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Semiconductivity and Diamagnetism of Polycrystalline Graphite and Condensed Ring Systems

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The analysis of results obtained from studies of electric resistivity as a function of temperature, and sample preparation, and of other available evidence, leads to a clarification of the electronic processes in the class of substances extending from condensed ring molecular solids to polycrystalline graphite. In all these solids, the electric current flows preferentially along the benzene-ring planes. Scattering of electrons is due to thermal lattice vibrations and to the boundaries of molecular planes, where electrons pass through potential barriers into the neighboring crystallites. These barriers are quite transparent in polycrystalline graphite and baked carbons, since the flow occurs along the carbon-carbon bonds, but are quite opaque in molecular solids where the barriers are due to the presence of foreign atoms attached at the periphery of the molecules.

In contrast with the infinite graphite crystal, systems of benzene-rings of finite dimensions possess a finite energy gap between the filled and the conduction bands, the energy gap steadily decreasing with increase of molecular size—from about 1 ev for molecules several benzene rings wide, to 0.2–0.3 ev for systems 30–40A in diameter and to 0.05 ev for graphite crystallites with diameters of the order of 1000A. When in the process of carbonization, foreign atoms are removed from peripheries, the carbon atoms left with free, unattached valencies play a role of donors, that is, become a source of conduction (excess) electrons. The concentration of such excess electrons increases as long as gases are driven out from the carbons, but starts decreasing as a result of growth of crystallite size for samples treated to higher temperatures. The complete interpretation of the dependence of resistivity on temperature is based on a combination of these three factors: scattering, concentration of the excess electrons, and concentration of holes and electrons activated from the lower band (over the energy gap).

The anisotropic component of the diamagnetism of condensed ring systems has a twofold origin: (1) diamagnetism of the filled band (closed shell) of resonance (π) electrons, which is proportional to the number of benzene rings in a molecule; and (2) the Landau diamagnetism of the free electrons and holes. The contribution of the Landau diamagnetism is by far the larger of the two for graphite, but decreases fast with the crystallite size and becomes negligible for molecules with diameters of 30A or below, due to an increase in the effective mass of carriers.

INTRODUCTION

THIS paper originated in an attempt to find a consistent picture of electronic processes in a large class of solids, which until recently has attracted comparatively little attention of physicists.[1] These solids are all made by heat-treating organic materials in a neutral or reducing atmosphere. They range from the so-called raw cokes obtained at the lower temperatures through materials, graphitic in structure, produced at the highest temperatures of treatment. No matter what the original organic substance is, if it remains fluid up to a relatively high temperature (~450°C), large condensed ring molecules are created in the heating process. At the setting temperature, some kind of polymer is formed in which the molecules are stacked parallel in groups like pennies in a bag full of money.[2] Higher heat treatment produces continuing growth of these molecules; at temperatures above 700°–800°C, these subsubstances, having lost most of the atoms or groups attached at the periphery of the molecules, become the so-called calcined or baked carbons. These are essentially solids built of very small (20–30A diam) turbostratic crystallites of graphite: packs of parallel graphite planes having no directional relationship to each other. Only at considerably higher temperatures, when the molecular planes reach a diameter of about 150A[3] a rotation starts to bring the planes into a regular directional arrangement and into a consecutive order corresponding to the large crystals of graphite.

Some of the organic substances solidify at a much lower temperature—for instance, the so-called hardening resins.[4] The early stabilization by crisscross bonding, impairs the growth of molecular planes in the heating process; the carbons thus obtained show a glassy structure and do not graphitize so easily. Several years ago, the author had introduced the name "hard carbons" in order to distinguish such materials from the highly crystallized carbon obtained from petroleum or coal tar pitches.[5] It must be realized, however, that there is a continuous transition from hard carbons to the soft, easily graphitizing materials, and that the term hard carbon covers quite a broad variety of structures.

I. GENERAL CONSIDERATIONS

As checked by a number of investigators, the resistance of graphite crystals in the direction parallel to the graphite planes is about $5\times10^{-5}\Omega$cm at room temperature. This value might be a little too high since it is possible that not all graphite layers are effective in carrying the current if a direct contact with each of them is not established in the experiment. The parallel resistivity varies probably linearly with temperature

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[1] See the preliminary note S. Mrozowski, Phys. Rev. **77**, 838 (1950).

[2] A wealth of information is contained in papers by Riley and his collaborators: Blayden, Gibson, and Riley, Proc. of the Conference on the Ultrafine Structure of Coals and Cokes, B C U R A London, 1943, and a number of other publications.

[3] R. E. Franklin, Acta Cryst. 4, 253 (1951).

[4] See for instance R. Houwink, *Elasticity, Plasticity, and Structure of Matter* (Cambridge University Press, London, 1937), p. 152.

[5] Recently Franklin (reference 3) suggested the name of "non-graphitizing carbons." Such a name does not seem appropriate, since these carbons do graphitize after all, although at correspondingly higher temperatures.

over a wide range. This has been found to hold for low temperatures,[6,7] and it seems almost certain from the study of polycrystalline graphites that the approximate linear relationship should hold up to the highest temperatures, the slope being about $1.7\times10^{-7}\Omega\text{cm}/°\text{C}$ or somewhat less.

Calculations made by Coulson,[8] and Wallace,[9] for an infinite lattice show that graphite along the plane is an intrinsic semiconductor with a zero activation energy and with a density of electronic levels decreasing to zero as one approaches the boundary between the filled and empty energy bands. However, the results of the more detailed calculations of Wallace cannot be considered as satisfying. For instance, no explanation of the temperature dependence of the anomalous diamagnetic susceptibility and of the linear temperature dependence of the electric resistivity is given. Furthermore, the ratio of the resistivity in two directions is calculated to be of the order of 100. The resistivity in the transverse direction is large and very difficult to determine. Only a lower limit can be obtained with the best crystals available. Krishnan and Ganguli[10] found for the two directions a ratio of resistivities equal to about 10^5. The transverse resistivity of graphite is therefore of the order of 3Ωcm or larger. Thus Wallace's estimate fails by a factor of 10^3. The general picture undoubtedly is correct, but the theory seems to require considerable refinements.

As a result of the great anisotropy of the graphite crystallites, the electric current flows in polycrystalline materials preferentially along the graphitic planes. Consequently, in the rest of this paper only this kind of flow will be considered. In comparing the resistivity of polycrystalline materials with each other or with graphite crystals, a number of corrections should be kept in mind:

(1) The increase in length of current path through the crystallites. Passing N planes of diameter d the zigzag path has a length Nd, but the direct distance is only $Nd\langle\cos\theta\rangle_{\text{Av}}$, where θ is the angle between the given direction and the graphitic plane, so that $f_1=1/\langle\cos\theta\rangle_{\text{Av}}$. For an isotropic material with a perfectly random distribution of the crystallite planes, the average increase is by a factor $f_1=4/\pi=1.28$. If the crystallites show any kind of alignment relative to a certain axis, for instance, if the planes of crystallites align parallel to the direction of extrusion, the factor along the axis becomes smaller and larger across (for a perfectly random distribution in the normal plane $f_1=\pi/2=1.57$). On the other hand, if the sample is made by compressing graphite powder, the crystallites align with planes normal to the direction of pressure and the factor becomes large for the axial direction and small (nearly 1) for a crosswise direction.

(2) Due to a disordered crisscross bonding between crystallites, some planes might happen not to carry any current, that is, might happen to be ineffective. It seems very improbable that in such a polymer any graphitic plane could remain completely unattached and ineffective, so that the assumption of every fourth plane being totally ineffective would probably exaggerate the situation. Thus, the correction factor f_2 will be somewhere between 1 and 1.33.

(3) The "real density" correction. It is known that the smaller crystallites of graphite have larger interplanar distances. Consequently, there are fewer graphitic planes per unit volume, and the so-called real density d of the material is lower than that of a graphite single crystal; the resistivity is consequently higher by a factor $f_3=(2.26/d)^{\frac{1}{3}}$. This is a small correction relative to the others and will not be considered further.

