typical primary peak shape is apparently associated with the trapping level near 0.3 ev characteristic of the zinc-sulfide-like crystal lattice. Where this 0.3-ev trap is the deepest trapping level present, no in-phase light emission at low frequencies is observed, since recombination occurs by field-controlled thermal release earlier in the voltage cycle.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of many of my colleagues and to thank particularly R. E. Halsted, P. D. Johnson, W. W. Piper, V. L. Stout, F. E. Williams, and J. R. Young for valuable discussion, and P. E. Pashler for continued encouragement. H. C. Froelich kindly supplied the electroluminescent phosphors.

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Thermoelectric Power, Electrical Resistance, and Crystalline Structure of Carbons*†

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The thermoelectric power Θ and the electric resistance R of soft and hard carbons were investigated as functions of heat-treatment temperature T_{ht} from 1000°C to 3100°C at three ambient temperatures T equal to 90°K, 305°K, and 573°K. The crystalline structure was studied by means of x-ray powder diffraction technique. For a given T, with increase of T_{ht} the thermoelectric power of soft carbons goes through a flat minimum at $T_{ht}\sim 1400$°C, increases quite fast to a maximum at about 2100°C, and subsequently drops down again and continues to do so up to the highest T_{ht}. The electric resistance is only very slowly decreasing (plateau) up to $T_{ht}\sim 2000$°C, with a subsequent rapid decrease up to the highest T_{ht} investigated. The positions of the maximum in Θ and of the corresponding knee in resistance (end of plateau) shifts to higher heat treatments with decrease of ambient temperature T. The thermoelectric power is proportional to temperature T in the range of heat treatments below the T_{ht} corresponding to the maximum in Θ. The observed dependence of Θ and of R on T_{ht} and T are in good agreement with Mrozowski's energy band scheme for carbons and graphites. A hard carbon prepared from phenol-benzaldehyde resin shows a two-stage graphitization with $\frac{1}{8}$ of the crystalline mass beginning to graphitize at $T_{ht}\sim 2200$°C and the remainder only above $T_{ht} = 2800$°C. Correspondingly the resistance curves show two plateaus ending one at $T_{ht}\sim 2200$°C and the other at $T_{ht}\sim 2800$°C. The dependence of Θ on T_{ht} is somewhat similar to that found in soft carbons.

I. INTRODUCTION

ELECTRICAL properties of carbons have been investigated extensively during the past sixty years. In 1916 La Rosa[1] reviewed the earliest work on the thermoelectric power of carbon and noted large differences in the values previously published by other investigators. In the same paper he also reported results of his measurements of the thermoelectric power for a purified[2] carbon at temperatures between 308°K and 823°K. He found that the thermoelectric power, relative to a platinum standard, had a positive sign and increased linearly with temperature. Knowing that carbon has a negative coefficient of resistance, which is characteristic of "variable conductors" (semiconductors), the linear increase, which is characteristic of metals, seemed anomalous to La Rosa. Comparing his results with those of his predecessors, La Rosa attributed the large disagreements in magnitude and temperature dependence (after normalization to the same standard) to possible experimental difficulties or the presence of impurities in the samples of the other investigators, rather than to differences in the manufacturing processes (arc lamp carbon rods, carbon filaments, etc.).

Gottstein,[3] who checked the validity of thermodynamic relationships between different thermoelectric effects for a number of semiconductors, reported the value of the thermoelectric power of natural graphite (unknown purity) to be $+9.76$ μv/°K with respect to copper when measured directly and $+9.97$ μv/°K when calculated from the measured values of the Peltier coefficient.

In the period between the two world wars, little was published on the thermoelectric behavior of carbons and graphite. Pirani and Fehse[4] reported the thermoelectric power of a highly graphitized ("metallized") incandescent lamp filament to be $+2.5$ μv/°K with respect to platinum. Some measurements were made also by Fukuda and Saito[5] on carbon films formed by thermal decomposition of aliphatic hydrocarbons in vacuo at about 1100°C. They reported the thermoelectric power as negative with respect to copper (the authors also claim a negative sign for graphite with

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[1] M. La Rosa, Nuovo cimento **12**, 284 (1916).

[2] M. La Rosa purified a commercial carbon rod by keeping it for nine hours at about 800°C in a stream of chlorine.

[3] G. Gottstein, Ann. Physik **43**, 1079 (1914).

[4] M. Pirani and W. Fehse, Z. Electrochem. **29**, 168 (1929).

[5] M. Fukuda and Y. Saito, Electrotech. J. (Japan) **2**, 129 (1938).

respect to copper), becoming more negative with increasing ambient temperature, with increasing decomposition temperature, or with higher carbon content in the original hydrocarbon. They also found that an increase in the degree of vacuum and in the rate of decomposition causes the power to become less negative and eventually to change sign.

Several years ago, Mrozowski[6] proposed an explanation of the electronic properties of carbons and graphite and their dependence on origin and heat treatment. In general, carbons can be divided into two main classes: soft and hard carbons. Soft carbons are made by pyrolysis of organic materials such as tars or pitches, which remain fluid up to above 400°C. They graphitize easily and show a platelet structure upon grinding to a very fine size.[7] Hard carbons are made from substances such as hardening resins, which solidify at an early stage in the pyrolytic process. Hard cokes graphitize only at very high temperatures and when ground break up into irregular but isotropic chunks.

The present investigation was undertaken in order to check certain predictions of Mrozowski's theory. Preliminary measurements,[8] which were performed at about 300°K, indicated that the thermoelectric power Θ *vs* platinum for various carbons and graphites showed a pronounced dependence on heat-treatment temperature T_{ht}.[9] For T_{ht} between 700°C and 3000°C, Θ was found to be always positive: first to decrease from a value of about 40 μv/°K at 700°C to about 5 μv/°K at 1400°C, then increase to about 30 μv/°K at 2100°C and finally to decrease again to a value of about 10 μv/°K for well-graphitized materials heated to 3000°C. Values for different soft cokes were found to be scattered only slightly around the above described curve. Θ for a hard coke showed a similar dependence but much less variation in magnitude.

According to the model[6] the dependence of Θ on T_{ht} is explained by three effects: (1) the decrease of Θ in the region of low T_{ht} as resulting from an increasing number of excess holes which are created by π electrons being trapped in the free valence σ orbitals on the periphery of crystallite planes; (2) the increase of Θ in the range 1400°C–2000°C as resulting from a decrease in the number of peripheral sites occurring with crystal growth; and (3) the decrease of Θ above 2100°C as resulting from an increase in the number of carriers (holes and electrons) as electrons are thermally excited into the conduction band. The position of the Θ maximum is determined by a balance between effects 2 and 3, and a shift in the position of the thermoelectric power maximum with a change in ambient temperature was expected. The purpose of the present investigation was to test this prediction.

