

Hall Effect and Magnetoresistivity in Carbons and Polycrystalline Graphites*

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The Hall constant and magnetoresistance of a carbon (soft type) were investigated as a function of heat treatment temperature, T_{ht} , (that is, crystallite size) at two ambient temperatures T (78° and 300°K). The maximum in the Hall constant shifts toward higher heat treatments as the ambient temperature is lowered, in much the same way as does the maximum in the thermoelectric effect. Anomalies in the Hall curves in the range $1600 < T_{ht} < 1900^\circ\text{C}$ are shown to be due to impurities. No magnetoresistance is detectable for $T_{ht} < 1700^\circ\text{C}$; the magnetoresistance was found to be negative in the range $1700 < T_{ht} < 2300^\circ\text{C}$ and to be positive and rapidly increasing with T_{ht} above that. For both ambient temperatures the maximum of negative

magnetoresistance occurs at about the same T_{ht} as the maximum of the Hall constant. Introduction of acceptors changes the magnetoresistance in the direction of lower T_{ht} . The value of magnetoresistance and of Hall constant show a sensitive dependence on the alignment of crystallites in the samples. The results are interpreted in terms of the band model. It is concluded that the lower (full) and upper (empty) bands are slightly overlapping in graphite crystals, and furthermore, that the negative magnetoresistance is due to holes in the lower band and the positive magnetoresistance as well as the high diamagnetic susceptibility are due to electrons in the upper band. Remarks about the thermoelectric effect and electrical resistance are also included.

I. INTRODUCTION

SEVERAL years ago an explanation was proposed for the mechanism of the electrical conduction in a broad class of solids, solids ranging from polymerized aromatic molecular solids through carbon materials and polycrystalline graphite up to single crystals of graphite.¹ In such solids the current follows preferentially along the aromatic planes (planar condensed benzene-ring systems); it is carried by π electrons excited into the upper (conduction) energy band and holes left behind in the lower π band (intrinsic carriers) and/or by holes already present in the lower (filled) π band (excess carriers). These last holes are due to trapping of π electrons in surface sites which, according to the proposed explanation, are identified with σ orbitals of the free unengaged carbon valencies on the peripheries of the condensed benzene-ring systems. As the size (diameter) of the aromatic planes increases with heat treatment of the solid to a progressively higher temperature, T_{ht} , the energy gap between the upper and lower π band gradually decreases and finally disappears completely when the crystallite size becomes of the order of 0.1μ . The variation of the energy gap, in conjunction with the changes in the number of surface traps, explains qualitatively the changes occurring with T_{ht} in electrical conductivity of aromatic solids and in other properties like thermoelectric and Hall effects at room temperature as well.^{1,2} Since the activation energy of π electrons into the upper band steadily decreases with increasing crystallite diameters, it was expected that the position of the positive maximum in the thermoelectric effect and in the Hall constant would depend on ambient temperature, shifting towards lower T_{ht} (smaller crystallite sizes) when the measurements are

performed at higher ambient temperatures. Recently Loebner³ reported the results of studies of the thermoelectric effect for carbons at different temperatures in which the occurrence of such a shift of the maximum was demonstrated. However, since the interpretation of the Hall constant is essentially simpler and since the measurements yield absolute values directly, it was felt worthwhile to check the existence of the predicted shift also for the Hall constant.

The Hall constant has been determined for well-graphitized materials by a number of investigators in the past.⁴ Only recently in three instances measurements have been extended over a range of crystallite sizes. Kmetko² and Donoghue and Eatherly⁵ investigated the Hall constant as a function of heat treatment T_{ht} , from the baked state up to graphitization, only, however, at room temperature. On the other hand, Kinchin⁶ studied the Hall constant at various ambient temperatures, but for graphites with crystallite diameters of 300 Å and above, that is, in the range of T_{ht} considerably outside the position of the maximum. Thus, a study of the Hall constant over a wide range of T_{ht} for at least two considerably different ambient temperatures seemed necessary to establish the presence of the effect expected.

Since no information as to the dependence of the magnetoresistivity on ambient temperature T and on heat treatment temperature T_{ht} (crystallite size) was available, measurements of resistance were performed concurrently with the Hall constant studies. The experiments yielded most interesting results,⁷ and in

³ E. E. Loebner, *Phys. Rev.* **102**, 46 (1956).

⁴ H. Zahn, *Ann. Physik* **16**, 148 (1905); G. Gottstein, *Ann. Physik* **43**, 1079 (1914); H. Kammerlingh Onnes and K. Hof, *Proc. Roy. Acad. Amsterdam* **17**, 520 (1915) were the early ones. More recently: G. Hennig, *J. Chem. Phys.* **19**, 922 (1951).

⁵ J. J. Donoghue and W. P. Eatherly, *Rev. Sci. Instr.* **22**, 513 (1951).

⁶ G. H. Kinchin, *Proc. Roy. Soc. (London)* **217**, 9 (1953).

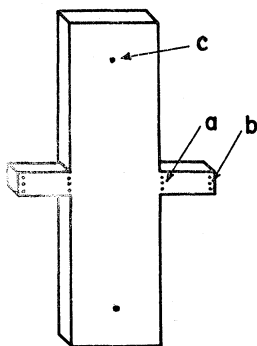
⁷ S. Mrozowski and A. Chaberski, *Phys. Rev.* **94**, 1427(A) (1954).

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¹ S. Mrozowski, *Phys. Rev.* **85**, 609 (1952) and Errata [*Phys. Rev.* **86**, 1056 (1952)].

² E. A. Kmetko, *J. Chem. Phys.* **21**, 2152 (1953).

FIG. 1. Shape of carbon plates used in this work. *a* and *b* are holes for determination of Hall constant, *c* for magnetoresistance.



consequence the work was extended to a study of the dependence on geometrical factors (alignment of crystallites) and also on the acceptor concentration, by studying the magnetoresistance of residual bisulfate compounds of carbon.