(4) The microporosity correction. In a crisscross arrangement, some spaces are left unfilled between crystallites. The voids are mainly formed as a result of a differential shrinkage in the process of cooling.[11] Since these voids represent less than 10 percent of the total volume, this correction $f_4=(2.26/d)^{\frac{1}{3}}$ is again quite small and in the following will be neglected $(1<f_4<1.03)$.

(5) The macroporosity, which is due to the method of preparation of carbons, consisting of empty spaces between particles of coke and pores left in larger particles of coke. The corresponding correction is not a simple function of the bulk density. For a reasonable evaluation, the original mix formula must be known. For average commercial products (coke flour mixes) the correction factor f_5 is around 1.5. Great caution is necessary since some of the materials prepared with small amounts of binder might require considerably larger corrections.

(6) Microcracks are created in cokes and especially in the binder coke during the baking process. These microcracks form a network all through the material[12] and probably are only partly sealed in the process of graphitization. The number of microcracks varies with the kind of treatment and, as found by us, the resistivity of the polycrystalline graphite is increased in the more unfavorable cases by as much as 25 percent.

Applying these corrections to an actual case of a commercial well-graphitized rod for the direction along the axis of extrusion: $f_1\leqslant1.28$, $f_2\leqslant1.33$, $f_5\cong1.5$, and $f_6\leqslant1.25$, it is found that the total correction factor is $f\leqslant3.25$. At a temperature of 900°K the resistivity of graphite is $\leqslant15\times10^{-5}\Omega$cm, and the corresponding resistivity of the polycrystalline rod should consequently be $\rho\leqslant48\times10^{-5}\Omega$cm. The temperature of 900°K is selected

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[6] W. J. de Haas and P. M. van Alphen, Proc. Roy. Acad. Amsterdam **34**, 70 (1931).

[7] H. Kammerlingh Onnes and K. Hoff, Proc. Roy. Acad. Amsterdam **17**, 520 (1915).

[8] C. A. Coulson, Nature **159**, 265 (1947).

[9] R. P. Wallace, Phys. Rev. **71**, 622 (1947).

[10] K. S. Krishnan and N. Ganguli, Nature **144**, 667 (1939).

[11] The existence and formation of these voids, as well as the influence of the differential shrinkage on the mechanical properties of carbons will be discussed elsewhere.

[12] As shown on electron micrographs obtained by E. Kmetko at our laboratory.

so as to fall into the linear range. The measured value for good rods without defects is about $70\times10^{-5}\Omega$cm, as may be seen in Fig. 2. Thus a considerable part of the total resistivity of the polycrystalline graphite is accounted for by the temperature lattice scattering in the graphite crystallites. The estimate given above shows, however, that at least one-third of the measured resistivity of the polycrystalline graphite at 900°K is due to other scattering processes.

This extra scattering must be due to the finite dimensions of crystallites and to intercrystalline contacts. The flow of carriers from one crystallite to another probably occurs at places of their nearest approach where the graphite planes belonging to the two crystallites are held together by peripheral C—C bonds, and where the carriers pass through low potential barriers. Some carriers are reflected by these barriers, however; furthermore, almost all carriers are scattered by the remaining parts of the crystalline boundaries (high barriers). Thus, this extra scattering is a process not easily amenable to calculations. A complicating factor is that the electric field is probably not uniform throughout the crystals, but is more concentrated in the neighborhood of the intercrystalline contacts (barriers). In the following sections, a simplified treatment of this extra scattering will be used in which the scattering by the crystal boundaries and the contact resistance will be regarded as two different processes. The splitting of the scattering, however, will be done only in order to separate in a purely formal way the part of the scattering which is variable (with temperature) from that part which is constant, and not too much meaning should be attached to each of these quantities separately.

Since carbons can be made with different microcrystallinic structures, that is with crystallites held together by variable numbers and distribution of C—C bonds, it could be expected that the real (corrected) resistivity is not simply a function of crystallite size, but might vary within large limits with the type of carbon structure. It is remarkable therefore that the crystallite size is found actually to be the greatly preponderant factor which determines resistivity of a solid carbon sample. According to the experience of the author, gained during his several years of association with the Research Laboratory of the Great Lakes Carbon Corporation and later at the University of Buffalo with a great number of laboratory prepared samples, the resistivities after being corrected for the effects 1, 5, and 6, correlate well with the widths of the assymetric x-ray diffraction line 110 (from which the size of the graphitic planes is estimated). In other words, the corrected resistivity can be quite accurately predicted from the microcrystal size and vice versa. There is even a better correlation of the shapes of the resistivity-temperature curves with the x-ray diffraction patterns. A definite evidence of individual differences among samples is available showing that other effects do have an influence, but the differences are relatively small and in the broad discussion of the problem of resistivity of polycrystalline carbons they will not be considered. However, they have to be brought into discussion when one desires to explain the nature of these individual differences. Some examples of such differences will be mentioned later.

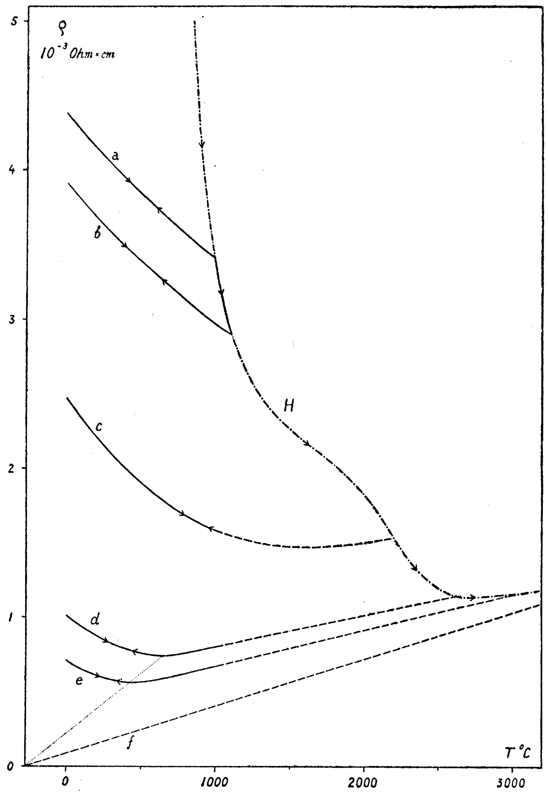

FIG. 1. Electric resistivity as function of temperature for a carbon rod treated to temperatures: (a) 1000°, (b) 1100°, (c) 2200°, (d) 2600°, and (e) 3000°C. Full lines mark the region in which the actual measurements were performed; broken lines represent the expected trend outside of this region. Line *f* is the limit to which the curves probably tend with increasing degree of graphitization. Curve *H* gives the variation of the resistivity during the heat treatment of the carbon (irreversible).

If a carbon is made from a mixture of coke, with addition of a carbon black, for instance, or if it is made using a binder which graphitizes differently from the coke—the correlation between temperature of treatment, the resistivity, and the type of x-ray diffraction pattern may be obscured or even may, in special limiting cases, become completely obliterated. The lack of knowledge of the composition of carbons and the mix formula according to which they were prepared can probably be blamed in many cases for the divergent opinions one finds in the literature on the subject of resistivity of carbons.