While this work was in progress, the results of two other investigations were published. Hirobayashi and Tayoda[10] measured the thermoelectric power of a phenol-formaldehyde resin coked in hydrogen gas to temperatures ranging from 700°C to 1000°C. They found the power to be positive with respect to lead, to decrease markedly with increasing heat-treatment temperature T_{ht} and to decrease with increasing temperature T between 300°K and 573°K. Their limited results supplement rather well our findings reported in Sec. III.B. Tyler and Wilson[11] investigated the thermoelectric power of three graphite samples (of unspecified heat treatments) as a function of temperature in the interval from 20°K to 280°K. They converted their Θ's, originally based on a copper standard, to absolute values, using the data for the absolute thermoelectric power of copper given by Borelius.[12] Tyler and Wilson found that the absolute thermoelectric power of two graphitized soft carbons was negative and had a minimum at about 30°K, whereas that of a graphitized mixture of lampblack with binder was positive, with a monotonic increase toward higher temperatures. They were unable to interpret the results obtained. Some measurements of thermoelectric power as a function of "graphitization," have been made by Eatherly,[13] but the data have not been published.

The influence of heat treatment on the electrical resistivity of carbons and graphite was recognized at an early date[14] and a number of reports can be found in the literature (for references, see reference 6). However, a complete series of electrical resistivity measurements for a wide range of heat treatments (500°–3000°C) has been given only for a soft carbon at room temperature.[6] In this work, measurements of electrical resistance were made at three ambient temperatures on soft and on hard carbon samples that had been heat-treated to successively higher temperatures, and the results are correlated with results of measurements of thermoelectric power on the same samples.

Numerous investigations of carbons with x-ray diffraction technique have been performed.[15] The structure of hard and soft carbons was extensively

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[6] S. Mrozowski, Phys. Rev. **85**, 609 (1952); **86**, 1056 (1952).

[7] E. A. Kmetko, Proceedings of the Conferences on Carbon, University of Buffalo (to be published).

[8] E. E. Loebner, Phys. Rev. **84**, 153 (1951); **86**, 1056 (1952).

[9] In this paper °C will be used for the temperature of heat treatment of carbons and °K will be used for the temperature at which their electrical properties were determined.

[10] H. Hirobayashi and H. Tayoda, J. Phys. Soc. (Japan) **7**, 337 (1952).

[11] W. W. Tyler and A. C. Wilson, Jr., Phys. Rev. **89**, 870 (1953).

[12] G. Borelius, *Hanbuch der Metallphysik* (Akademische Verlagsgesellschaft, Leipzig, 1936).

[13] W. P. Eatherly, Phys. Rev. **85**, 768(T) (1952).

[14] C. A. Hansen, Trans. Am. Electrochem. Soc. **16**, 335 (1909).

[15] See for instance: B. E. Warren, Phys. Rev. **59**, 693 (1941); R. E. Franklin, Acta Cryst. **3**, 107 (1950); **4**, 253 (1951); G. E. Bacon, Acta Cryst. **1**, 337 (1948); **3**, 137, 320 (1950); **4**, 558 (1951); H. T. Pinnick, Phys. Rev. **94**, 319 (1954). See also papers by B. E. Warren, by J. C. Bowman, and by L. D. Loch and A. E. Austin in *Proceedings of the Conferences on Carbon* (University of Buffalo, to be published).

investigated by Franklin,[16] who found a two-phase and three-phase graphitization in most hard carbons. X-ray diffraction studies were made in this work for comparison and completeness. In the case of a phenol-benzaldehyde coke (hard carbon), an extreme case of two-phase graphitization has been found and the dependence of the thermoelectric power and resistance on heat treatment investigated.

II. EXPERIMENTAL

The general experimental method can be outlined as follows: The samples were first treated to the desired temperature T_{ht}; this was followed by measurements of the thermoelectric power Θ and resistance R at three temperatures T; x-ray diffraction patterns of powder taken from rods of the same heat treatment were obtained; the samples were then heat-treated to the next higher temperature T_{ht}, the measurements performed, and so on.

A. Samples and Heat Treatment

In earlier stages of this work[8] it was shown that all investigated soft cokes and soft carbon rods, originating from different organic materials have essentially the same Θ *vs* T_{ht} dependence. Therefore, a single batch of commercial baked carbon rods was used throughout this investigation. On the other hand, carbonized and heat-treated phenol-benzaldehyde resin was used to study the behavior of a hard carbon. Since there are considerable variations among the hard carbons, phenol-benzaldehyde carbon (PB-carbon) cannot be considered representative of the entire class of hard carbons. It is, however, one of the hardest carbons known, thus greatly differing from the soft cokes.

The soft-carbon samples consisted of rods 6 inches long and $\frac{1}{4}$ inch in diameter from National Carbon Company, Fostoria, Ohio.

The hard-carbon samples consisted of rods 6 inches long and $\frac{1}{2}$ inch in diameter. They were prepared by baking (to 1000°C) an extruded mixture of calcined (at 1000°C) phenol-benzaldehyde coke particles and phenol-benzaldehyde resin binder. The "green" PB-carbon rods were baked in a quartz-tube furnace which was packed with a mixture of coke flour and white sand.

Both types of samples were heat treated in steps of 200°C or 300°C, to temperatures ranging from 1200°C to 3100°C. The treatment was performed in a graphite-tube furnace filled with high-purity nitrogen gas. The temperature of the samples was determined using a Leeds and Northrup optical pyrometer. After the desired temperature was reached, the samples were held at that temperature from two to four minutes (soaking time). They were then left in the furnace and allowed to cool slowly.

B. Apparatus

The measuring equipment was designed to enable an easy interchange of samples, and to allow the electrical measurements to be carried out in a furnace as well as in a Dewar flask without disturbing the samples and the leads.