II. EXPERIMENTAL AND RESULTS

A. Hall Constant

For the studies of the Hall constant, samples were cut out in the longitudinal direction from $\frac{3}{4}$ -inch-diameter National Carbon Company baked rods (essentially soft carbon type), heat-treated previously to a given temperature (4 samples for each heat treatment T_{ht}). The heat treatment consisted throughout this work of a gradual increase of temperature up to the maximum in about 2 to 4 hours and holding for 10 minutes at the top temperature T_{ht} , all in an atmosphere of pure nitrogen. The samples were plates about 3.7 cm long, 0.6 cm wide, and 0.1 cm thick and having side arms for the Hall effect potential leads (Fig. 1). The ends of the plates were clamped by means of flat beryllium copper springs which served as current leads. A direct current of $\frac{1}{2}$ amp was used, the Hall potential being measured by means of a potentiometer. Platinum potential leads were inserted into fine holes drilled in the carbon material (see Fig. 1; points *a* and *b* indicated on the arms), and pairs of holes were selected which differed in potential the least in the absence of the magnetic field. The small residual potential difference resulted in asymmetric deflections for the two directions of the magnetic field, due to the presence of magnetoresistive effect. This asymmetry, however, cancels out when the average of the two readings is taken; this was checked by using the compensation method of Breckenridge and Hosler⁸ on a number of occasions. For measurements at room temperature, the sample had to be protected from air convection currents, which introduced some scattering into the results. The low-temperature measurements were performed by immersing the sample with all the leads directly into liquid nitrogen. Two different magnets were used as

⁸ R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 753 (1953).

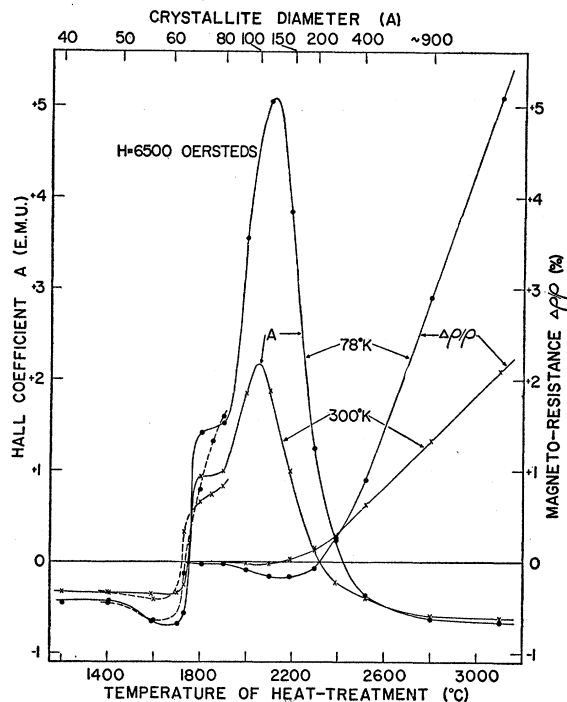


FIG. 2. Dependence of the Hall constant A and magnetoresistance $\Delta\rho/\rho$ on heat treatment of the carbon for two ambient temperatures. Dashed curves in the region $T_{ht}=1650$ – 1900°C correspond to chlorinated specimens.

sources of magnetic field: the smaller one with pole-pieces 3 inches in diameter, and the larger one with 8-inch-diameter poles. The second one, with a 2-inch pole separation, permitted the attainment of fields to about 14 000 oersteds. The field intensity was determined by means of a fluxmeter; the fluxmeter coils were standardized, at a field around 3300 oersteds, using proton resonance.

The Hall voltage was taken as an average of four readings (magnetic field and current through the sample being reversed) at a number of fields ranging from 2000 up to 10 500 oersteds. For all heat treatments, no dependence of the Hall constant on the field strength has been detected which would be greater than the limits of errors of the measurements for both the room and liquid nitrogen temperature. For the given dimensions of samples, no correction is necessary for the finite ratio of the length to width.⁹ The average values for the Hall constant as directly calculated from the data are plotted as a function of heat-treatment temperature T_{ht} in Fig. 2. Since the size of carbon crystallites grows with increasing heat treatment and since it is believed that the electronic properties of carbons are actually mainly a function of the size, the approximate diameter of crystallite planes is given on top of Fig. 2. However, this is done for orientation purposes only, the data being mostly taken from the work of Pinnick¹⁰ who

⁹ J. Volger, Phys. Rev. **79**, 1023 (1950).

¹⁰ H. T. Pinnick, Phys. Rev. **94**, 319 (1954).

determined the sizes by x-ray diffraction for a set of rods of a very similar, but not identical composition.

Most of the points on Fig. 2 represent the results obtained on several samples. The Hall constant is positive in the range of T_{ht} between 1750 and 2400°C. The position of the maximum shifts with the ambient temperature as expected on the basis of the behavior in the thermoelectric effect.³ To the left of the maximum both curves reveal a very interesting structure, with a hump around 1800°C in both and a minimum at 1650°C for the low-temperature curve. The hump appears in the range where the so-called puffing takes place, presumably due to evolution of sulfur from the carbon material. The fact that its position is independent of ambient temperature seemed to support the suspicion of such an origin. A thorough purification of some carbon samples before heat treatment was attempted by heating the samples in a slow stream of chlorine gas mixed with nitrogen for about $\frac{1}{2}$ hour at a temperature of 1200°C. After such cleaning process, the samples were consecutively heat-treated to increasing temperatures in a stream of nitrogen and the Hall constant after each heat treatment determined. The results are given in Fig. 2 in the form of dashed curves. It is evident that the purification has greatly reduced the hump, although by no means removed it completely. Consequently one has to conclude that the hump must be due to impurities in the carbon material; this might not be true in relation to the minimum around 1650°C, although certainly more experiments are necessary to clarify this point. The purified samples show in the region of the maximum Hall effect values lower than the nonpurified samples, but after so many consecutive heat treatments these samples were yielding less reliable results anyway (chlorinated samples gradually crumble), so that no special significance could be attached to this observation.