II. POLYCRYSTALLINE GRAPHITE

A system of resistance-temperature curves as they are found for solid carbon is presented in Fig. 1. All five curves were obtained by actual measurements from room temperature up to 1100°C for the same petroleum coke laboratory rods treated successively to five different temperatures—1000°C, 1100°C, 2200°C, 2600°C, and 3000°C. The two lowest curves correspond to a graphitized material, and their shape is typical of graphitized carbons of any kind. These curves have definite mimima beyond which at higher temperatures the relationship becomes linear. The slopes of these lines are steeper for higher degrees of graphitization. A number of years ago Nishiyama[13] published a system of resistance-temperature curves for carbon filaments graphitized to temperatures 2000°C, 2500°C, and 3000°C. Though his curves are similar to mine, they are incorrect in a number of important respects. It can be seen from Fig. 1 that the crossing point of the line extrapolated to 0°K with the ordinate axis is always positive (in Nishiyama's curves it becomes negative for high degrees of graphitization) and decreases steadily with increase of the graphitization temperature. The increase of the holding time t (for $t \geqslant 10$ min) in graphitization has an influence in decreasing resistivity, less, however, than was found by Nishiyama. The resistivity at the minimum seems to be a linear function of the temperature (dotted curve), at least for highly graphitized samples.

It seems obvious that the first step is to look at electron scattering processes for an explanation of this type of behavior. Wallace[9] has shown that for the model of a two-dimensional intrinsic semiconductor with zero energy gap, the resistivity in graphitic planes is $\rho = A/kT\tau$, where $A = h^2c/16\pi e^2k \ln 2$ with $c = 6.75$A (double distance of graphite planes). Wallace's formula shows that $(N/m)_{\mathrm{eff}} = kT/Ae^2$, the proportionality with temperature being a quite general result independent of the character ot the change of the density of electronic states with energy near the Brillouin zone corners. The scattering probability by thermal vibrations of the lattice $1/\tau_e$ must vary as T^2 in order to give a linear relationship $\rho = aT$ found experimentally for large graphite crystals. Wallace did not investigate the temperature dependence of the mean free path and left this question unsolved. It so happens that the case of graphite is quite unique, since the scattering probability by the lattice vibrations $1/\tau_e$ is proportional to TE and the velocities of all electrons being the same, the mean free path depends on the energy E of the scattered electron $l \cong 1/TE$. This is a simple consequence of the linear relationship between the energy and the momentum vector at the Brillouin zone corners, the number of states per unit energy and unit surface in k-space being independent of energy.[14] Since $\bar{E} \cong kT$, we find $1/\tau_e \cong T^2$ as required.[15]

If the crystal has a finite dimension L (or has lattice defects), the probability of scattering at the boundaries $1/\tau_b$ will be, for the same reason as above, proportional to E. This time, however, no additional proportionality, with temperature, will be present, since the scattering is caused, not by thermal vibrations, but by the permanent boundary of the crystal. In order to get the total resistivity of the polycrystalline graphite, a member representing the resistance of all intercrystalline contacts also should be included. The scattering at the contacts is not uniform in all directions so that the arguments used above are inapplicable,[14] and all that can be said is that this contribution is probably a decreasing function of temperature and that its importance should rapidly increase as the crystallite sizes decrease. Thus, the resistivity should be $\rho = (A/kT)(1/\tau_e + 1/\tau_b) + c(T) = aT + b + c(T)$, where the constant contribution of the boundary scattering is inversely proportional to the dimensions of crystallites.

The system of curves (Fig. 1), however, cannot be represented by such a formula for two reasons: (a) the contribution $c(T)$ increases with decrease of the size of the crystallites; therefore, for a definite temperature T the slope of the curves ρ *vs* T should increase as we go to less graphitized samples. This is not found to be true in Fig. 1. The slope at room temperature, for instance, is found to be about independent of the degree of graphitization for samples graphitized up to 3200°C. (b) The experimental curves join the linear relationship at higher temperatures so quickly without the curvature extending over a wide temperature range, that this immediately suggests the presence of some kind of exponential factor.[16]

An exponential relationship cannot be due to scattering processes. Such a relationship will be obtained, however, if the graphite crystals should happen to possess a finite energy gap ΔE between the filled and empty energy bands. Thus, we are led to the conclusion that the Coulson-Wallace result is true only for infinitely large crystals of graphite. For small crystals of graphite, consequently, $\rho = [aT + b + c(T)]e^{\Delta E/2kT}$ with ΔE decreasing to zero with increase of the size of the graphite crystals. Such a relationship will remove the objection (b); it will, however, still be subject to objection (a). However, if it is assumed that there are excess electrons in the upper energy band, the objection (a) can also be satisfied, as will be shown below, and a good explanation of the curve ρ *vs* T obtained.

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[13] Z. Nishiyama, Z. Physik **71**, 600 (1931).

[14] W. Shockley, *Electrons and Holes in Semi-Conductors* (D. Van Nostrand and Company, Inc., New York, 1950). See the discussion of the conditions under which the mean free path is independent on energy (p. 493) and the formula (29).

[15] In a rigorous calculation of the resistivity, τ should not be taken out from under the integral, as was done by Wallace (see reference 9) (his Eqs. (3.11) and (3.12)). The temperature dependence, however, turns out to be the same for both procedures, so that the simplified treatment is given here.

[16] Two attempts were made recently to interpret the shape of the resistivity curves purely by scattering processes, both leading to identical formula $\rho = aT + (b/T)$. D. Bowen [Phys. Rev. **76**, 1878 (1949)] has overlooked, in derivation of the formula, the energy dependence of the scattering probability, and the existence of intercrystalline barriers, furthermore, he was unaware of objections (a) and (b). S. Mizushima and J. Okada [Phys. Rev. **82**, 94 (1951)] obtained the relationship from an analysis of Nishiyama's incorrect curves.

Figure 2 gives a resistivity curve for well-graphitized commercial graphite. This curve is a combination of results obtained by Goetz and Holser,[17,18] (temperature range 12°K–300°K) and by Powell and Schofield[19] (1400°C–2500°C), with a central part (0°–1000°C) fitted from the author's own data. It is unfortunate that no studies of resistivity have been made which would cover the whole range using the same sample of graphite. The author believes, however, that the general relations are brought out sufficiently well by such fitting of data. The whole curve from 150°K to highest temperatures can be represented by an empirical formula

$$\rho=(aT+b)/(r+e^{-\Delta E/kT}) \qquad (1)$$

with $a=3.5\times10^{-7}\Omega\text{cm}/°\text{C}$, $b=1.7\times10^{-4}\Omega\text{cm}$, $r=\frac{1}{5}$, and $\Delta E=600k=0.05$ ev.

This relationship can be interpreted in the following way: two scattering processes contributing to the resistivity at temperatures above 150°K are the thermal lattice scattering and the boundary scattering, the latter being approximately independent of temperature. The number of carriers consists of a constant number of excess electrons, n_e, and a variable number of electrons, n, activated from the lower band over the energy gap ΔE and a corresponding number of holes; therefore, the expression $re^{\Delta E/kT}$ represents roughly the ratio of the number of excess electrons to the number of activated electrons and holes.

The linear (high temperature) part of the curve corresponds to temperatures for which $kT>\Delta E$, where the number of activated electrons and holes is so large that the presence of a few excess electrons and of the energy gap is immaterial and the type of the curve becomes essentially similar to the one for a single graphite crystal. To the left of the resistivity minimum as we proceed towards lower temperatures, the number of activated electrons decreases due to the finite width of the gap. Here the resistivity would increase very strongly (exponentially), were it not for the excess electrons whose presence comes to be more and more felt in cutting down the rate of increase. Finally, below 150°K a stage is reached where there are so few activated electrons and holes that the current is conducted exclusively by the excess electrons. From there on down, either the number of carriers remains constant or decreases due to immobilization of the excess electrons on the surface sites. The immobilization of the excess electrons takes place, however, at considerably lower temperatures (~5°K, see Sec. V). The existence of the finite energy gap might lead to a rounding off of the Brillouin zone energy peaks (see Sec. VI) and change the linear into a parabolic relationship just near the corners of the zone. It seems that this cannot be the cause of the observed increase of resistivity at low temperatures and that the deviation of the expression (1) from the experimental curve below 150°K is mainly due to the contact resistances $c(T)$. Goetz and Holser[17] and Buerschaper[18] found that the ratio of the resistivities in a direction transverse to and parallel to the extrusion axis is a function of temperature. Goetz and Holser found that this ratio increased from 1.87 at room temperature to a value 2.03 at the lowest observed temperature (12°K). Extruded rods have a preferential arrangement of crystallites parallel to the axis. The higher resistivity in the transverse direction is partly because of this arrangement. In the transverse direction, the actual path length is larger (more zigzagging); consequently, the variation of the resistivity ratio with temperature shows that the resistance due to intercrystalline barriers (contacts) increases more for slow electrons if the change in direction of the flow of the current at the barriers is larger. Thus, the existence and a temperature dependence of the contribution $c(T)$ at low temperatures seems to be demonstrated by their experiments.