The mounting of the samples is depicted in Fig. 1. Figure 1(a) shows the setup for measurements above room temperature, and Fig. 1(b) shows the setup for measurements below room temperature. The carbon sample was held firmly between two graphite heater blocks by means of removable graphite screws (collars) whose heads were machined as shown in Fig. 1. Several sets of screws were available to accommodate both types of samples and to assure a good thermal contact between the sample and the heater blocks, irrespective of the dimensional changes of the samples caused by heat treatment. Nichrome wire spiral heating elements were wound around and insulated from the two graphite heater-blocks. The bottom block (*H*I) rested on steatite rings, held by set-screws at the ends of two heavy-walled quartz tubes which were about $\frac{3}{8}$ inch in diameter. These quartz tubes formed the skeleton of the assembly, passing through both graphite blocks as well as through a lavite cover, from which the assembly was suspended by the use of set-screws. The lavite cover had an offset flange which rested on the rim of the 2-inch quartz tube furnace during the high-temperature measurements and on the flange of the copper housing during the low-temperature measurements. Leads from the two heaters and from thermocouples TC numbers 1 through 4 passed through the upper heater-block and the lavite cover. Electrical and thermal contact was achieved by a press fitting of the thermocouple junctions into drilled holes. Two kinds of thermocouples were used: TC 1 and TC 2 were platinum to platinum-10% rhodium thermocouples, while TC 3 and TC 4 were alumel to chromel *P* thermocouples. The thermocouple wires were connected to copper leads by immersing their ends into mercury filled test tubes which were kept in a bath of melting ice. The copper leads were connected to the terminals of a type *K*-2 potentiometer via an eight-position all-copper rotary selector switch. Positions (1) through (4) of the switch served for electrical contacts to thermocouples TC 1 through TC 4, while positions (5) and (6) allowed the emf between the platinum leads of TC 1 and TC 2 to be determined. This emf was either the Seebeck voltage (thermal emf) of the platinum-carbon-platinum differential thermocouple alone (no outside voltage applied to the sample) or an applied voltage producing a current flowing in series through the sample and a 0.1-ohm standard resistor (without temperature gradient imposed on the sample). Switch positions (7) and (8) served to connect the potential leads of the standard resistor into the measuring circuit, thus

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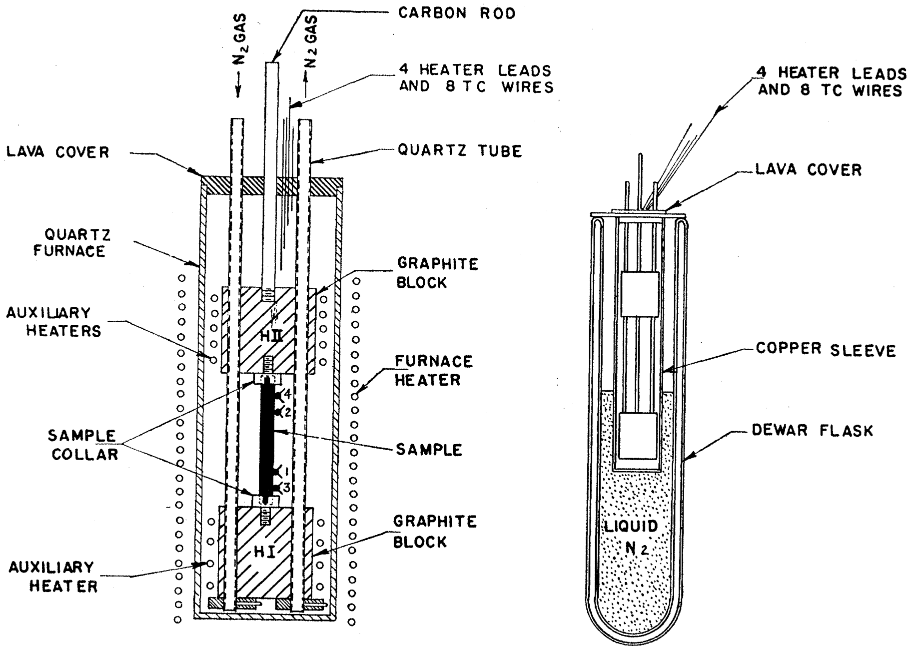
[16] R. E. Franklin, Proc. Roy. Soc. (London) **209**, 196 (1951).



(a) (b)

FIG. 1. Mounting of the sample for measurements of the Seebeck effect and of the resistance. (a) Quartz tube furnace for high temperatures; (b) Dewar flask for low temperatures.

making possible a potentiometric determination of the sample's resistance.

A slow flow of nitrogen gas was maintained through the two heavy-walled quartz tubes to flush the interior of either the furnace or the copper housing in order to prevent oxidation at elevated temperatures and water vapor condensation at low temperatures.

It was noted during test runs that after prolonged heating to and above temperatures of 800°K, the portions of platinum wire which were close to the measuring junctions of TC 1 and TC 2 became very brittle (a possible cause of the brittleness might be diffusion of carbon atoms into platinum). Since the use of a platinum standard offered many advantages, structural changes in the platinum leads were avoided by restricting the studies to temperatures below 600°K.

C. Electrical Measurements

The temperatures T_1 and T_2 were determined by employing thermocouples TC 1 and TC 2 located in small holes drilled in the sample (see Fig. 2). The temperature difference T_2-T_1, controlled by means of heaters HI and HII, did not exceed 12°K. This temperature difference was so small that standard tables of the Seebeck voltage of platinum to platinum-10% rhodium thermocouples could not be used because their tabular intervals are too large. Consequently the values of T_1 and T_2 were calculated using the formulas of Roeser and Wenzel.[17] However, these formulas only apply to temperatures above the ice point. For temperatures below the ice point the differential Seebeck voltage of the platinum to platinum-10% rhodium thermocouple decreases gradually to zero at about 200°K and then becomes negative at lower temperatures. Because of this sign reversal, the Pt-Pt/Rh thermocouple is commonly not used for determination of temperatures below the ice point. However, our low-temperature measurements were made in the narrow range between 84°K and 96°K, where the thermoelectric emf of the Pt-Pt/Rh thermocouples has a sufficiently steep slope. The platinum thermocouples TC 1 and TC 2 were calibrated between 75°K and 105°K against the base metal thermocouples TC 3 and TC 4, which in turn had been standardized at the boiling points of nitrogen and water and the melting point of ice. TC 1 and TC 2 enabled the determination of T_1 and T_2 with sufficient accuracy. During the initial cooling of the sample, the temperature was checked by using TC 3 and TC 4 while TC 1 and TC 2 were used below 100°K.

The thermoelectric power Θ of the carbon rod relative to platinum was determined from plots of the Seebeck voltage of the platinum-carbon-platinum differential thermocouple, against the temperature difference T_2-T_1. The average temperature of the sample, $T=(T_1+T_2)/2$, was kept nearly constant during each run and also the same for all runs in a series (for a given $T=90$°K, 205°K, 573°K). A typical plot of the thermal emf ϕ *vs* (T_2-T_1) for the three temperatures T of two soft-carbon samples, heat-treated to 1400°C, is shown in Fig. 3.

The determination of Θ from the slope eliminated a

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[17] W. F. Roeser and H. T. Wenzel, J. Research Natl. Bur. Standards **10**, 275 (1935).