In the high heat-treatment range (above 2700°C), the results, although being well reproducible for each sample, revealed a considerable scattering from sample to sample. Samples highly heat treated show little temperature dependence in the Hall constant (Fig. 2) but they vary not only in the amount of change with temperature, but even in its direction. No sample was found which would show as great a change in Hall constant as observed for polycrystalline graphite by Kinchin (Fig. 1 of reference 6). It has been found that in some cases an apparent extra temperature dependence is due to the Hall probes being located too close to the main cross section of the plate or still more so too close to the corners (positions *a*, Fig. 1). It has been noticed furthermore, that handling the samples directly by hand, or rubbing their surface with emery paper, changes the Hall constant slightly, all the changes being not sufficient, however, to explain the scatter of results. One has to conclude that the differences are real and due to the nonuniformity in composition of the

original carbon material, which becomes noticeable only after the material has been graphitized. As will be evident later, acceptor or donor impurities in small concentration affect strongly the electronic properties of graphite, but not that of corresponding material heat treated to lower temperatures. It might be that some impurities of this kind survive through the graphitization process.

For very highly purified Ceylon graphite, ground and compressed into a plate under pressure of 10 tons/square inch, with the magnetic field perpendicular to the surface of the flakes, values for the Hall constant of -1.9 and -4.2 emu were found at the room and liquid nitrogen temperatures respectively. A very small change in the Hall constant was observed in this temperature range for natural graphite by Kinchin.⁶ Evidently a strong temperature dependence is obtained only for very pure specimens.

B. Magnetoresistance

Concurrently with the determinations of the Hall constant, measurements of the magnetoresistance were performed for all samples. The measurements are easily reproducible for well-graphitized materials. However, in the lower heat-treatment range, where the magnetoresistance effect for the fields available was very small, considerable difficulties were encountered at first, until it was realized that a very firm contact between the potential probes and the sample is essential for the success. When the magnetic field is turned on and off, slight induced currents in the probe circuit are sufficient to move the point of contact and completely falsify the results. The probes were therefore firmly imbedded into the samples by pushing them into undersized holes (points *c* in Fig. 1). The circles in Fig. 2 indicate the reproducibility of the results obtained. The two curves correspond to two ambient temperatures, the $\Delta\rho/\rho$ values being obtained for a magnetic field of 6500 oersteds. Quite unexpectedly, a negative magnetoresistance was found to be present for carbons in the range where the Hall constant reaches its positive maximum. It seems very significant that the minima of magnetoresistance almost coincide (they are shifted by about 20°C towards higher T_{ht}) with the Hall effect maxima. More than that, for lower heat treatments

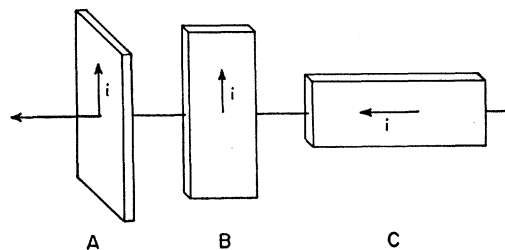


FIG. 3. Three arrangements for the determination of the magnetoresistive effect.

even a dip corresponding to the hump in the Hall curve at 1800°C can be seen, when the low-temperature magnetoresistance curve is plotted on an enlarged scale.

The field dependence of the magnetoresistance at room temperature has an exponent of 1.75 for all heat treatments from 2300°C up; for lower ones the effect is too small for a study in a sufficiently wide range of field strengths. At liquid nitrogen temperatures the exponent is variable: It is close to 2 when $\Delta\rho/\rho$ is small, decreases to 1.75 for larger values of $\Delta\rho/\rho$ (for both positive and negative magnetoresistance effects), and drops even below 1.60 for well-graphitized samples and for high magnetic fields ($>10\,000$ oe). For the last samples, the exponent increases up to 2 at around 1000 oersteds, and seems even to increase further for still lower fields.

A series of tests was made with the carbon samples arranged with the main surface of the sample parallel to the magnetic field (cases *B* and *C* and intermediate, Fig. 3) in order to investigate the parallel Hall effect.¹¹ The current through the sample was 0.5 amp, the sample was rotated around the normal, and the Hall voltage was determined for different positions. As expected, no difference of potential between the Hall probes was present when the direction of the current was parallel to or perpendicular to the field. A maximum value is observed for the 45° position. The parallel Hall effect was detectable only for well-graphitized samples, since the potential difference is quite small. For a field of 11 400 oe and the 45° arrangement, a potential difference of 9 μv at room temperature and 24 μv at liquid nitrogen were found for a sample of $T_{ht}=3100^\circ\text{C}$, the arm with negative potential being on the side of the pole piece from which the current entered the sample. The sign is independent of the direction of the magnetic field, as expected for this type of an effect.

C. Influence of Alignment of Crystallites

During these last experiments the magnetoresistance was also checked, and it was noticed that for some samples the magnetoresistance effect was slightly larger when the sample was perpendicular than when it was parallel to the field (the current in both cases being perpendicular to the field, cases *A* and *B*, Fig. 3). The ratio of the magnetoresistances for the two positions was independent of temperature and for such a small effect, was very well reproducible. It was furthermore found that the samples showing this variation are only the ones which have been cut out from the carbon rod off the central axis (cuts type *Ib*, Fig. 4) the axial cuts (*Ia*) showing no change in magnetoresistance when rotated around the axis parallel to the direction of the current. This experiment demonstrated the great sensitivity of the magnetoresistance to the relative alignment of crystallites in the sample (carbon particles

¹¹ C. Goldberg and R. E. Davis, *Phys. Rev.* **94**, 1121 (1954).

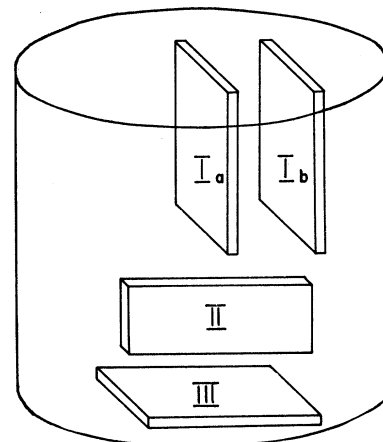


FIG. 4. Different types of cuts from a cylindrical piece of extruded carbon.

being aligned in the process of extrusion of the carbon rods prior to baking¹²), and therefore additional experiments were performed to gain more information about the influence of this geometrical factor.