A slow decrease of the combined resistivity contributions b and $c(T)$ with increase of temperature in the range above 500°C could, in conjunction with the exponential factor, explain the changes in the linear slope with degree of graphitization (Fig. 1). On the other hand, the type of thermal vibrations of small crystallites might be sufficiently different from the larger ones to give such a variation.

As calculated by Wallace,[9] the number of activated electrons per atom at room temperature is of the order 2×10^{-4} or 2×10^{-3} (the lower value obtained for the

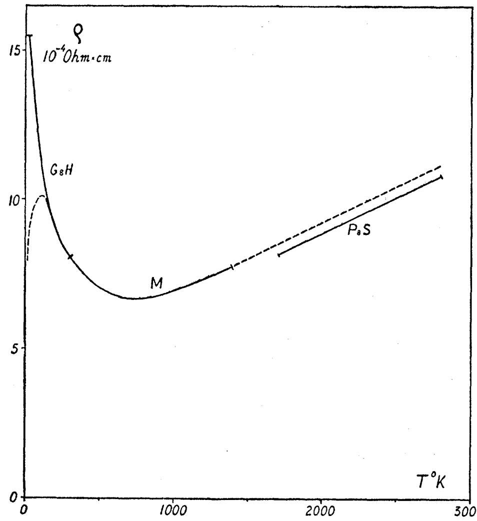

FIG. 2. Electric resistivity of polycrystalline graphite (carbon heat-treated to about 2900°C) as function of temperature. Experimental results due to: G&H—Goetz and Holser (see reference 14), *M*—the author, P&S—Powell and Schofield (see reference 16). Broken curve is calculated from Eq. (1) of the text.

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[17] A Goetz and A. Holser, Trans. Am. Electrochem. Soc. **82**, 391 (1942).

[18] R. A. Buerschaper, J. Appl. Phys. **15**, 452 (1944). Buerschaper's results are believed to be either erroneous or obtained for a different type of carbon. His curve for baked carbons cannot be fitted with ours.

[19] R. W. Powell and F. H. Schofield, Proc. Phys. Soc. (London) **51**, 153 (1939).

plane model is probably the more reliable of the two, since the tridimensional model leads to an inacceptable ratio $\rho_{\parallel}/\rho_{\perp}$). Due to the existence of a gap, the number of activated electrons and holes will be reduced for the polycrystalline graphite by the factor $e^{-\Delta E/kT}$ (Fermi level near the bottom of the conduction band). Multiplying this by the ratio of the number of excess electrons to the number of activated electrons and holes $re^{\Delta E/kT}$ (see above), we find the number of excess electrons roughly to be of the order 8×10^{-5} or 8×10^{-4} per atom (lower value preferred).

Formula (1) can be derived under very simplified assumptions for the region where $n_e \gg n$; that is, where the Fermi level is located close to the bottom of the conduction band. Strictly speaking, it is not applicable to the rest of the curve. It does, however, give a linear dependence for $kT > \Delta E$ as required and it is believed that the rigorous solution which should be obtained by using the Fermi-Dirac statistics and considering the variation in the position of the Fermi level and of the quantity $(N/m)_{\text{eff}}$ with temperature would yield a curve similar in shape to the one given by (1). Therefore, it is hoped that ΔE as determined from fitting (1) with the experimental curve should differ not too much from the real width of the gap.

III. BAKED CARBONS

The dependence of resistivity on temperature for baked carbon rods has been measured by many investigators. As in the case of graphitized rods there is, however, only one instance known to the author where a system of curves relating to the same sample treated to different temperatures was obtained. This was done by Powell and Schofield,[19] who measured the resistivity of baked rods to temperatures over 2000°C. However, their results are not in agreement with expectations and are probably erroneous. Crossings of curves occur only when there is either cracking or oxidation of samples, and their results show many such irregularities which, under correct experimental conditions, should not appear. It seems possible that the admixture of 20 percent lampblack in their carbons was in some way responsible for these irregularities.

A system of curves starting from baked carbon up to polycrystalline graphite was given in Fig. 1. The baked rods studied were petroleum coke laboratory-prepared samples with no component treated to a temperature higher than 1000°C. This is an important point to consider since commercial products contain particles which have been calcined to 1200–1300°C and consequently are mixtures of cokes treated to different temperatures (binder is baked only to 1000°C!). Unfortunately, the author has not investigated the complete series of curves for different intermediate treatments, and the measurements were performed only from room temperature up to 1100°C. For the latter reason, the remaining parts of the curves (*c*), (*d*), and (*e*) in Fig. 1 represent the probable trend of curves as can be expected on the basis of Powell's and Schofield's[19] curve for graphitized material and from the known temperatures at which the curves end (temperatures of heat treatment determine the general trend of curve *H*). We are in the process of preparing more extensive studies of such systems of curves for carbon rods and also for cokes at our laboratory. The upper part of Fig. 1 is given here only because these preliminary results for baked carbons deviate essentially from those of Powell and Schofield.

If the interpretation of the resistivity curves for graphitized materials suggested above is accepted, the character and shape of the system of curves in Fig. 1 can be easily understood. When the curve for a baked carbon is extrapolated beyond the line of treatment, it becomes evident that a minimum in resistivity would not be reached below 2000°C. Thus, from the position of the minimum, the estimated energy gap between the occupied and conduction bands is of the order of 0.2 ev or more. Studies of thermoelectric power performed recently at our laboratory by E. Loebner[20] show that the power at room temperature is negative and about equal for both baked and graphitized states.[21] Assuming the effective mass of carriers in the baked state to be $m \leq m_{\text{eff}} \leq m/6$ (see Sec. VII) a concentration of electrons 2×10^{-2} to 10^{-3} per atom is calculated from Loebner's results. On the other hand, at room temperature, the number of activated electrons for a gap 0.2 ev wide is about 1×10^{-7} and at 1000°C about 2.6×10^{-5}. It means that the conduction of baked carbons is due almost entirely to a constant number of excess electrons throughout the whole range for the curves (*a*) and (*b*) (Fig. 1).

It is seen then, that the decrease of the resistivity in curves (*a*) and (*b*) Fig. 1 is caused primarily by a decrease in scattering. These curves are essentially analogous to the low temperature part of the curve for polycrystalline graphite (below 150°K, Fig. 2). The dimensions of crystallites being smaller by a factor of more than 20, almost the whole resistance of the baked carbons is due to boundary scattering and contact resistances. Since the relative contributions of b and $c(T)$ are not known, the exact form of the function $c(T)$ cannot be estimated from the experimental data.

As mentioned before, different types of baked carbons show about the same resistivities when observed values are multiplied by the correction factors f_1, f_5, and f_6. The individual differences are real, however, as can be seen from the slopes of the curves resistivity *vs* temperature. Hard carbons in the baked state show a steeper slope—the relative decrease becomes, for very hard carbons, as much as 25 percent (for soft carbons 22 percent, see Fig. 1).

Figure 3 gives the variation of the room temperature

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[20] E. E. Loebner, Phys. Rev. **84**, 153 (1951).