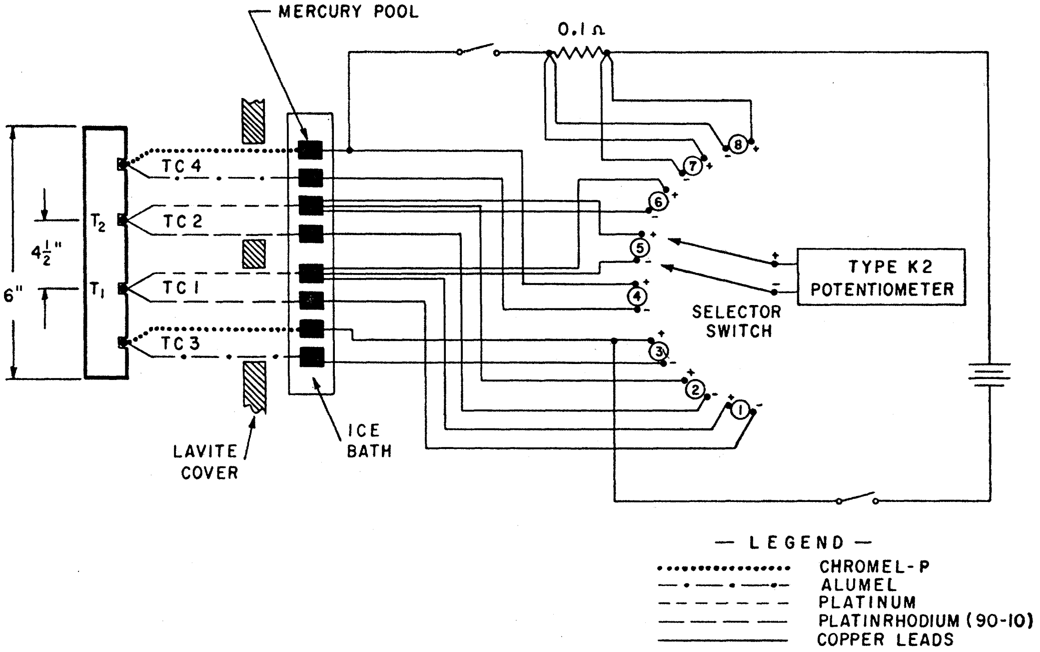

FIG. 2. Electrical circuit for potentiometric determination of Seebeck voltages and resistances, including rotary selector switch and the thermocouple arrangement at the sample.

number of errors. An estimate of the magnitude of these errors can be made from the intercept of ϕ on the temperature-difference axis. These errors are probably due to the difference in the characteristics of thermocouples 1 and 2 and temperature gradients in the junctions themselves.

The mean square deviation of the experimental points from the interpolated straight line was always only a few hundredths of a μv/°K, giving an error smaller than 2%. This error is mainly due to the operator's inability to make three simultaneous emf determinations while the thermal gradient, and therefore all the emf's, are changing slowly with time. Another contributory factor to the error is probably the average temperature T which varies somewhat throughout the measurement.

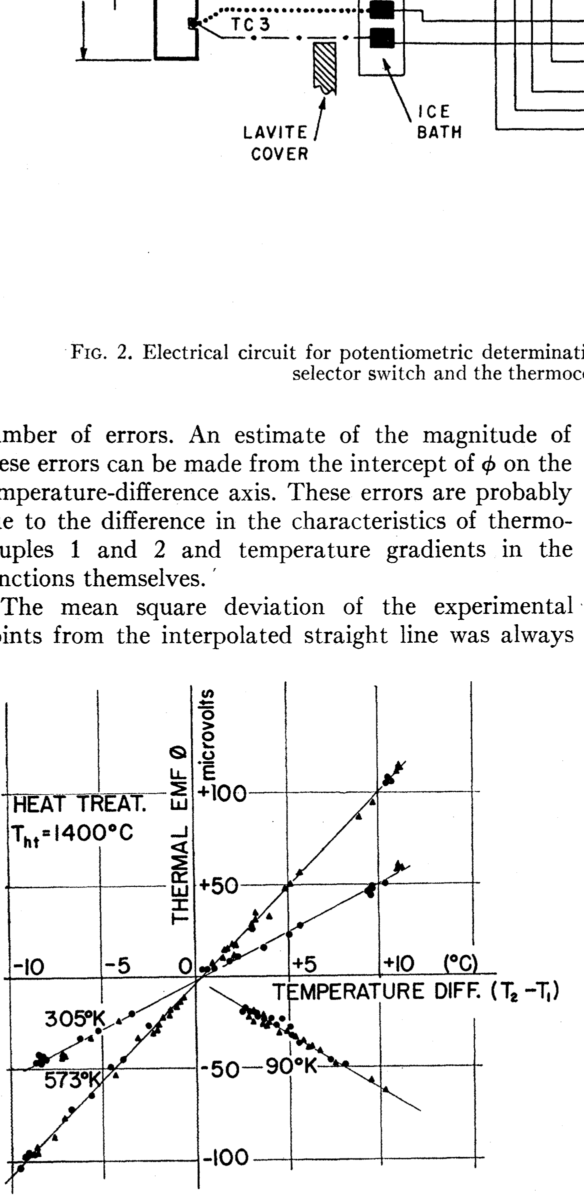

FIG. 3. Three typical plots of the Seebeck voltage ϕ *vs* temperature difference (T_2-T_1) measured at 90°K, 305°K, and 573°K for two soft carbon samples heat-treated to 1400°C: The symbols ● and ▲ represent experimental points for sample 1 and for sample 2 respectively. The thermoelectric power (*vs* platinum) at the respective temperature is obtained from the slope of each line.

The electrical resistance R of a $4\frac{1}{2}$-in. long section of the carbon sample was determined from a potentiometric comparison between the voltage drops across the sample (TC 1 and TC 2) and across a standard 0.1-ohm resistance carrying the same current. The resistance was measured while the temperature difference (T_2-T_1) was changing at a rate of about 0.1°K/minute (a condition deviating somewhat from equilibrium) and the time of the measurement was chosen to coincide as nearly as possible with the sign reversal of (T_2-T_1). An average of two readings, taken with the current flowing in opposite directions and corrected for the thermal emf generated, was used to evaluate the resistance.

D. X-Ray Techniques

The crystal structure of the samples was determined by x-ray diffraction powder techniques using a Norelco Geiger Counter X-Ray Diffractometer. The Cu K_α radiation was filtered by a nickel foil. The integrated x-ray intensities of the lines were obtained by planimetering the recorded traces after a graphical subtraction of the radiation background. The width of asymmetric lines was determined by direct measurements at half-maximum intensity and also by dividing the planimetered area of the lines by their maximum intensity. Both procedures yielded the same relative variations in the width with heat treatment. Since the elaborate scheme of corrections worked out by Franklin[15] and others was not introduced in this work, no claims as to the absolute accuracy of the results are made.