The magnetoresistance was measured for the carbon sample and current both perpendicular to magnetic field (*A*), for the sample parallel but the current perpendicular (*B*), and finally for the sample and current parallel to the magnetic field (*C*).

It was checked first that the ratios of the three values for *A*, *B*, and *C* are independent of the strength of the magnetic field and independent of temperature. They do, however, change with heat treatment. For instance, a sample type *Ib* heat treated to 2100°C was subsequently graphitized to about 2850°C. Measured at a field of 11 400 oe, the ratio *A* to *B* increased from 1.02 to 1.06 and the ratio *B* to *C* increased from 1.74 to 2.12, thus indicating an increase in alignment of crystallites with their growth in heat treatments, the conclusion being in best agreement with the results of x-ray diffraction studies concerning the alignment of crystallites in platelets of a soft carbon (see Fig. 5 in reference 12). Another variant of the experiments was to cut samples from rods in three directions *I*, *II*, and *III* (Fig. 3) and investigate all in arrangement type *A*: It was found that the magnetoresistance and Hall constant for cuts *I* and *II* are about the same and for cut *III*, lower by about 37% and 18%¹³ (irrespective of heat treatment and ambient temperature). The ratios of resistance at liquid nitrogen to that at room temperature were found slightly different for different cuts; no consistent differences were found between cuts *I* and *II* or *III* which would be in any way distinctive for the two cases of flow of current relative to the extrusion axis as was observed by Goetz and Holser.¹⁴

In order to gain some rough information about the

¹² See a paper by S. Mrozowski in *Proceedings of the Conferences on Carbon*, University of Buffalo, Buffalo, 1956, p. 31.

¹³ This last result agrees with an observation by Kinchin (reference 6).

¹⁴ A. Goetz and A. Holser, *Trans. Am. Electrochem. Soc.* **82**, 391 (1942).

magnetoresistance of a single crystal of graphite and its dependence on direction of the current and on the field relative to the crystal, a rectangular plate was cut from a highly purified lump of Ceylon graphite as closely parallel to the surface of the flakes as possible. At 11 400 oe, for the three arrangements, the following three ratios $\Delta\rho/\rho$ were obtained: (A) 0.13, (B) 0.08, and (C) 0.03. The difference between A and B demonstrates the confinement of the current to the graphitic planes; the fact that C is different from zero is due to the electrons diffusing along the plane and not moving exclusively in the direction of the current. Since it was suspected that the alignment of the flakes throughout such a plate was not perfect, some very highly purified Ceylon graphite was ground and then compressed into a plate under pressure of 10 tons/square inch. For such a plate, the following results were obtained: (A) 0.168, (B) 0.058, and (C) 0.033, thus showing that a good alignment is essential in the case of the current flowing perpendicular to the field, the values of A and B being respectively larger and smaller in this case. A smaller difference between cases B and C is also to be expected for a very good alignment. Thus, for a disordered

assembly of Ceylon graphite crystals an intermediate magnetoresistance should be expected, about equal to an average of the three figures A, B, and C, or about 0.086. This seems a reasonable figure, since for a well graphitized sample ($T_{ht}=3100^\circ$), $\Delta\rho/\rho=0.058$ was found at the same field strength.

D. Acceptors

Changes in the Hall constant of polycrystalline graphite caused by introduction of acceptors were studied by Hennig.⁴ Kmetko² investigated the corresponding changes in thermoelectric power, extending the range to carbons heat treated as low as 1400°C. It seemed worthwhile to investigate correspondingly the magnetoresistance, since this is a property of polycrystalline graphite which varies very strongly in the range of high heat treatments. Also, the behavior in the region of negative magnetoresistance was of interest. A set of rods, variously heat treated and containing various amounts of residual bisulfate acceptors, prepared and used by Pinnick and Kiive¹⁵ in their work on diamagnetic susceptibility of carbons, was kindly loaned by Mr. Kiive to the authors for these experiments. The results of the measurements for a transverse magnetic field of 12 700 oe are presented in a graphical form in Fig. 5. One can see that the effect of introduction of acceptors is strongly dependent on the heat treatment of the carbon sample and on the ambient temperature. In Fig. 6, the magnetoresistance for untreated samples is plotted as a function of heat-treatment temperature. The slight difference in the curves Fig. 6 and Fig. 2 is due to a difference in carbon material and heat-treatment procedure. Comparing the various curves of Fig. 5 with Fig. 6, one sees that introduction of acceptors produces changes equivalent to a decrease in heat treatment. Oxidation levels corresponding to

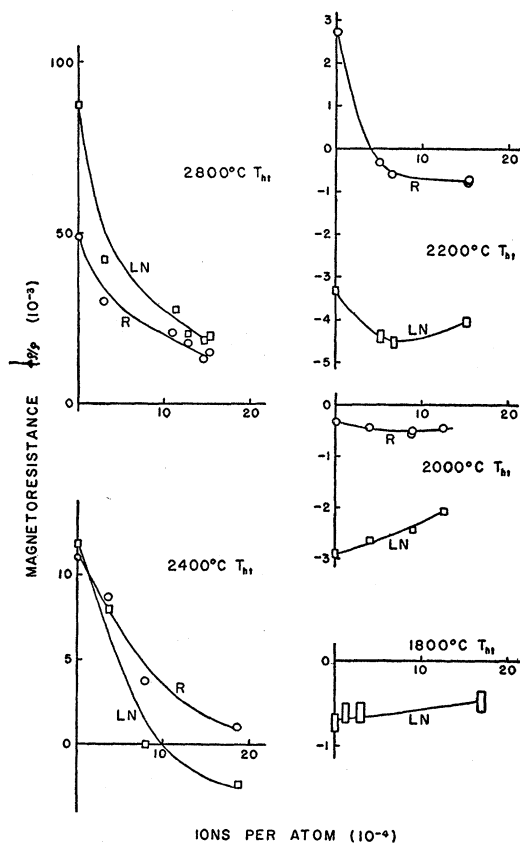


FIG. 5. Influence of introduction of bisulfate ions into the carbon structure on the magnetoresistance for differently heat-treated samples of carbon. LN—liquid nitrogen, R—room temperature.