[21] That it is negative for both states was found some time before by E. Man in our laboratory by rough experiments on the Hall effect.

resistivity of a carbon as a function of temperature of treatment. The part below 1100°C was obtained using raw cokes, and the part above 1000°C using commercial and laboratory carbon rods. The curves were fitted to overlap in the range 1000–1100°C. Three distinct regions are easily recognizable. The first is the region of the extremely rapid decrease from the raw state to a baked state. This occurs parallel to a strong evolution of gases and a considerable shrinkage of the material and is due to the transformation of the molecular solid, which is an intrinsic semiconductor with a large gap (see Sec. IV), into the baked carbon, which is an excess semiconductor with a high concentration of free electrons. The fast increase of the number of carriers is demonstrated by the strong drop of the thermoelectric power for samples treated from 700°C to 1000°C.[20] This transition occurs for all carbons (soft and hard) in the same temperature region; it will be further discussed in Sec. IV.

The second region is the flat plateau from about 1000°C to 2000°C. A very small change in resistivity is observed, although the size of crystallites (diameter) grows from about 25A up to almost 150A.[3] The expected decrease of the resistivity (scattering) due to growth of crystallites is compensated, however, by a decrease in concentration of the excess electrons. In fact, Loebner[20] found an increase of thermoelectric power in this range. The plateau is remarkable, since it occurs for most types of carbons. It extends to somewhat higher temperatures (by several hundred degrees) for hard carbons, which are more difficult to graphitize. The existence of the plateau is quite a general feature; in his experience the author has found only one type of carbon which showed a steady decrease of resistivity with increase of degree of graphitization. Also, once the author prepared a special carbon type which showed an increase of resistivity with increase of degree of graphitization (slightly rising plateau). These anomalous cases can be easily explained by variations in the mutual relation between the growth of crystallites and the concentration of excess electrons. The fact, however, that in most cases a good compensation of the two effects results in the formation of a plateau is remarkable in itself, and it seems compelling to look for a deeper meaning of this relationship. This question will be taken up again when the origin of the excess electrons is discussed.

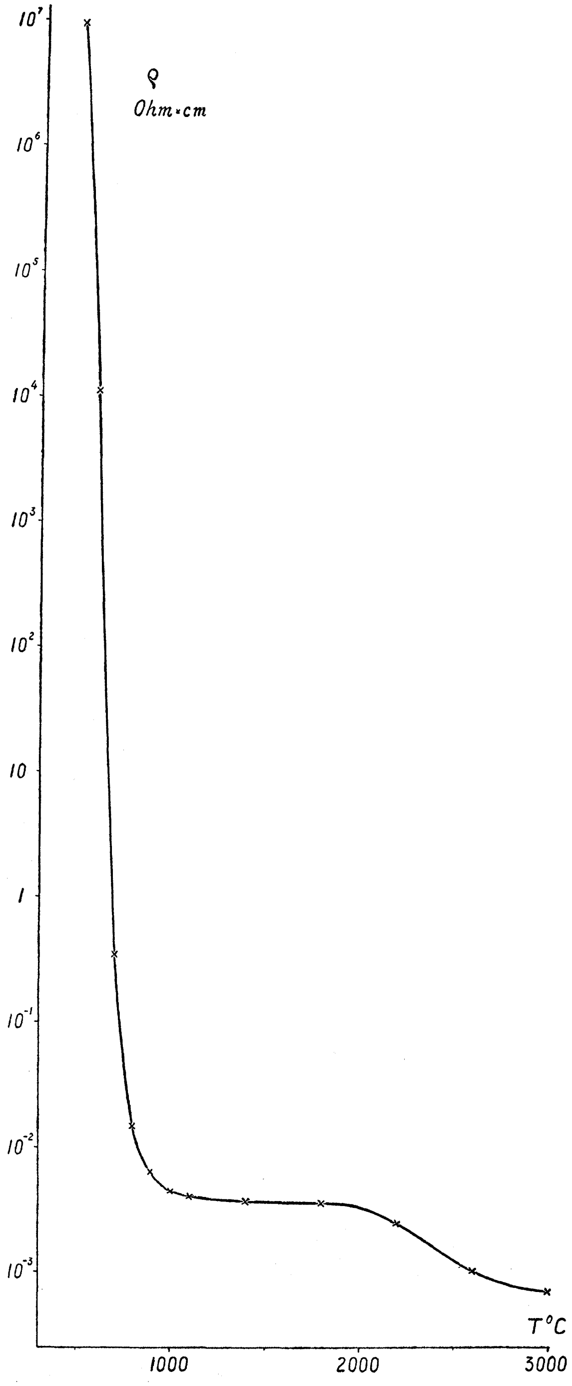

FIG. 3. Electric resistivity of a carbon at room temperature as function of the heat-treatment.

The third region shown in Fig. 3 corresponds to the graphitization of samples. Here the microcrystalline size increases strongly with temperature of treatment. The drop in resistivity above 2000°C is due to a further decrease in boundary and contact scattering, and to the overbalancing of the continuing decrease in number of excess electrons (from about 2×10^{-2} or 1×10^{-3} in the baked state to $\sim8\times10^{-5}$ for 2900°C graphite samples) by the increase in activation of electrons from the lower band, since the energy gap decreases steadily with increase of crystallite size and for samples treated above 2000°C the width of the gap becomes so small that considerable activation occurs at room temperature. The total concentration of carriers in polycrystalline graphite ($\sim1.5\times10^{-4}$ for 2900°C sample) is smaller than in the baked state, but the effective masses of carriers are also smaller. The factor $(N/m)_{\text{eff}}$ comes out to be about 2–4 times smaller than for the baked state. This

TABLE I. Energy gap in condensed ring systems as obtained from temperature variation of resistivity in ev.

Temperature of treatment °C		300	350	425	500	520	450	630	690	700	715	800
Sandor[a]	Coal coke								0.144			0.042
Akamatu and Inokuchi[b]	8–9 rings 1.06–0.75											
Mizushima and Okada[c]	Pitch coke					0.2					0.06	
Kmetko[d]	Pyrolysed cellulose			0.80	0.62		0.41	0.22		0.09		0.03
		Energy gap from infrared absorption										
Kmetko[d]	Pyrolysed cellulose	1.2	0.9	0.7	0.5		0.35	0.25		0.2		

[a] See reference 22.
[b] See reference 23.
[c] See reference 16.
[d] See reference 24.

explains the previously puzzling fact, that the resistivity drops from the baked to the graphitized state, only by a factor of about 6, when the crystallite sizes differ by a factor of 20 or more. The difference in the factor $(N/m)_{\mathrm{eff}}$ clarifies the matter and shows that, after all, the contribution of the boundary scattering and of contact resistances $[b+c(T)]$ is about inversely proportional to the crystallite size, as expected. Correcting the resistivities for lattice scattering $(a-\frac{1}{3}\cdot f)/(e-f)=7$ and multiplying by the ratio of $(N/m)_{\mathrm{eff}}$ we get in fact the factor 21, as required.