III. RESULTS

A. Soft Carbons[18]

1. *Thermoelectric Power*

The results of the thermoelectric power determination for soft carbons are shown in Fig. 4. Three curves give the dependence of the thermoelectric power Θ (referred to platinum) on heat treatment, at $T=90°\mathrm{K}$, 305°K and 573°K. On this graph, the lowest heat treatment of the commercial carbon rods is indicated by horizontally extended ovals since the accurate value of the baking temperature and the temperature of calcination of the coke it was made from was not known. Similarly, a spread in the values of Θ found for different samples at a definite T_{ht} is indicated by the height of the ovals.

Each of the three curves in Fig. 4 has the same general shape; a shallow minimum at T_{ht} equal to about 1400°C, and a relatively sharp maximum around 2100°C. The lower the average temperature T, the higher is the heat treatment T_{ht} corresponding to the maximum: for T equal to 573°K the maximum is located at 1980°C, for 305°K at 2050°C, and for 90°K at 2180°C. Studies made with another batch of rods in a narrow range of heat treatment (not included in Fig. 4) have helped to locate the exact position of the maxima.

It is convenient to divide the whole heat-treatment range for each curve Fig. 4 into two regions, region I extending from lowest T_{ht} up to T_{ht} corresponding to the maximum of the thermoelectric power and region II extending from there on up to the highest T_{ht} used. Carbons of region I are usually called baked carbons, and those of region II, graphitized carbons or polycrystalline graphite because, as it happens, regions I and II correspond to a basic difference in structure (see Sec. III. A. 3). No sharp division exists between the two regions, as the position of the thermoelectric power maximum shifts with the temperature of measurement. That this division is not artificial and corresponds to a difference in type of electronic mechanism can be seen from the different temperature dependence of the thermoelectric power in each of the two regions.

From Table I it can be seen that within region I the experimentally determined increment in the thermoelectric power, due to an increase in the heat treatment parameter T_{ht}, is roughly proportional to the absolute temperature T. The increment in the thermoelectric power is defined by

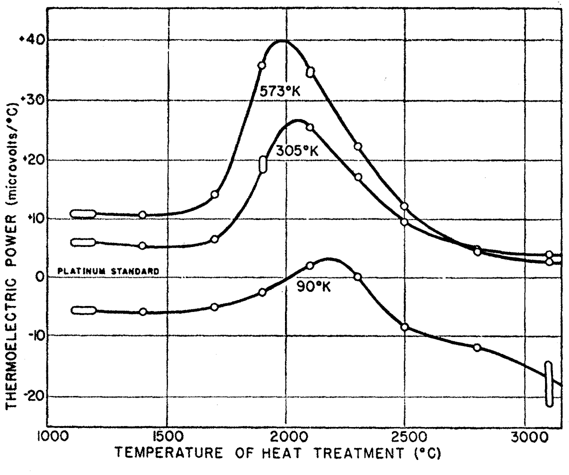

FIG. 4. Thermoelectric power Θ of soft carbon rods 1 and 2 *vs* platinum obtained at three average temperatures T(°K) as a function of heat-treatment temperature T_{ht}.

$$\Delta\Theta=\Theta(T_{ht}^{i},T)-\Theta(T_{ht}^{j},T), \qquad (1)$$

where $\Theta(T_{ht}^{i},T)$ stands for the thermoelectric power of a carbon heat treated to temperature T_{ht}^{i} and determined at temperature T with respect to platinum. $\Delta\Theta$ is then the change in the absolute thermoelectric power of a carbon (determined at an ambient temperature T) as produced by a variation of its heat treatment from T_{ht}^{i} to T_{ht}^{j}. It can be seen from Table I that, within the experimental error, $\Delta\Theta/T$ is independent of T.

For graphitized carbons and graphite, the relation between the thermoelectric power and the temperature is not so simple as for baked carbons. This can be seen from Fig. 4. For high values of T_{ht}, the 305°K and 573°K curves approach small values of Θ whereas the 90°K curve decreases towards considerably lower values. The possible influence of impurities on the thermoelectric power in carbons was checked by purifying one baked rod (from the same batch) by the method of La Rosa.[2] The thermoelectric power was determined before and after purification in the initial baked state, as well as after heat treatment to 2100°C. The resulting values agree within experimental error with the values for the unpurified carbons.

TABLE I. The thermoelectric power increment $\Delta\Theta$ due to varying heat treatment H and its dependence on temperature T.

			$\Delta\Theta$ in μv/°K			$\Delta\Theta/T$ in μv/°K$^2\times10^3$	
			T			T	
T_{ht}^{i}	T_{ht}^{j}	90	305	573	90	305	573
1900	1700	3.43	11.47	21.96	38.2	37.8	38.6
1900	1400	3.95	12.70	25.37	43.9	41.7	44.2

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[18] The results for soft carbons were reported at the North Carolina meeting of the American Physical Society; see E. E. Loebner, Phys. Rev. **91**, 243(A) (1953).

2. *Electrical Resistance*

The electrical resistivity of polycrystalline carbons depends on the degree of their porosity. Corrections necessary for the calculation of the real resistivity of polycrystalline carbons and graphite were enumerated by Mrozowski.[6] The results reported in this paper have not been corrected for small changes in the porosity, weight, or size of the samples, which were induced during the heat treatment. Thus, after each heat treatment, a small decrease in weight of the sample was found. It amounted to about 1% of the rod's weight. Because of the unavoidable oxidation and mechanical losses, the cumulative reduction of weight through successive heat treatments resulted in an over-all loss up to 10% at 3100°C.

The relative electrical resistance R/R_0, of the same soft-carbon rods discussed in the previous section, is shown in Fig. 5 as a function of the heat-treatment parameter T_{ht} determined at the same three ambient temperatures T. R_0 represents the initial resistance of the carbon before any heat treatment, the resistance being determined at 90°K.

Each curve of R/R_0 *vs* T_{ht} has essentially the same shape. After an initial decrease, a typical plateau follows, extending from T_{ht} about 1200°C to a knee which occurs around 2100°C. The lower the average temperature T at which Θ was determined, the higher the heat treatment T_{ht} at which the knee occurs and the higher the radius of curvature of the knee. The shift in position of the knee in the resistance curve corresponds to the shift of the position of the maximum in the thermoelectric power curve. On the other hand, it seems that the position of the low T_{ht} end of the resistivity plateau is not appreciably affected by T.

3. *Structure*

The structure of the soft carbons used in this study and its dependence on heat treatment were determined from a series of x-ray diffraction runs.

