Evidence of Single-Crystal Characteristics in Highly Annealed Pyrolytic Graphite

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(Received September 5, 1961)

It is demonstrated that massive specimens of pyrolytic graphite heat-treated at 3600°C may exhibit electrical characteristics comparable to those of the best single crystals presently available. Low-field magnetoresistance data taken perpendicularly to the *c* direction of these specimens yield average carrier mobilities (1.3×10^4 cm²/v-sec at 300°K; up to 8×10^5 cm²/v-sec at 4.2°K) in substantial agreement with Soule's and McClure's results for the layer planes of highly purified natural graphite. In conjunction with temperature dependence studies of the zero-field resistivity, it is found that the carrier density reproduces the theoretically predicted behavior down to 77°K, but departs at lower temperatures. Plausible interpretations of this discrepancy and of the "knee" in the resistivity curve are briefly discussed.

I. INTRODUCTION

OWING to a combination of features such as anisotropy, semimetallic conductance, and enormous mobilities in the basal planes, single-crystalline graphite may have remarkable potentialties.[1] Naturally occurring graphites are found in the form of small soft flakes that contain a substantial amount of impurities and require extreme care in handling. Attempts to grow synthetic single crystals of reasonable size have hitherto met with only partial success. As a result of this situation, experimental studies of graphite crystal properties refer to a few specimens of natural origin and questionable perfection.

Pyrolytic graphite (PG), produced by cracking methane on a carbon surface heated to around 2100°C, is made up of relatively well-aligned packets of hexagonal atom networks,[2] but exhibits characteristics that are far from single-crystalline.[3] It has recently been shown, however, that concurrently with graphitization, heat treatment at temperatures above 2500°C further enhances the preferred orientation of PG.[4] This trend was interpreted as lending support to the conjecture that temperatures exceeding 3250°C might induce crystallite alignment, growth, and ordering to an extent compatible with the notion of mosaic structure. The purpose of this note is to demonstrate that the electrical properties of PG specimens recrystallized at 3600°C indeed justify their classification as mosaic single crystals of graphite. Our measurements refer primarily to the variations with temperature of zero-field resistivity and low-field magnetoresistance perpendicularly to the *c* direction. In addition, they have been employed to obtain information about the carrier density and mobility behavior in synthetic as compared to natural "single" crystals.

II. EXPERIMENTAL PROCEDURE

The two specimens considered in this investigation are both rectangular and roughly 5 by 2.5 by 1 mm in size; they were cut with a thin razor blade from a PG plate deposited at 2380°C (20 mm Hg pressure) and subsequently annealed for half an hour in a graphite crucible inductively heated to 3600°C.[5] Since the material is easily deformed by manipulation, sample preparation involved potting in a resin prior to shaping by means of a sandblast unit and copper-plating of the exposed surfaces. After mounting in a cryostat, basal-plane resistivity and transverse magnetoresistance were measured as a function of temperature from 330° down to 4.2°K, using a constant current of 250 ma and applying a magnetic field maintained at 2520 gauss across the thickness of the sample.

III. DATA AND RESULTS

Different methods of attempting to ensure adequate crystal-electrode contacts resulted in resistivity values lying between 60 and 75 μohm-cm at room temperature, or well within the range reported for the *a* axis direction of Ceylon graphite.[6] Some difficulties were experienced in obtaining reproducible absolute values; this was not seriously investigated, because resistivity versus temperature dependence, as well as magnetoresistance, should provide more sensitive "measures" of the crystalline perfection.

Figure 1, for instance, gives a plot of the ratio of resistance at a temperature T to the resistance at 0°C,

[1] B. Lax, Bull. Am. Phys. Soc. **6**, 58 (1961); E. H. Putley, *The Hall Effect and Related Phenomena* (Butterworth, Inc., Washington, 1960), p. 211; A. R. Ubbelohde and F. A. Lewis, *Graphite and its Crystal Compounds* (Oxford University Press, New York, 1960), p. 25.

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

[3] C. A. Klein, Revs. Modern Phys. (to be published); also available as Raytheon Technical Report R-58 (unpublished).

[4] O. J. Guentert and S. Cvikevich, *Proceedings of the Fifth Conference on Carbon, The Pennsylvania State University, 1961* (to be published).

[5] For a description of the annealing procedure, see J. R. Diefendorf, *Proceedings of the Fifth Conference on Carbon, The Pennsylvania State University, 1961* (to be published).

[6] The lowest value reported for small crystals of North American origin is 39 μohm-cm. [W. Primak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).]

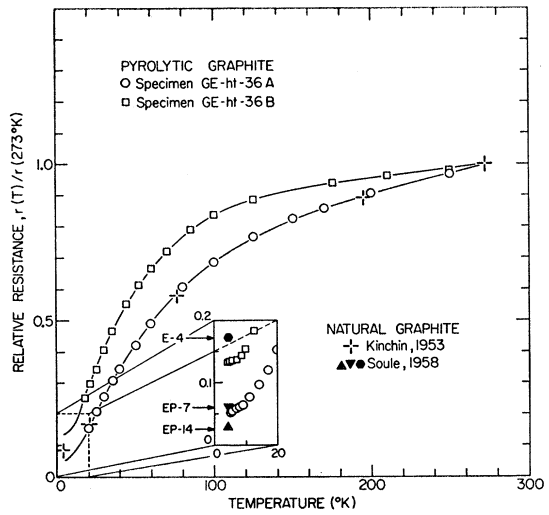

FIG. 1. Temperature dependence of the basal plane resistivity of highly annealed pyrolytic graphite. For comparison, some typical indications relative to single-crystalline graphite of natural origin are also included. The very low temperature data were plotted on an enlarged scale in order to conveniently record the leveling-off below 10°K.