IV. CONDENSED RING MOLECULAR SOLIDS

Figure 1 has not been extended to samples of coke treated to temperatures below 1000°C because raw cokes have very high resistivities (see Fig. 3) and the corresponding curves could not be conveniently included in this graph. The interesting characteristic of these samples is that as the temperature of the treatment decreases the curves ρ *vs* T become steeper and steeper; (in fact, many times steeper than the curve (*a*) in Fig. 1). The great steepness of the curves for compressed raw coal coke has been noticed by Sandor.[22] Sandor believed the effect to be due to the existence of some kind of nontransparent intermolecular potential barriers and calculated their height by fitting the experimental curves with the exponential formula $e^{\Delta E'/kT}$. Sandor found $\Delta E'$ to be 0.072 ev for a 690°C coke and 0.021 ev for a 800°C coke. In the author's opinion such a large variation on the $\Delta E'$ value indicates that Sandor's interpretation of the exponential relationship is incorrect since $\Delta E'$ cannot be in any way connected with barriers, which, after all, consist of contact regions between molecules. Some molecules, in the solidified substance, are bound by C—C valence bonds to neighbors and these contacts do not represent high barriers. In the rest of the contacts the carbon ring systems are separated by peripheral foreign atoms (H, N, O) and these are the opaque barriers partly responsible for the high resistance of this substance. The high resistance barriers are high, but narrow (~10A), and therefore have some transparency for the conduction electrons. The transparency of such barriers is proportional to the energy of the electrons, and its temperature dependence is overshadowed by the exponential variation. Furthermore, these barriers decrease in numbers but not in quality as the size of the condensed ring systems increases and therefore cannot be the cause of the variation of $\Delta E'$. If, however, it is assumed that condensed ring systems are intrinsic semiconductors with an energy gap $\Delta E(\Delta E=2\Delta E')$, then the experimental temperature variation can be understood as a variation in the number of activated carriers and represented by the factor $e^{\Delta E/2kT}$. Akamatu and Inokuchi[23] reached independently the same conclusion in interpreting their results on resistivities of violanthrone and pyranthrone powders under pressure. Their work is remarkable since the experiments were performed with substances of uniform molecular structure. The resistivity of condensed ring systems has been investigated recently also by Mizushima and Okada[16] and in our laboratory by Kmetko.[24] In all cases, the variation of the resistivity with temperature is approximately exponential and the ΔE values found by these authors are collected in Table I.*

Our interpretation has been directly confirmed by the work of Kmetko,[24] who has shown the existence of a close agreement between the ΔE values obtained from curves of the resistivity and from the position of the edge of a continuous absorption band in the infrared. Kmetko's infrared values are included for comparison in Table I.

As can be seen, the size of the energy gap decreases as the condensation process progresses. The interesting feature is the general agreement between different authors who worked with different original starting substances—and also the individual differences, which directly correlate with the degree to which these substances resist graphitization (hardness).

The ΔE values in Table I decrease as we go from raw cokes towards baked carbons. For samples treated above 600°C, however, the slope of the resistivity curves does not yield the real value of the energy gap, the slope

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[22] J. Sandor, Proc. Conf. Ultrafine Structure of Coals and Cokes, London, 1944, p. 342.

[23] H. Akamatu and H. Inokuchi, J. Chem. Phys. 18, 810 (1950).

[24] E. A. Kmetko, Phys. Rev. 82, 456 (1951).

* *Note added in proof.*—Shortly H. Inokuchi investigated the resistivities of a number of aromatic substances, from 6 up to 10 ring systems, and found gaps ranging from 1.7 to 0.75 ev. [Bull. Chem. Soc. Japan 24, 222 (1951)].

becoming smaller due to the presence of the increasing numbers of excess electrons. In fact, as mentioned before, Loebner[20] has shown that for samples treated to 700°C and higher the thermoelectric power becomes measurable and decreases strongly in absolute value as one proceeds toward the baked state. For samples treated 700°C or above, Kmetko[24] found an increasing continuous absorption all through the infrared which must be due also to the presence of increasing numbers of free electrons. For samples treated below 600°C, no excess electrons are present; the resistivity and infrared values vary in a parallel manner, the infrared values being lower since the absorption edge gives information about the smallest gaps and the resistivity about the largest ones in a mixture of molecules of different sizes.

The great drop in room temperature resistivity by a factor 2×10^9 (Fig. 3) from $10^7\Omega$ cm for raw cokes (500°C samples) to around $5\times10^{-3}\Omega$ cm for baked carbons (1000°C samples or higher) is to a great extent due to the increase in number of carriers. Raw cokes (treated below 600°C) are essentially intrinsic semiconductors with a very large energy gap; consequently, the number of activated electrons is very small; for instance, for a 0.6 ev gap, the number is of the order 10^{-9} per carbon atom at room temperature. Baked carbons, on the other hand, have, as calculated before, about 10^{-3} excess electron per carbon atom or more; thus, a change in resistivity by a factor 10^6 is explained by the variation in number of carriers. The rest of the variation in resistivity is undoubtedly due to a process of a gradual replacement of the high opaque intermolecular barriers by low resistance C−C contacts, which occurs at the time when the peripheral gases are driven out in baking.

V. THE ORIGIN OF EXCESS ELECTRONS

The great regularity with which the resistivity of organic substances drops over the range of coking from 500°C where they are practically insulators to about a 0.005Ω cm for baked carbons (1000°C) requires explanation. No matter what the impurities in the parent organic substance are, the drop occurs always at the same temperatures and leads to approximately the same resistivity (corrected for f_1, f_5, and f_6). This regularity forces us to look not to the impurities for a source of the free conduction electrons (excess electrons), but to the carbon itself. A clue to the origin of excess electrons is furnished by the results previously mentioned, which show that the excess electrons appear in great numbers at the time when most of the peripheral gases are driven out of the carbon. The molecular condensation process is not fast enough to take care of all the newly formed free valence bonds on the peripheries; furthermore, many molecules are not in favorable positions relative to their neighbors, so that a great number of free peripheral valence bonds are left without having anything to be attached to. Consequently, a strong valence adsorption and also a chemical activity would be expected for carbons and polycrystalline graphite. But this is not what is observed in experiments. The adsorption of carbons is mainly of molecular Van der Waals type. For instance, baked (calcined) carbon blacks show in adsorption a very small percentage of chemical bonds.[25] The adsorption of radon on graphite crystals is about uniform around the crystal; in catalysis the whole surface of microcrystals is equally effective without preference for the edges.[26] Calcined cokes and graphite resist oxidation very well. They are also remarkable in that there is no formation on their surface of any oxide films at room temperature. The free peripheral carbon valences do not seem to be present where they are expected; consequently the peripheral carbon atoms have changed their state into a different hybridized state which does not show the activity of an unsaturated valence.

Some information about the process of transformation into this new hybridized state is obtained from experiments of Savage and Brown.[27] They showed that graphite, ground up mechanically, has the power of attaching hydrogen and other gases by a chemical bond at the freshly created peripheries along the broken surface. The power is lost after the carbon has been heated to temperatures above 800°C. The author had similar experiences with the oxidation of ground carbons. Evidently there is some activation energy necessary to induce the transition from the regular state with three valence bonds in a plane into this new hybridized state, which seems to be the more stable of the two. When gases are driven out in the baking (calcining) process, the temperature is sufficient to form this more stable state right from the start, and therefore no chemical activity in the calcined or graphitized carbon is detectable at room temperature.

It is suggested here that the carbon atoms in this new state are the source of the excess electrons. The formation of the excess electrons can be pictured as follows: when the atom attached to the peripheral carbon is removed, the energy of the electron taking part in the bond is raised. When tied in a bond the electron belongs to the energy band of the planar valence electrons of graphite; when, however, the valence becomes free, the electron is lifted above the filled band of the resonance electrons to a level higher in energy than the bottom of the conduction band. From this state the electron jumps into the conduction band, if the activation energy necessary to change the state of the atom happens to be supplied by the heat vibrations. In the bottom of the conduction band, the electron is almost free; a very small amount ϵ of kinetic energy will suffice to tear it away from the positive ion left behind. Consequently, this electron will, at very low temperature, be bound in

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[25] Beebe, Biscoe, Smith, and Wendell, J. Am. Chem. Soc. **69**, 95 (1947) and **72**, 40 (1950).

[26] U. Hofmann and W. Hoper, Naturwiss. **32**, 225 (1944).