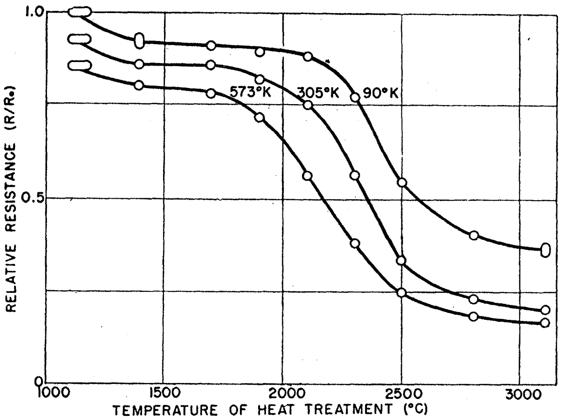

FIG. 5. Relative resistances R/R_0 of soft carbon rods 1 and 2 obtained at the three average temperatures T(°K) as a function of heat-treatment temperature T_{ht}.

The great width of the (002), (10), and (11) lines for $T_{ht}=1100$°C indicates that baked carbons contain crystallites of very small dimensions. Since the (10) and (11) lines are asymmetric, one concludes that these crystallites are turbostratic, i.e., they are composed of stacks of parallel but randomly rotated graphitic planes. The diameter of the graphite planes was calculated from the width of these asymmetric lines by using Warren's formula.[15] The average number of graphitic plane layers in a stack forming the crystallite was determined from the broadening of the (002) line.

The decrease in line width which occurs with heat treatment to higher temperatures indicates growth in crystallite size while the appearance of the (101) and other (*hkl*) ($l\neq 0$) lines results from the rotational ordering of the planes into the three-dimensional lattice of graphite. This process of rotational orientation is found in soft carbons to start for heat treatments above 1700°C and its completion is estimated to occur at about 2500°C.

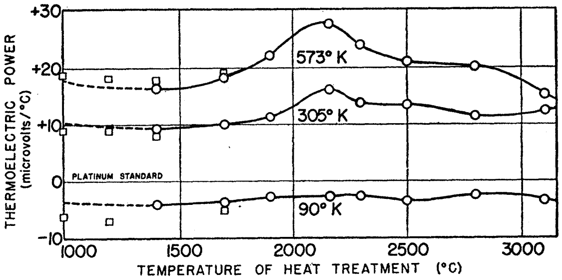

FIG. 6. Thermoelectric power Θ of hard carbon samples 5 and 6 (designated □) and 7 and 8 (designated ○) *vs* platinum obtained at three average temperatures T(°K) as a function of heat-treatment temperature T_{ht}.

Measurements of the width of the (002) line showed that the L_c dimension of the crystallites increased from just a few layers in the 1100°C carbon up to hundreds of layers for $T_{ht}>2300$°C. The diameter L_a of the crystallites was determined at the lowest heat treatments from the asymmetric broadening of the (10) and (11) reflections with the help of Warren's formula. At somewhat higher heat treatments the apparent crystallite diameter was estimated from the broadening of the symmetrical contribution of the (100) reflection to the (10) line using the conventional formula; and for higher heat treatments, where the (101) contribution begins to overlap considerably with the (100) contribution, the broadening of the symmetrical (110) reflection was used for the estimate of the diameter. In general, above 2300°C such size determination becomes unreliable and a high-precision technique is necessary. It was found that the diameter L_a changes essentially at the same rate as the L_c dimension, though at higher heat treatments the crystallites tend to have a higher L_c/L_a ratio. The position of the (002) line was found to shift to higher angles with an increase in the heat-treatment temperature. This indicates a decrease in the apparent interlayer spacing from a value above 3.6 angstroms for T_{ht} about 1100°C to around 3.4 angstroms for T_{ht} about 2500°C, while it remains relatively constant from 2500°C up to 3100°C. All the changes observed were essentially similar to those described by Franklin[15,16] and are in good agreement with the results of Pinnick[15] obtained with the same type of carbon.

B. Hard Carbons[19]

1. *Thermoelectric Power*

Graphs of Θ *versus* T_{ht} for phenol-benzaldehyde carbon are given in Fig. 6 for three values of T. The squares on the diagram indicate values obtained with two rods used in the early stages of the experiments. These samples unfortunately broke during the course of the investigation. The circles indicate values obtained with two other rods of the same batch, which were originally heat-treated to 1400°C.

The curves in Fig. 6 show the following similarities to those of the soft carbons in Fig. 4: They all have a shallow minimum for $T_{ht}\sim 1400$°C and a maximum around 2200°C; for lower T the maximum occurs at higher T_{ht} (for $T=573$°K the maximum is located at 2120°C, for 305°K at 2160°C, and for 90°K at 2220°C). In the heat-treatment range I the increments are again roughly proportional to the absolute temperature.

However, the PB-carbon differs from soft carbons in a number of ways: For the same T the maxima occur at a somewhat higher heat-treatment temperature T_{ht}; furthermore, the variation in the thermoelectric power, due to change in T_{ht}, is in general small; finally the curves show a complicated behavior in the range of higher values of T_{ht}.

2. *Electrical Resistance*

Graphs of R/R_0 against T_{ht} are presented in Fig. 7 for the three values of T. They refer to the same PB-carbon samples described in the previous section.

The dashed line at the low-T_{ht} end of one curve is an extrapolation of the electrical resistance of the second pair of rods (represented in Fig. 6 by circles); the extrapolated values were obtained using the relative changes in resistance observed for the first pair of rods.

The PB-carbon curves on this graph show again similarities to those of soft carbons (see Fig. 5): All curves exhibit an initial decrease followed by a typical plateau, which extends in this case to around 2200°C; as for soft carbons the knee of the curve, which terminates this plateau, occurs at lower values of T for higher heat treatments; the position of the knee of the resistance curve corresponds roughly to the position of the maximum on the thermoelectric power curve.

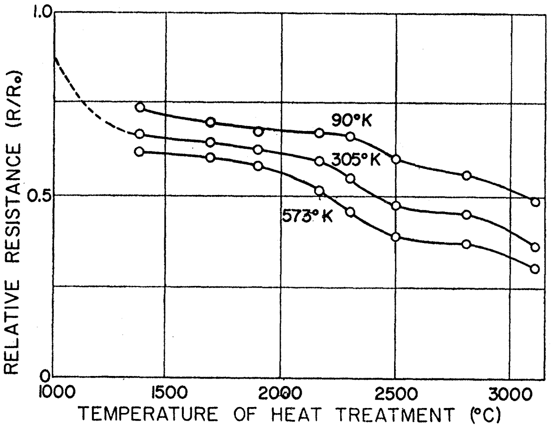

FIG. 7. Relative resistances R/R_0 of hard carbon rods 7 and 8 obtained at three average temperatures T(°K) as a function of heat-treatment temperature T_{ht}.