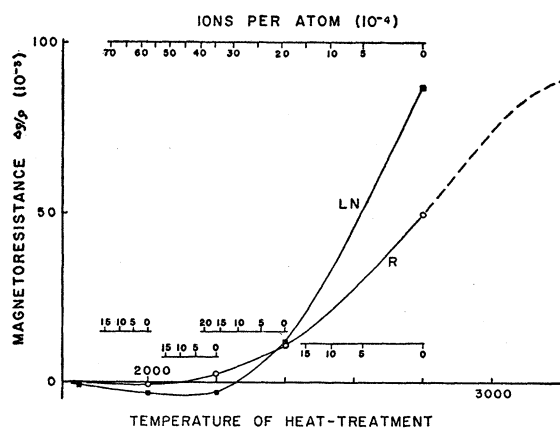


FIG. 6. Schematic drawing illustrating the relative influence of introduction of acceptors (bisulfates) and of change in heat treatment on the magnetoresistance. LN—liquid nitrogen, R—room temperature.

¹⁵ H. T. Pinnick and P. Kiive, Phys. Rev. **102**, 58 (1956).

changes in heat treatment are indicated in Fig. 6 for each investigated group of rods. These different scales are roughly combined in a unified single scale given at the top of the figure, which should permit one to estimate approximately the number of acceptors necessary to induce a desired change in magnetoresistance. It can be estimated from it, for instance, that in order to execute a shift from $T_{ht}=2800^{\circ}\text{C}$ to the minimum in the curve at room temperature, about 60×10^{-4} acceptors per carbon atom are necessary. The scale is probably not quite correct, since when one goes to lower heat treatments the crystallite size decreases and as a result the total resistance increases because of increase in boundary scattering, while on the other hand for the increasing concentration of acceptors the resistance falls. A direct comparison of $\Delta\rho$ instead of $\Delta\rho/\rho$ is maybe more appropriate; this will slightly change the estimated scale in the Fig. 6 and decrease the concentration corresponding to the minimum to about 50×10^{-4} , but definitely to not less than that. This number seems to be in poor agreement with the concentration of acceptors corresponding to a maximum in the Hall effect (25×10^{-4} , reference 4) and in the thermoelectric effect (30×10^{-4} , reference 2), as observed for well-graphitized samples. This discrepancy should not be disturbing, however, since the whole band structure changes with heat treatment^{1,15} and the two cases are strictly not comparable anyway.

III. DISCUSSION

A. General Remarks

Because of the great anisotropy of crystallites of graphite, all the electronic properties of polycrystalline carbons are a function of the relative alignment of crystallites in the sample. Furthermore, they are also dependent on the porosity of the material. Kinchin⁶ has pointed out a number of corrections which have to be introduced in order to compare the Hall constant of single crystals to that of polycrystalline materials and has tried to estimate roughly their magnitude. Until, however, the nature of such corrections is well understood and their magnitude obtainable with reasonable accuracy, not much importance can be attached to the absolute values of the Hall constant and of the magnetoresistance, and their differences for different carbons. Fortunately, however, for a broad explanation of the changes occurring in carbons with change in heat treatment, with change in ambient temperature, with introduction of acceptors, etc., the knowledge of the relative changes in these constants is sufficient. The results reported in this paper help to clarify a number of features of the general problem and to formulate more precisely the difficulties which will have to be resolved before the nature of electronic processes in carbons and polycrystalline graphites is understood in detail.

The general band model as briefly described in the

introduction consists of two main features¹⁶: a variable energy gap between two electronic bands, and the presence of deep surface traps. The first of these is of importance mainly for the explanation of the electronic processes in aromatic molecular solids, the second for the processes in carbons and graphites. The results of various experiments lead to the conclusion that carbons and graphites, no matter how pure they are, possess a great number of electronic traps. These traps are the carbon valencies which are not engaged in cross-bonds and which are present mostly on the peripheries of crystallites: Electrons from the π band jump into these σ orbitals, forming spin pairs and thus quenching the chemical activity of these free valencies. The holes created in the π band are mobile and diffuse away from the periphery, leaving the carbon atoms with an electronic arrangement analogous to that of the nitrogen atom in the pyridine ring. When a carbon atom is missing on the inside of a graphitic plane, as might happen as the result of neutron irradiation, freezing-in of lattice vacancies by quenching or simply in the process of growth of crystallites by fusion of neighbors, three free valencies per vacancy are available as traps. Because of Coulombian repulsion, however, probably one and not more than two electrons will be accommodated in the narrow space of the vacancy; taking in addition, the vacant π -electron state of the absent carbon atom, it is to be expected, therefore, that an average from two to three excess holes in the band will correspond to each vacant carbon site. When two almost-parallel crystallites (in twisted position) fuse together at the peripheries in the process of growth, heat-resistant screw dislocations will frequently be formed, which might leave many valencies along the axis unsaturated. One can see therefore that even in well-graphitized pure carbon materials a great number of these σ traps will be available.

An extrapolation of the curve of Fig. 6 to high heat treatment based on Fig. 2 (up to 3100°C) and on the estimated magnetoresistance for a disordered arrangement of large graphite crystals, in conjunction with an extrapolation of the upper scale of Fig. 6, makes it clear that the well-graphitized artificial polycrystalline graphites contain maybe as much as 1×10^{-3} hole per carbon atom or more. Thus, one can see that a direct comparison of the results for such graphites with the theoretical predictions for perfect graphite crystals is not possible. As an illustration of this situation, the results of the recent work by Keesom and Pearlman¹⁷ can be taken. The authors found a linear term in the specific heat of graphite at very low temperatures: an approximately linear term is actually expected for partly overlapping bands, but no comparison with the

¹⁶ Graphs presenting in a schematic way the changes occurring with heat treatment were given in McMichael, Kmetko, and Mrozowski, *J. Opt. Soc. Am.* **44**, 26 (1954), Fig. 1 and reference 3, Fig. 9.

¹⁷ P. H. Keesom and N. Pearlman, *Phys. Rev.* **99**, 1119 (1955).

theoretical predictions is possible until the concentration of excess holes in the particular piece of artificial graphite they used is obtained from other experiments. In fact, it seems very probable that the main contribution in their case was due to these excess holes and not to the intrinsic carriers as assumed by these authors.