[27] R. H. Savage and C. Brown, J. Am. Chem. Soc. **70**, 2362 (1948).

some sort of a surface state with a very low energy of activation ϵ. It seems possible, then, that the existence of this activation energy ϵ is responsible for the strong variation of conductivity of carbons observed at very low temperatures.[28]

Thermoelectric studies of carbons[20] have shown that the concentration of excess electrons decreases for cokes treated above 1400° with increasing temperature. This decrease could well be the result of a gradual driving out of impurities by heating; these impurities might be supplying some excess electrons present in addition to the carbon's own sources. If this decrease in the number of excess electrons should be caused by a foreign matter, it would be difficult to understand why the formation of the plateau, Fig. 3, for most of the reasonably pure carbons (not too impure), is such a regular occurrence. It seems very improbable that in all these varieties of carbons investigated a definite concentration of a certain impurity was present. Furthermore, it was estimated from the thermoelectric power of carbon that the concentration of the excess electrons is about $10^{-2}-10^{-3}$ per atom. If there are that many excess electrons due to the peripheral carbon atoms, large amounts of impurities would be necessary to change definitely the general trend of correlations. (On the other hand, the properties of polycrystalline graphite should be much more sensitive to impurities, since this substance possesses a much lower concentration of excess electrons.) It seems attractive to the author to ascribe the existence of the resistivity plateau to processes occurring in the carbon itself, and to blame impurities for smaller deviations from the general relationship and for the few anomalous cases observed.

As discussed above, the excess electrons present in pure carbons are due to those peripheral atoms which happen not to be bonded to neighboring crystallites. The proportion of the nonbonded peripheral atoms to the total number of atoms in a crystallite will certainly decrease with the growth of crystallites. Let it be assumed that the nonbonded ones constitute a certain constant proportion of all peripheral atoms. The concentration of excess electrons will then be inversely proportional to the linear dimensions of crystallites. On the other hand, the contribution of the contact resistances between crystallites to the total scattering will also be about inversely proportional to the dimension of crystallites—thus there will be a cancellation of the two factors and a resistivity independent of size of crystallites will be obtained. On the other hand, if the proportion of nonbonded to bonded peripheral atoms increases with the size of crystallites, then the concentration of excess electrons will decrease less with increase of crystallite size, but the contribution of the contact resistances will also be larger for large sizes (less intercrystalline bondings), so that, again, a resistivity plateau will be obtained. Thus, the general occurrence of the plateau can be understood irrespective of the variations in the polycrystalline structure of carbons.

The quantitative agreement is not unreasonable. Loebner's data give about 1.35 for relative change in number of excess electrons for samples heated to 1400°C and 2200°C. Pinnick's x-ray crystallite size determination[29] for the same carbons gives an increase by a factor 2.6 for the diameter in the direction of the graphite plane. When one considers the presence of activated electrons from the lower band in the 2200°C carbon, the disagreement of the two numbers does not seem to be serious, especially if one notices that 2200°C is located already beyond the end of the resistivity plateau and that in the evaluation of thermoelectric data, the variation of the effective mass of carriers has been neglected.

VI. THE NATURE OF THE ENERGY GAP

Wallace[9] has expressed the opinion that the existence of the zero energy gap between the filled and empty bands is presumably a consequence of the symmetry of the graphite lattice and is independent of the approximations considered. If so, the energy gap should not be different from zero for crystals of finite dimensions unless a deviation from hexagonal symmetry is introduced into the system of benzene-rings by peripheral tensions, or some other reasons. Since the electronic energy rises linearly at the corners of the hexagonal Brillouin zone, there will be a tendency for a crystal of finite dimensions to change its shape so as to round off the sharp energy peaks in the Brillouin zone corners, the decrease in the electron energy being used up to distort the benzene-rings system. Thus a finite energy gap would be formed as observed experimentally in polycrystalline graphite.[30]

It is hard to understand how the molecular planes can be sufficiently distorted as to acquire such large energy gaps as observed. It seems that these gaps are real energy gaps at the Brillouin zone boundaries and not merely manifestations of the discontinuity in molecular electronic energy levels. The calculated distances of levels, assuming a free electron plane box model, are at least by one order of magnitude too small for that. Moreover, in polymerized substances like carbons the electronic levels are broadened by bonding of molecules to their neighbors and coupling of their vibrations to such an extent that the discrete structure inside the bands becomes wiped out. Thus the continuous appearance of the infrared and visible absorption is probably real and not simulated by a dispersion in molecular sizes. Bonding of molecules to the neighbors brings distortions in the system. The differential shrinkage in cooling[11] leads to existence of large strains inside of polycrystalline graphite. It seems probable that these strains affect the size of the gap and are responsible for

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[28] Giauque, Stout, and Clark, J. Am. Chem. Soc. 60, 1053 (1938).

[29] H. T. Pinnick, unpublished results.

[30] The author is indebted to Dr. G. H. Wannier of the Bell Telephone Laboratories for pointing out to him this possible explanation.

the slow decrease in the size of the gap from the baked to the graphitized state. Single crystallites of graphite, or crystallites less strained, as, for instance, in graphitized carbon blacks, might have considerably smaller energy gaps.

In studying the ultraviolet spectra of unsaturated hydrocarbon chains, Kuhn[31] reached the conclusion that the lowest electronic absorption frequency in the spectrum can be represented by an empirical relation which definitely points toward the existence of an energy gap at the Brillouin zone boundary of an order 2 ev for molecules 15 carbon atoms long. Kuhn has proposed an explanation based on the assumption that the presence of the free ends of the molecule stabilizes preferentially one of the resonating structures, thus introducing a double periodicity into the lattice and breaking the series of electronic levels into distinct groups (or bands). It seems doubtful that a variation in bond length, large enough to give an energy gap of the size 1–2 ev, is really present in such molecules.[32] Kuhn's explanation, however, is very interesting, to say the least, especially in light of the recently detected deviations of the graphite lattice from hexagonal symmetry, deviations which according to Hoerni and Weigle[33] possess a double periodicity along the carbon chains (direction of motion for zero energy gap in graphite). These deviations might be in some way related to the finite size of the energy gap in polycrystalline graphites; it is felt, however, that the whole problem at the present stage requires a thorough theoretical clarification.

VII. DIAMAGNETIC ANISOTROPY[34]

The existence of the energy gap and the presence of excess electrons are factors which have to be taken into consideration when an explanation of the diamagnetic properties of large aromatic systems is attempted. Pauling[35] was the first to realize that in order to reconcile the values of the anisotropic component found for susceptibilities of benzene and other small aromatic molecules on the one hand and for graphite on the other, some new assumptions have to be made about the motion of resonance electrons. He proposed a semiclassical theory of induced currents in the benzene-ring network which leads to a very rapid increase in the anisotropic component with the size of the molecule. The value corresponding to graphite is reached according to Pauling for molecular diameters of about 40A. The increase is definitely too rapid: already for pyrene (4 benzene rings) Pauling's theory gives a value larger than experimental by 60 percent. The susceptibility found in experiments for baked carbons with molecular diameters about 40A represents only a small fraction of the susceptibility of the large graphite crystals. Grinding the graphite crystals to a size below 1 micron decreases measurably the susceptibility.[36] In a study of carbons of different origin Miwa[37] has shown that, very roughly, the susceptibility increases linearly with the molecular size and rises to about 30 percent of the graphite value for crystallite planes of about 200A diameter (70A thickness). Even for polycrystalline graphite, the susceptibility is still considerably below the limiting value.