The PB-carbon graphs differ from those of soft carbon in the important respect that in addition to the regular plateau, there is a second plateau-like region, terminated by a second knee occurring between 2800°C and 3100°C. The temperature dependence of the position of the second knee could not be established from the available data. It can be seen that in general the relative resistance changes less for hard carbons than for soft ones in the investigated range of heat treatments.

3. *Structure*

X-ray diagrams for heat treatments from 1400°C to 3100°C differ considerably from the ones for soft carbons. For corresponding T_{ht} the x-ray diffraction lines for PB-carbon are much broader than for soft carbons; for example, the diffraction pattern of a PB-carbon heat treated to 3100°C, resembles roughly the pattern for a soft carbon heat-treated to 1700°C. In addition, the (002) diffraction line for the PB-carbon shows a complex structure, which has an interesting dependence on heat treatment.

With increasing T_{ht}, a sharp component gradually emerges superimposed on the large-angle side of the broad (002) line. Because of its sharpness, the sharp component can roughly be separated from the broad component by graphical means. The relative integrated intensities of the sharp and the broad (002) components are given in Fig. 8 as a function of heat treatment. There is no indication of the existence of the sharp peak at 1400°C, while at 1700°C it is clearly detectable and increases in relative intensity to a value of about 13% of the total combined areas at about $T_{ht}=2200$°C. Above this heat treatment, the ratio of the areas of the sharp to broad component increases relatively slowly. For $T_{ht}>2800$°C, the integrated intensity of the sharp peak starts growing faster again at the expense of the broad component so that the broad component's area shrinks to about 43% at 3100°C. It should be noted

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[19] The results for hard carbons were reported at the Detroit meeting of the American Physical Society; see E. E. Loebner, Phys. Rev. 94, 1435(A) (1954).

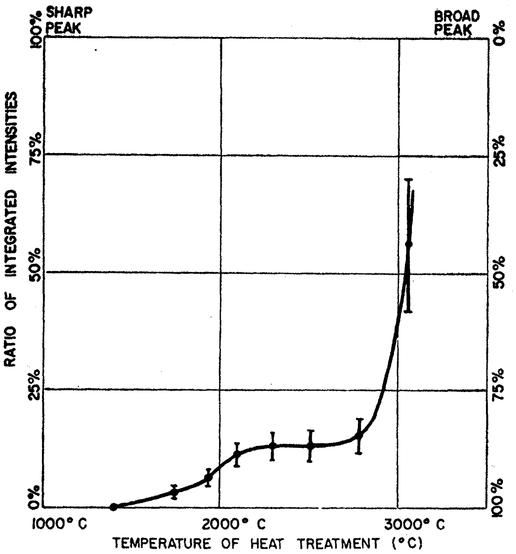

FIG. 8. The relative ratio of the soft and hard carbon phases in the phenol-benzaldehyde carbon (sample 5) heat-treated to successively higher temperatures T_{ht}(°C).

that the above percentages refer to the fraction of carbon atoms participating in the layer structures and not to all atoms present.

The width and the position of the sharp (002) component depend on T_{ht} in a way similar to that observed for the (002) line of soft carbons. However, for low T_{ht}, the peak is located at somewhat higher angles than in the case of correspondingly heat-treated soft carbons.

Inspection of the diagrams shows that the line width of the broad component decreases quite slowly as the parameter T_{ht} increases, indicating a much less pronounced crystallite growth than that which was found in soft carbons. Results for the half-width of the broad (002) component suggest that the stacks of the graphite molecular layers grow from about four layers at 1400°C to about 20–25 layers at 2800°C; while their diameter, determined from the (10) asymmetrical line, increases from about 40 A at the 1400°C heat treatment to about 90 A at 2800°C. For T_{ht} greater than 2800°C, the broad component decreases further in width as well as in intensity. No tendency for a mutual rotational alignment of the graphite plane layers was found for the broad component. On a number of recordings, for which the Geiger counter operated with a relatively low extraneous background count, the peak of the (10) line profile showed an additional weak but narrow component, resembling somewhat the composite structure observed for the (002) reflection. The interlayer spacing of the graphitic layers, as determined from the position of the broad (002) line, decreases with increasing T_{ht}, but at all times remains much larger than the spacing in soft carbons.

In addition, up to heat treatments of 2100°C, an amount of background scattering which points to the presence of a relatively larger amount of disorganized carbon is observed. Some such scattering can be observed even for $T_{ht}=2800$°C.

Since the relative amount of the sharp (002) component had been found to be about 14%, it seemed necessary to determine whether it might not be the binder which graphitizes more easily than the coke particles themselves (the binder constitutes just about 14% of the substance). Consequently, particles of the coke from which the rod was made were treated to 2000°C and then studied with x-rays. The same intensity ratio for the sharp to broad components was found as before.

It was also held possible that the presence of iron impurities might have promoted the growth of the soft phase below $T_{ht}=2200$°C by catalytic action. It has been checked by chemical analysis[20] that the amount of ferromagnetic impurities was considerably smaller than 0.1%. Although the possibility of catalysis cannot be excluded completely it does not seem to be probable. Considering the extensive studies of Franklin,[16] the two-phase graphitization seems to be a characteristic property of the coke itself.

IV. DISCUSSION

The results, described in the previous section, clearly indicate that there is a correlation between the thermoelectric power, electrical resistance, and structure of solid carbons. Since there are considerable differences in the structure and properties of soft and hard carbons, these two types will be discussed separately.

A. Soft Carbons

The dependence of the electrical resistance and thermoelectric power on heat treatment T_{ht} and ambient temperature T can be explained on the basis of the energy-band model[6] which was proposed a few years ago. In this model, electronic conduction is restricted to a direction parallel to the benzene-ring planes. A one-dimensional energy-band diagram, showing the forbidden energy gap and the position of the Fermi level as a function of heat treatment (or diameter of the condensed benzene-ring plane), is given in Fig. 9. Values of some of the physical constants for soft carbon are included below the diagram.