B. Hall Constant

Figure 2 shows that the Hall constant is almost independent of temperature for the lowest heat treatments. It seems probable that for a pure specimen in absence of the anomalies around $T_{ht}=1650^{\circ}\text{C}$ and 1800°C the constant will continue to be temperature independent up to $T_{ht}\sim 1800^{\circ}\text{C}$. Such a behavior is expected from the band model. For these heat treatments the number of traps is very large, the Fermi level is depressed far below the top of the band, and the conduction is essentially of one carrier semimetallic type. The proportionality of the thermoelectric power with absolute temperature³ is in best agreement with this view. As the Fermi level gradually rises with increasing heat treatment (decrease in number of traps), it crosses the inflection curve (Hall effect changes sign), and finally comes close enough to the top of the band, so that electrons begin to be activated into the upper band. This last process seems to start at room temperature for T_{ht} greater than 1800°C (the two Hall curves separate); it is only around $T_{ht}=2050^{\circ}\text{C}$ that a balance between the decrease in number of excess holes and the increase in activated electrons is reached, leading to a maximum in the Hall constant. For lower ambient temperature, such a balance will be reached when the Fermi level is located higher, that is, for higher heat treatments. The observed shift of the position of the maximum in Hall constant (Fig. 2) and in the thermoelectric effect³ not only supports this prediction but permits one to draw an important conclusion concerning the structure of energy bands in graphite. If, for a perfect graphite crystal, the two energy bands just touch (as in Wallace's theory), then, with decreasing ambient temperature, the maximum should move towards higher T_{ht} indefinitely, tending toward perfectly graphitized material for 0°K . This is because at a sufficiently low temperature, that is, when kT is smaller than the depression of the Fermi level, a positive Hall constant will always be obtained no matter how small (if only finite) the number of excess holes is; in other words, because the Hall constant at 0°K tends to infinity as the Fermi level approaches the corners of the zone. On the other hand, if the energy bands partly overlap, the Hall effect maximum will tend to a finite T_{ht} value with decrease of ambient temperature: The limit will be reached when the Fermi level crosses the lower limit of the upper band. For overlapping bands in highly graphitized substances, no change in sign of the Hall effect even down to the lowest ambient tempera-

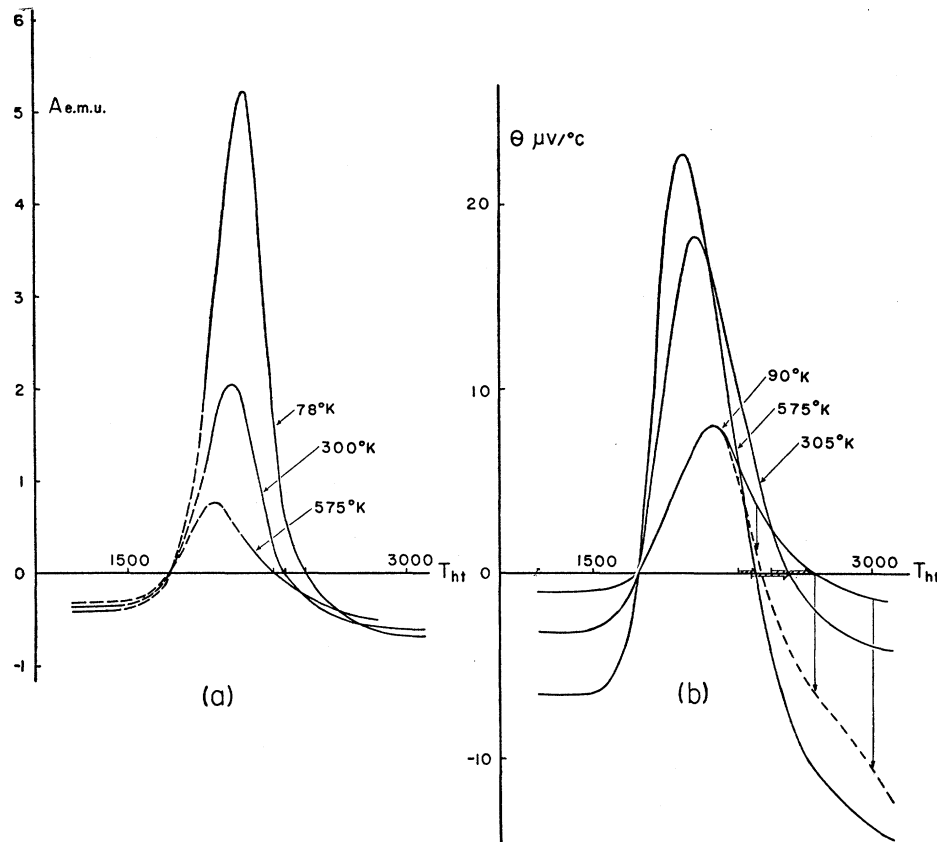
tures is expected. The slow rate at which the maximum shifts with decrease of ambient temperature seems to point very strongly towards the second alternative. Extrapolating very roughly the temperature dependence to 0°K , one finds it reasonable to assume that for soft cokes around $T_{ht}=2300^{\circ}\text{C}$ the Fermi level crosses into the upper band. Combining this information with the results of Sec. IID, one can say then that the Fermi level for a perfect graphite crystal is located above the lower limit of the upper band by about 2 to 3×10^{-3} electrons per atom (combined number for both overlapping bands).

The change of the Hall constant from the positive maximum to negative values for well-graphitized substances is due to the increasing contribution of the more mobile negative carriers in the upper energy band. In order to explain the temperature dependence of the Hall constant for well-graphitized materials, Kinchin⁶ assumes the existence of electron traps above the Fermi level; it is hard to see what the nature of such traps could be. In view of the unclarified situation as to the temperature dependence of the Hall constant for the well-graphitized materials (see Sec. IIA, and the discrepancies in ours and in Kinchin's⁶ results between artificial and natural graphite), it seems too early to look beyond the changes in concentration of free carriers and their mobilities for an explanation of this dependence.