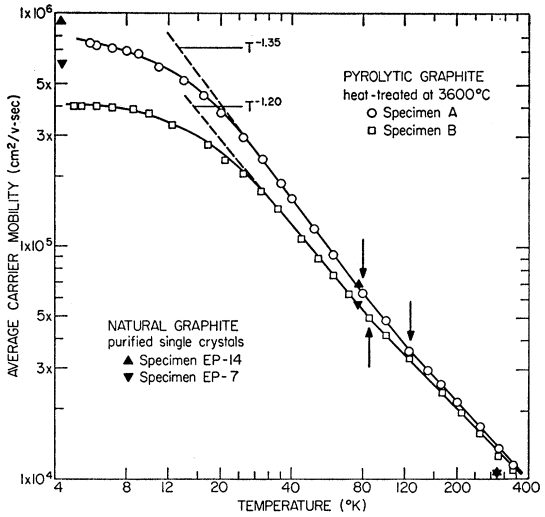

FIG. 2. Average carrier mobility in the layer planes of highly annealed pyrolytic graphite as determined from magnetoresistance measurements at 2520 gauss. The arrows mark breaks in the temperature dependency over the lattice scattering region. The natural graphite values are those derived by McClure (reference 10) and are based on galvanomagnetic data taken by Soule (reference 9).

in confrontation with natural graphite data. The two PG curves exhibit familiar single-crystal characteristics,[7] in particular the "knee" at approximately 100°K, but differ enough to emphasize the effect of slight structural variations. Above 20°K, sample A behaves actually in full agreement with Kinchin's[8] observations on a Travancore graphite flake. Soule's[9] $\rho(4.2°K)/\rho(273°K)$ ratios, on the other hand, imply that our sample B must be superior to his Essex County specimen E-4, whereas sample A might even compare with highly purified single crystals such as EP-7 or EP-14 (see insert of Fig. 1). In the next paragraph it will be shown that the magnetoresistance measurements do support this contention.

Soule[9] has pointed out that the low-field magnetoresistive coefficient should provide a good approximation of the average carrier mobility along the layer planes of graphite, or more precisely that

$$(\mu_e\mu_h)^{\frac{1}{2}}=(\Delta\rho/\rho_0)^{\frac{1}{2}}\times 10^8/H, \qquad (1)$$

if one uses laboratory units. In Fig. 2 we have plotted $(\mu_e\mu_h)^{\frac{1}{2}}$ vs T as deduced from Eq. (1) on the basis of our PG data, together with single-crystal results as indicated by McClure's[10] analysis. We note the following: (1) In highly-annealed PG the mobilities are exceedingly large, $(\mu_e\mu_h)^{\frac{1}{2}}$ progressing from 1.3×10^4 cm²/v-sec at 300°K up to almost 1×10^6 cm²/v-sec at liquid helium temperatures, in harmony with EP-7 and EP-14.[11] (2) Below 25°K, the temperature dependence shows evidence of ionized impurity scattering contributions mainly for specimen B, as expected in view of the resistivity behavior. (3) At higher temperatures, the mobilities obey $T^{-\alpha}$ laws with values of α that recall Soule's observations on single crystals before shifting to values ($\alpha\approx1.0$) more closely representative of metallic lattice scattering mechanisms.

Considering the close correlation established in Figs. 1 and 2 with Soule's and McClure's work,[9,10] we have reasons to believe that Eq. (1) yields acceptable average mobility values for our specimens. We may therefore estimate the total carrier density (electrons plus holes) by writing

$$n=[e\rho_0(\Delta\rho/\rho_0)^{\frac{1}{2}}\times10^8/H]^{-1}, \qquad (2)$$

and observe its temperature dependence by plotting $n(T)/n(300°K)$ as in Fig. 3. On the same diagram we have drawn a curve labelled "ideal graphite," which illustrates the results of theoretical calculations based upon the three-dimensional band structure model.[12] Above 77°K, the over-all agreement must be considered quite satisfactory. At lower temperatures, however, the dip-featured behavior of PG falls out of line. Measurements on natural single crystals are not sufficiently

[7] For a discussion, see R. R. Haering and S. Mrozowski, *Progress in Semiconductors*, edited by A. F. Gibson (John Wiley & Sons, Inc., New York, 1960), Vol. 5, p. 273.
[8] G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, 9 (1953).
[9] D. E. Soule, Phys. Rev. **112**, 698 (1958).
[10] J. W. McClure, Phys. Rev. **112**, 715 (1958).
[11] According to McClure (reference 10), at 4.2°K Kinchin's specimen may have an average carrier mobility of about 7×10^5 cm²/v-sec—this is very close to our figure for sample A and rather gratifying in the light of Fig. 1.
[12] J. W. McClure and L. B. Smith, *Proceedings of the Fifth Conference on Carbon, The Pennsylvania State University, 1961* (to be published).