The large graphite susceptibility does not seem to be due to an effect present in smaller aromatic systems. Examination of experimental data obtained for small aromatic molecules[38] shows that the molar anisotropic component of susceptibility is proportional to the number of rings in the systems. Quantum-mechanical calculations of London[39] and Brooks[40] performed for a few of the simplest molecules are in rough agreement with the experimental data.[41] The molar anisotropic component for benzene is $\Delta\chi_B = -54\times 10^{-6}$ and for the other molecules roughly a multiple of this, with small deviations probably due to the specific molecular ring arrangement. Extrapolating this to larger aromatic molecules, it is expected therefore that aromatic molecules have, in general, molar susceptibilities $\Delta\chi \cong n\cdot\Delta\chi_B$ where n is the number of benzene-rings. This result seems to be a natural consequence of the fact that the resonance electrons form closed shells in aromatic molecules and fill exactly a Brillouin zone. For a full Brillouin zone the diamagnetism should be proportional to the molecular volume, that is, to the number of benzene-rings.†

This closed shell diamagnetism of London type is not the main cause of the large diamagnetism of graphite. The anisotropic component of susceptibility for a graphite crystal is -30×10^{-6} per gram, that is -720×10^{-6} per benzene-ring mole; this is about 13.5 times larger than the diamagnetism of the closed shell of resonance electrons. Per gram atom the susceptibility of graphite (-360×10^{-6}) is even superior to the susceptibility of bismuth (-315×10^{-6}). Ganguli and Krishnan[42] have studied the temperature dependence of the susceptibility of graphite and attempted to explain it by assuming that the resonance electrons form a free two-dimensional electronic gas. The general theoretical formulas for the Landau diamagnetism of free electrons, as developed by Stoner, have been adapted by

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[31] H. Kuhn, J. Chem. Phys. **17**, 1198 (1949). See also, J. R. Platt, J. Chem. Phys. **17**, 484 (1949).

[32] C. A. Coulson, Proc. Roy. Soc. (London) **A169**, 413 (1939).

[33] J. Hoerni and J. Weigle, Nature **164**, 1088 (1949). See also J. S. Lukesh, Phys. Rev. **80**, 226 (1950).

[34] See the preliminary note: S. Mrozowski, Phys. Rev. **80**, 123 (1950).

[35] L. Pauling, J. Chem. Phys. **4**, 673 (1935).

[36] C. H. Gregory, thesis, California Institute of Technology (1935); J. R. Rao, Indian J. Phys. **6**, 241 (1931).

[37] M. Miwa, Science Report, Tohoku University **23**, 242 (1934).

[38] K. Lonsdale, Proc. Roy. Soc. (London) **159**, 149 (1937).

[39] F. London, J. phys. et radium **8**, 397 (1937).

[40] H. Brooks, J. Chem. Phys. **8**, 939 (1940) and **9**, 463 (1941).

[41] See also R. McWeeny, Proc. Phys. Soc. (London) **64**, 261 (1951).

† *Note added in proof:*—Recently ovalene (10 compact rings) has been found to have a magnetic anisotropy of -616×10^{-6} by Akamatu, Inokuchi, and Handa [Nature **168**, 520 (1951)].

[42] W. Ganguli and K. S. Krishnan, Proc. Roy. Soc. (London) **117**, 168 (1941).

them to the case of an existence of a crystalline field with the energy surfaces $E=(h^2/2m)(\alpha_1 k_x^2+\alpha_2 k_y^2+\alpha_3 k_z^2)$. The formulas lead to a perfect agreement with experiments, when it is assumed that $N_{\rm eff}\alpha_1\alpha_2=1$; furthermore, by fitting the theoretical curve to the experimental results a very low degeneracy temperature of 520°K is obtained. The remarkably good agreement between the experimental and the theoretical curves makes it difficult to believe the agreement to be fortuitous. On the other hand, Ganguli and Krishnan's theory is unacceptable since, for instance, it leads to a large electronic specific heat of the order of 2 kcal/mole! Ganguli and Krishnan were not aware of the decrease in the density of electronic levels to zero at the Brillouin zone boundary between the occupied and empty bands; they treated the electronic gas as in a metal and assumed all resonance electrons to be effective.

It appears, however, that by a reinterpretation of the constants in the Ganguli-Krishnan theory, a reasonable picture of the diamagnetism of graphite can be obtained. This diamagnetism is due to the Landau diamagnetism of holes in the lower band and electrons in the conduction band. The effective number of electrons and holes is small ($N_{\rm eff}\sim 10^{-3}$) and their effective mass for the motion in the direction of the graphite plane also small. From the Ganguli-Krishnan relation $N_{\rm eff}\alpha_1\alpha_2=1$ obtained by fitting their high temperature data with theoretical formula, the effective mass is $m_{\parallel}=m/\alpha_1$-$m/\alpha_2=m/30$ of the order required by Wallace's[9] calculations. The degeneracy temperature is low since the electrons and holes have approximately Maxwellian velocity distributions. From the second Ganguli-Krishnan relation $\alpha_3 N_{\rm eff}=\alpha_1\alpha_2\alpha_3 N_{\rm eff}^2=(1/190)^3$ obtained by fitting their low temperature data with theoretical formula, taking for low temperatures $N_{\rm eff}\sim 10^{-4}$, it is found $1/\alpha_3\cong 700$, that is, a mass about 25 times larger for the motion across the graphite planes than obtained by Wallace, but this is just what is expected, since Wallace's calculations yield a too high conductivity across the planes. The remaining other difficulties of the Ganguli-Krishnan theory are also removed; in the modified model the electronic specific heat is small (about 100 times smaller) and the free electron paramagnetism is also negligible in comparison to the diamagnetism ($3/\alpha_1\alpha_2\cong 1/300$).

In this modified Ganguli-Krishnan theory the numbers $N_{\rm eff}$ and α_1, α_2 are functions of temperature; it so happens, however, that the relation $N_{\rm eff}\alpha_1\alpha_2=1$ is independent of temperature since $N_{\rm eff}\sim(kT)^2$ and $1/m_{\parallel}\sim\alpha_1=\alpha_2\sim(kT)$. (See Wallace[9]). The cancellation of the temperature dependence is the direct reason for the excellent agreement of the Ganguli-Krishnan theoretical curve with experimental data over the whole range of temperatures. The theory as given by Ganguli and Krishnan and modified here is certainly not sufficiently refined to give anything but a rough description of the effects, especially in view of the use of the ellipsoidal expression for the energy surfaces.

In order to explain the decrease of the diamagnetism with crystallite size, it is necessary to assume that the effective masses of carriers increase as the size of the crystallites decreases. This might be caused by the increase in the concentration of excess electrons (shift of the Fermi level) or the rounding off of Brillouin zone corners, or both. For crystals of finite size formation of the finite energy gap and rounding off of the Brillouin zone energy peaks (corners) will bring about a decrease in the curvature of the energy surfaces (decrease in α_1 and α_2) near the zone corners. Similarly, the presence of an excess of electrons or holes will shift the position of the Fermi level into regions of smaller curvature of the energy surfaces. The Landau diamagnetism being proportional to $N_{\rm eff}\alpha_1\alpha_2$, we see by substituting $N_{\rm eff}=10^{-2}$ for the baked state, that a decrease of the susceptibility by a factor 10 to 20 in comparison to graphite (as required by Miwa's[37] results) leads to effective masses $m_{\rm eff}\cong m/2$ to $m/3$ in crystallites of about 30A diameter. On top of the Landau diamagnetism, there is the diamagnetism of the full band (shell) of resonance electrons present, which is a function of the molecular size: 2.2×10^{-6} for graphite, decreasing to 0.245×10^{-6} per gram for a pure disordered benzene ring polymer.

It is felt that at this time it is more important to gather some additional data on susceptibilities of carbons under different conditions than to try to develop the theory further. We are now in our laboratory preparing to investigate some well-defined carbon and graphite samples.

CONCLUSION

In the process of developing a consistent picture of electronic processes in carbonized substances up to graphite it was shown above that the experiments lead us to assume (1) the existence of a finite energy gap between the occupied and empty bands, and (2) the presence of excess electrons due to peripheral carbon atoms with free, unattached valencies. Both these assumptions, as well as the proposed theory of the diamagnetic susceptibility of carbons and graphite require a thorough, theoretical study. Further experimental verifications beyond those reported in this paper are in process of preparation at our laboratory.

It should be pointed out here that considerations presented in this paper can be further extended and applied to carbon systems which have undergone deformations or atomic displacements. The transformation of a free valence electron into an excess conducting electron being connected with an energy of activation and with a dissipation of the energy difference might be a factor which should be taken into consideration in thermochemical studies when properties of carbons with strongly differing crystallite sizes are compared.

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