C. Thermoelectric Effect

In Fig. 7(a) the two smoothed out Hall curves of Fig. 2 are redrawn and a curve for $T=575^{\circ}\text{K}$ is added, the data for which were taken from Fig. 2 of the work of Kinchin,⁶ by plotting Kinchin's values as a function of crystallite size as given by Kinchin in his Table I and translating the crystallite sizes into corresponding T_{ht} values as found for our specimens. The probable extension of this curve to lower T_{ht} is included in the form of a dotted curve. In Fig. 7(b), the corresponding variation of the absolute thermoelectric effect with T_{ht} is given. Two curves for the ambient temperatures of 573 and 305°K are taken directly from the experimental data of Loebner.³ One can see that in the two carrier region ($T_{ht}>2200^{\circ}\text{C}$), the crossover points differ considerably from the crossovers for the Hall constant, being shifted towards higher T_{ht} . A predicted full curve for $T=90^{\circ}\text{K}$ is drawn in Fig. 7(b) in agreement with this general trend, and the actually experimentally obtained by Loebner³ is given roughly in Fig. 7(b) in dashed form. The increase in the absolute value of the effect at low temperatures for well-graphitized specimens was explained as "phonon drag" effect³; the heavy arrows in Fig. 7(b) show that the "phonon drag" effect for an ambient temperature of 90°K is already present at $T_{ht}=2300^{\circ}\text{C}$ (this is for quite small crystallites of about 200 A), increases greatly with the size of crystallites, and above T_{ht}

FIG. 7. (a) A system of smoothed-out (in the impurity anomaly region) Hall curves. Curves for $T=78^\circ\text{K}$ and 300°K were taken from Fig. 2; data for the continuous part of the $T=575^\circ\text{K}$ curve were taken from Kinchin.⁶ (b) Curves for thermoelectric effect for $T=573^\circ\text{K}$ and 305°K as found by Loebner,³ and a curve for $T=90^\circ\text{K}$ as expected from the trend of the Hall curves (continuous). The dashed curve is the one actually obtained by Loebner for $T=90^\circ\text{K}$. The vertical arrows indicate the contribution of the "phonon drag" effect.



$=2500^\circ\text{C}$ constitutes the predominant contribution to the thermoelectric power.

The temperature dependence of the thermoelectric effect, as roughly expected on the basis of the band model discussed above for well and poorly graphitized specimens, is given in Fig. 8 in the form of continuous lines. The continuous lines in the upper part of this scheme were obtained in a qualitative way for the model (touching bands) by observing that for sufficiently low temperatures a metallic type of behavior is expected, with steeper slopes for higher locations of the Fermi level, and a maximum moving towards lower temperatures (compare the discussion of the Hall constant in Sec. B), the following decrease being due to activation of electrons into the upper band. For sufficiently high temperatures, when the detailed structure of the bands at the zone corners becomes immaterial, the behavior has to become metallic again (see next section) with the thermoelectric power being negative (greater mobility of electrons than holes); this is why the curves are about linear and cross the zero axis instead of tailing off asymptotically to zero. The exact shape of the continuous curves at low temperatures for heat treatments of 2600°C and above will strongly depend on the type of the model considered; since, however, the main contribution to the thermoelectric power is due to the "phonon drag" effect in this range,

no effort was made to deduce the correct shape of the curves 2600°C or of that for 3000°C . The dotted curves represent the expected behavior when the presence of an increasing "phonon drag" effect with increasing crystallite size is included. The scale at the left was chosen so as to fit the experimental data of Loebner [Fig. 7(b)]. Curves of type No. 0, 4, 5, and 6 were found for artificial graphite by the North American Aviation group.¹⁸ Figure 8 is given here to point out that for intermediate heat treatments curves of type No. 2 are expected, and that their exact shape in the low-temperature range might yield additional information about the heat treatment for which the Fermi level crosses into the upper band.

D. Electrical Resistivity

The conclusion reached in Sec. IIIB as to the Fermi level crossing into the upper band already for poorly graphitized specimens seemingly invalidates the explanation of the temperature dependence of resistivity for artificial graphites proposed several years ago.¹ Actually this is not so. The main point of the explanation was that the increase in resistance of the poly-

¹⁸ See Fig. 8 in J. E. Hove, *Proceedings of the Conferences on Carbon* (University of Buffalo, Buffalo, 1956), p. 125. Actually, the two figures are not exactly comparable, since the crystallite sizes at irradiation do not change in a similar manner as in the original heat treatment process.

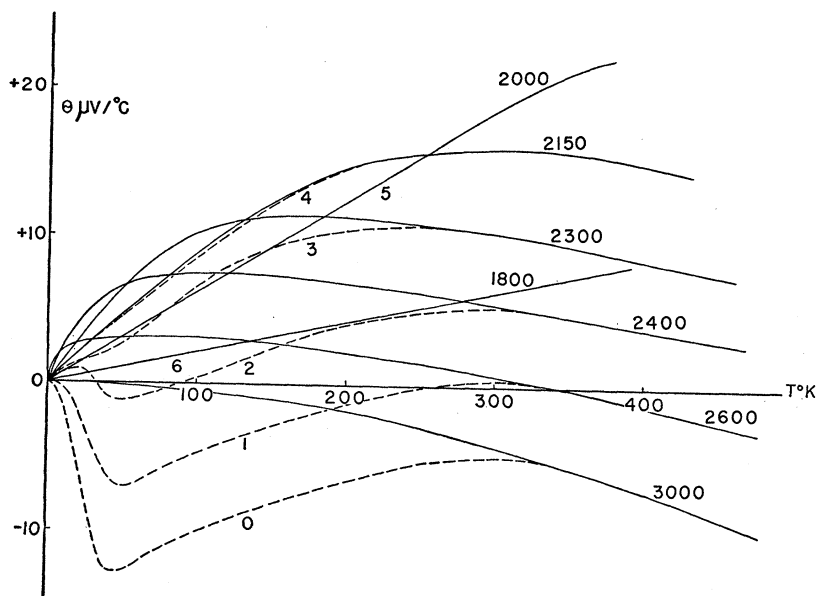


FIG. 8. Temperature dependence of the thermoelectric effect for differently heat-treated carbons as expected for the band model of carbon without (continuous curves) and with the contribution of the "phonon drag" effect (dashed curves).