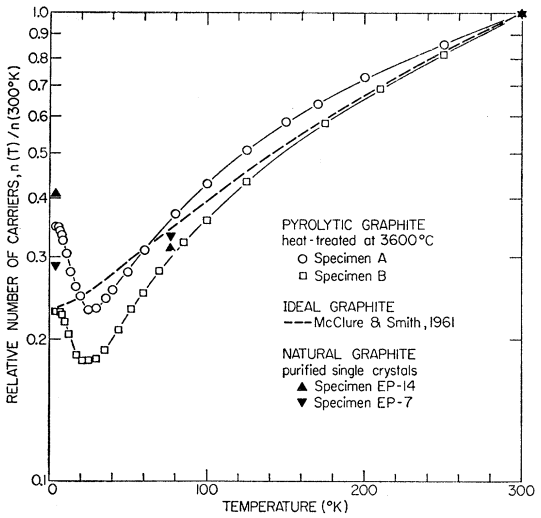

FIG. 3. Temperature dependence of the carrier concentration in highly annealed pyrolytic graphite confronted with ideal and natural single-crystal results. The natural graphite points are as indicated by McClure's magnetoconductivity-tensor analysis of Soule's measurements. Note that for the sake of clarity the ordinate is expressed on a logarithmic scale.

complete to permit comparison with our results; still, they point to a similar state of affairs.[13]

IV. DISCUSSION

In the absence of accurate information about residual defects in crystals of near-ideal graphite,[14] one might tentatively associate low-temperature complications with the defect configuration of specific samples. Although theoretical studies of the influence of various imperfections on transport properties of graphite have not yet been made, an explanation of the carrier density variations seems to require the presence of electron traps that cause the Fermi level to shift in such a way as to reduce the number of free carriers, up to liquid hydrogen temperatures.[10,15] Beyond that range, on the other hand, the total carrier concentration rises smoothly and almost linearly as in polycrystalline material.[16] Thus, it is perhaps legitimate to attribute the *knee* in the resistivity curve of single-crystalline graphite to the *break* in the temperature dependence of the mobility, since both phenomena occur in the region between 80° and 120°K (compare Figs. 1 and 2).

V. CONCLUSION

In summary, we have shown that galvanomagnetic measurements yield convincing evidence to support the claim that heat-treating PG can result in a synthetic graphite with essentially single-crystal characteristics.[17] Since natural near-ideal crystals of graphite are uncommon, a convenient and abundant supply of comparatively large specimens of highly annealed PG appears to be of consequence. A serious problem is that x-ray techniques do not reveal all the crystal defects, and imperfections of various kinds may have a particularly marked influence on properties conditioned by the electron band structure of graphite.[7] Indeed, a comparison of the room-temperature resistivities of our specimens with values obtained on small single crystals (see Section III) intimates crack-like perturbations in the conduction networks.[18] In order to reach definite conclusions, however, more refined methods of diagnosis are required. It might not be premature to speculate that a correct interpretation of the carrier concentration discrepancies at very low temperatures will ultimately lead to a sensitive crystal perfection test in graphite.

ACKNOWLEDGMENTS

Acknowledgments are due to J. W. McClure for his stimulating comments at the recent Carbon Conference and to L. B. Smith for supplying the theoretical carrier density equation in advance of publication.

[13] In polycrystalline as-deposited pyrolytic graphite the carrier concentration was found to decrease even more sharply with increasing temperature between 4.2° and 20.5°K. [C. A. Klein and W. D. Straub, Phys. Rev. **123**, 1581 (1961).]

[14] For instance, quenched-in vacancies introduced during heat-treatment [G. R. Hennig, J. chim. phys. **57**, 872 (1960)].

[15] It is interesting that in order to interpret low-temperature Hall effect anomalies, Kinchin (reference 8) was led to postulate the existence of impurity-induced acceptor levels in the conduction band.

[16] See Fig. 2 of the reference cited in footnote 13.

[17] To some extent this is also borne out by x-ray diffraction studies, as indicated by a c-axis spacing of 3.355 A in our specimens [O. J. Guentert (private communication)]. In this connection we note that the diamagnetic susceptibility of pyrolytic graphites recrystallized at temperatures between 3200° and 3600°C was found in general agreement with data reported for natural single crystals [D. B. Fischbach, Phys. Rev. **123**, 1613 (1961)]. It ought to be emphasized, however, that galvanomagnetic studies on PG specimens heat-treated at 3250°C yield carrier mobilities that are not yet characteristic of single-crystalline graphite [C. A. Klein and W. D. Straub (to be published)].

[18] Presumably caused by a slight buckling of the layers where strains have been released on recrystallization. [L. C. F. Blackman, J. F. Mathews, and A. R. Ubbelohde, Proc. Roy. Soc. (London) **A258**, 329 (1960)].