "fit" is the fact that the conjunction of decreasing mobility values and increasing carrier densities accounts for the flattening out of the electrical resistance of polycrystalline graphite, as the temperature approaches the absolute zero.[9] The temperature dependence characteristics of synthetic and

---

[6] G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, 9 (1953). Note that according to Fig. 1 of this paper the magnitude of the Hall coefficient increases with temperature between 4.2° and 20.5°K; this is consistent with our evidence on the carrier density behavior at these temperatures.

[7] P. Nozières, Phys. Rev. **109**, 1510 (1958).

[8] Y. Uemura and M. Inoue, J. Phys. Soc. Japan **13**, 382 (1958).

[9] Reynolds, Hamstreet, and Leinhardt, Phys. Rev. **91**, 1152 (1953).

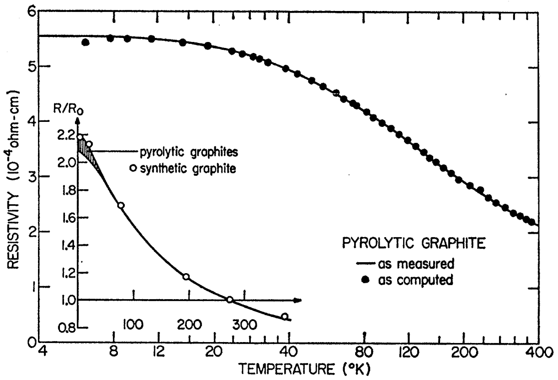

FIG. 3. Basal plane resistivity of a pyrolytic graphite specimen deposited at 2500°C. The filled circles are as given by Eq. (4) with parameters based on the indications of Figs. 1 and 2. The open circles illustrate how a synthetic specimen graphitized at 2600°C (reference 6) compares on a relative resistance scale with pyrolytic graphites deposited at $2300° < T_d < 2600°C$.

pyrolytic materials do namely coincide, although the conductivities differ by a factor of 3 or more, depending upon density and orientation. It may be pointed out that this substantiates Bowen's hypothesis[10]: In a conventional polycrystalline graphite the current carriers move perpendicularly to the *c* axes of the individual crystallites and are not exposed to multiple scattering effects in the areas of contact. Finally, a confrontation of Figs. 1 and 2 leads to the conclusion that large changes in the carrier mobility—that means crystallite size—do not induce noticeable carrier density variations. We believe that an interpretation of the polycrystalline graphite behavior in terms of near-ideal crystallites whose boundaries act in the manner of potential barriers is therefore justified.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to S. Cvikevich and O. Guentert for supplying adequate pyrolytic graphite specimens as well as most valuable indications on structural aspects of these materials.

---

[10] D. Bowen, Phys. Rev. 76, 1878 (1949).

PHYSICAL REVIEW VOLUME 123, NUMBER 5 SEPTEMBER 1, 1961

Thin-Film Elucidation of the Electroluminescence Process

W. A. THORNTON
Research Department, Westinghouse Electric Corporation, Bloomfield, New Jersey

(Received April 24, 1961)

Very thin sulfide films emit light only on alternate half-cycles of the voltage sine wave, whereas the emission of thicker films and phosphor powders is quite symmetrical with polarity. This asymmetry of emission, together with clipping or dc bias of the applied voltage, is used to confirm unambiguously that the excitation and recombination steps in electroluminescence are separable and occur sequentially and under different field configurations, and that the recombination is field-driven.

INTRODUCTION

ELECTROLUMINESCENCE in zinc sulfide is a complex process which is not yet well understood. In this paper it is shown that the behavior of very thin zinc sulfide films confirms in a relatively unambiguous way long-standing ideas that the excitation and recombination steps in electroluminescence are (a) separable and occur sequentially and under different field configurations,[1,2] and (b) that the recombination is field-driven.[3–6]

EXPERIMENTAL PROCEDURE

The electroluminescent films[7] used here are of zinc sulfide activated with copper and chlorine, and in some cases manganese in addition, made by a two-step evaporation-firing process on tin-oxide coated glass. Film thickness is about 1 μ. Aluminum was vaporized directly on the finished film to form the rear electrode, except in one case where an intermediate plastic (PVCA) film was interposed. The powder phosphor layers used for comparison are conventional sprayed dispersions of equivalent powder phosphors in PVCA.

An RCA-6217 photomultiplier and cathode follower with dc coupling was used for light detection; the signal from this circuit was introduced into a high-gain dc amplifier (y) of a Tektronix type 535 oscilloscope and the voltage applied to the phosphor was also used as the external (x) sweep. A careful check for extraneous

---

[1] W. R. Watson, J. J. Dropkin, and A. T. Halpin, Abstract No. 38, Electrochemical Society Meeting, Chicago, May, 1954.

[2] J. F. Waymouth and F. Bitter, Phys. Rev. 95, 941 (1954).

[3] W. A. Thornton, Phys. Rev. 102, 38 (1956).

[4] W. A. Thornton, Phys. Rev. 103, 1585 (1956).

[5] H. A. Klasens, *Proceedings of the International Conference on Semiconductors and Phosphors, Garmisch, 1956*, edited by M. Schön and H. Walker (Interscience Publishers, New York, 1958).

[6] P. Zalm, Philips Research Repts. 11, 353 (1956).

[7] W. A. Thornton, J. Appl. Phys. 30, 123 (1959).