crystalline graphites when the temperature is lowered is not due to an increased scattering but to a decrease in an effective number of carriers. As the temperature is lowered, the number of carriers decreases towards a limiting value determined by the number of excess holes present (traps), and thus the resistivity will first increase and then reach a plateau or a maximum beyond which it might slowly decrease, the exact behavior being dependent on the temperature dependence of boundary and lattice scattering in this range. Since in the previous work¹ the resistivity was fitted with an empirical expression by extrapolating the scattering factor from the 0°–1000°C range into the low temperatures, there can be no wonder that the calculated curve deviated at temperatures below 100°K from the experimental one. If one assumes, however, that at low temperatures scattering depends less strongly on temperature than in the 0°–1000°C range, the experimental results such as those obtained by Reynolds *et al.*¹⁹ find a simple explanation. It is easy to see that no reasonable assumption about scattering alone can furnish an explanation of the maximum found by Reynolds *et al.*

The empirical expression was interpreted in the original paper, reference 1, as indicating the existence of an energy gap ϵ between the filled and empty bands. It was soon after realized that ϵ does not have to be a gap but is just the activation energy of electrons into the upper band. But even this seems to be too restrictive. Actually, when there is a deep minimum in the density of energy levels and the Fermi level is located by an amount ϵ below it, the influence of the existence of this shift ϵ on the number of effective carriers has to disappear at temperatures $T \gg \epsilon/k$, that

is, for kT something around several times ϵ . When the minimum is due to a slight overlap of bands, and the electrons have a larger mobility than holes, even for a Fermi level located in the overlap region but somewhat off-center, a resistivity curve with a minimum will be obtained. In other words, according to the new interpretation, ΔE as calculated from the resistivity minimum gives roughly a value several times greater than the position of the Fermi level relative to its position in a perfect graphite crystal (for the Fermi level at the lower limit of the upper band ϵ turns out to be of the order of 0.03 to 0.02 eV). The explanation of changes due to introduction of donors remains essentially the same as proposed previously.²⁰

E. Negative Magnetoresistance

Although no explanation of the mechanism of the negative magnetoresistance can be given, the close correlation of the two—magnetoresistive and Hall effects—seems very significant and suggests that negative magnetoresistance is associated with holes and positive magnetoresistance with electrons. When with increasing heat treatment the Fermi level crosses the inflection curve (Hall effect zero) and gradually moves upward, the negative magnetoresistance increases, and probably continues to increase all the way up to the top of the band, where the curvature of the energy surfaces is the greatest. However, as soon as electrons are activated into the upper band, a positive magnetoresistance appears which being greater per carrier, soon overbalances the effect of holes. The combined effect of the two increases towards a limit which corresponds to a perfect graphite crystal. For a Fermi level above

¹⁹ Reynolds, Hemstreet, and Leinhardt, *Phys. Rev.* **91**, 1152 (1953).

²⁰ S. Mrozowski, *J. Chem. Phys.* **21**, 492 (1953).

this position, the magnetoresistance might decrease since the Fermi level is moving away from the bottom of the upper band, that is, into the region of lesser curvature, and closer to the top of the lower band. This is an interesting conclusion; experiments designed to test this prediction are in preparation.

F. Diamagnetic Susceptibility

The diamagnetic susceptibility of graphite is not only very high (much too high to be explainable on the grounds of Landau-Peierls theory as applied to the Wallace-Coulson model), but also shows a remarkable independence on crystallite size above a certain limit. Recently Pinnick and Kiive¹⁵ have shown that this limit is slightly temperature-dependent, and varies with temperature similarly to the variation of the position of the maximum for the Hall constant. The system of curves for the temperature variation of susceptibility, as obtained by Pinnick and Kiive for differently heat-treated samples of a soft carbon, is reproduced in Fig. 9; and on top of their system of curves two heavy curves are drawn which correspond respectively to the positions of the maximum and of the zero Hall constant. One can see that the maximum susceptibility (plateau) is not obtained at any temperature unless the Hall constant is negative, that is, unless the concentration of electrons in the upper band is sufficiently great. The apparently conflicting facts of a large change in magnetoresistance in the same range in which the Hall effect varies slightly but the susceptibility is about constant (plateau) will perhaps be reconciled in terms of a four-carrier band model (two

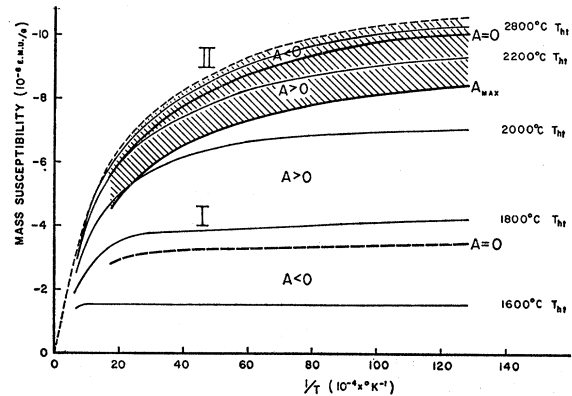


FIG. 9. Temperature dependence of the diamagnetic susceptibility of carbons as obtained by Pinnick and Kiive¹⁵ for differently heat-treated carbons. The shaded area covers the two-carrier conduction. The two heavy curves correspond to the location of maximum Hall constant A and to the zero Hall constant. The dashed heavy curve for $A=0$ corresponds to the Fermi level crossing the inflection curve.

types of holes and two types of electrons), such as obtained recently by Johnston²¹ and by Horton and Tauber.²² In general, it is hoped that experimentally established relations between different electronic effects in carbons such as presented in this paper will make possible an unambiguous selection of the proper band model for graphite.

²¹ D. F. Johnston, Proc. Roy. Soc. (London) **227**, 349, 359 (1955).

²² G. K. Horton and G. E. Tauber (to be published). The authors are indebted to Dr. Horton and Dr. Tauber for the opportunity of seeing the manuscript.