Benzene-ring layers of the carbon crystallites are formed from small aromatic molecules by condensation. Mrozowski[6] assumes that the energy gap between the two bands, which is large for small aromatic molecules, decreases gradually with increase of molecular size (crystallite diameter) throughout the range from raw cokes through baked carbons and polycrystalline graphite, and finally disappears for infinitely large

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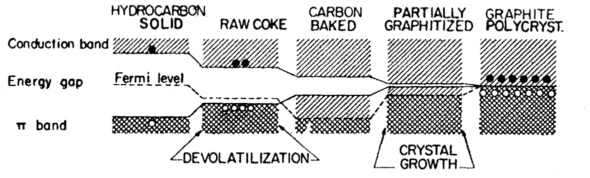
[20] The chemical analysis was carried out by R. L. Adamczak of the Chemistry Department, University of Buffalo.

graphite crystals or may even end in an overlap of the π and conduction bands.[21] In fact, it was shown by Akamatu and Inokuchi and by Kmetko[22] that molecular solids with condensed aromatic structures are intrinsic semiconductors whose energy gap decreases with increasing molecular size. An additional assumption made is the presence of surface electron traps created by the removal of hydrogen and other radicals which leave free some of the peripheral valences in the aromatic layers (many of the peripheral valences are not free, being engaged in polymeric-type inter-crystalline bonding). The chemi-desorption of peripheral hydrogen and other radicals takes place when the organic substances are subjected to temperatures above 600°C, and leads therefore to an excess p-type conductivity in the condensed-ring structure.[23]

Previously reported measurements on carbons and graphite[8] have shown a fast decrease of the positive thermoelectric power with increasing T_{ht} in the region between 750°C and 1000°C, and were interpreted to indicate an increase in the concentration of excess holes in the π band. Indeed, the concentration of carriers in the π band must become very high around 1400°C, when almost all the volatile constituents are driven off and the concentration of peripheral traps becomes high. Θ decreases to a very small value of the order of magnitude of the thermoelectric powers of metals. This has been indicated in the one-dimensional energy band diagram by a strong depression of the Fermi level (Fig. 9). At this stage ($T_{ht}\sim 1400$°C), all peripheries are bare. From here on, subsequent growth of crystallites will tend to decrease the relative number of peripheral sites (for each crystal the number of peripheral free valence sites probably increases in proportion to the circumference of a layer, see reference 6). Thus a depletion in the number of excess carriers results, which leads to an increase of Θ. This is represented in the diagram by a rising of the Fermi level toward the top of the π band.

When the Fermi level is located far below the top of the π band, a proportionality of the absolute thermoelectric power with the absolute temperature T is expected. This indeed was found in experiments (see Sec. III of this paper). Consequently, it can be concluded that baked carbons in the central part of region I have a very high concentration of one type of carrier[24] and should be classified rather as p-type semimetals than excess semiconductors.



	HYDROCARBON SOLID	RAW COKE	CARBON BAKED	PARTIALLY GRAPHITIZED	GRAPHITE POLYCRYST.
Energy gap	~1.0 - 0.5 ev	~0.5 - 0.3 ev	~0.1 ev	<0.01 ev	< 0 ev
Crystal size	<25A	~25A	~50A	~200A	>1000A
Heat treatment	<500°C	~600°C	~1200°C	~2200°C	>3000°C
Thermoel. power	(-)	+	−	+	−

FIG. 9. One-dimensional energy band diagram representing the band model for carbons. With increasing crystallite size (and heat treatment) the energy gap decreases. The depletion of the Fermi level depends on the concentration of the peripheral carbon valence bonds, which increases with increasing chemi-desorption of gases and decreases with increasing crystallite diameter.

The value of the absolute thermoelectric power of the platinum leads (chemically pure) which were used throughout this investigation was not exactly known. Therefore the absolute thermoelectric power for carbons has been estimated roughly by referring to the Hall coefficient curve which was found for the same carbons to be only slightly dependent on temperature in region I and to change sign from negative to positive with increasing heat treatment at $T_{ht}=1750$°C.[25] Since this is a one-carrier region, the crossover of the absolute thermoelectric power should be located for all three T's also at about $T_{ht}=1750$°C. Actually, if one uses the values of the absolute power for pure platinum,[26] one finds that all three curves have a common crossover at $T_{ht}=1700$°C. This is a small difference and of no significance for the conclusions reached in this paper. The curves so obtained of the absolute thermoelectric power of soft carbons for the three ambient temperatures are given in Fig. 10.

It can be seen from this graph that for T_{ht} in the range 900°C to 1750°C the sign of Θ is negative. For a single-carrier p-type conduction, the negative sign indicates that the Fermi level is depressed so low that it becomes located (at least partially) below the E *vs* $\mathbf{k}$ inflection surface. This conclusion is somewhat unorthodox but quite consistent with the metallic characteristic of carbons in region I.

In region II ($T_{ht}>2250$°C), the conduction is due to two carriers: holes in the lower π band and electrons

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[21] C. A. Coulson and R. Taylor, Proc. Phys. Soc. (London) **A65**, 815 (1952); S. Mrozowski, J. Chem. Phys. **21**, 492 (1953); Phys. Rev. **92**, 1320 (1953); D. F. Johnston, Phys. Rev. **93**, 1420 (1954).

[22] J. Akamatu and H. Inokuchi, J. Chem. Phys. **18**, 810 (1950); E. A. Kmetko, Phys. Rev. **82**, 456 (1951).

[23] It is interesting to note that H. K. Henisch and M. Francois [in *Semiconducting Materials* (Academic Press, Inc., New York, 1951), p. 234], who studied the thermoelectric power of selenium, conclude that the free holes in selenium do not originate from impurities but somehow from the crystalline structure itself. However, they do not suggest a specific model which would explain the generation of the holes. It seems that the study of carbons might help to disentangle cases of amorphous phases of other elements for which the process of crystallization occurs in a narrower range and at an appreciably lower temperature and hence cannot be as easily and systematically investigated.

[24] This, after being made plausible by considerations presented in a paper by Mrozowski (reference 6), was shown also to be correct by the experimental work of E. A. Kmetko, J. Chem. Phys. **21**, 2152 (1953).

[25] S. Mrozowski and A. Chaberski, Phys. Rev. **94**, 1427(A) (1954).

[26] See for instance the diagram on p. 207 in the book by A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953).

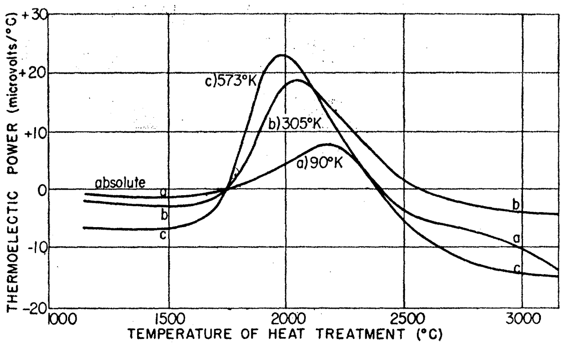

FIG. 10. The absolute thermoelectric power Θ of soft carbon rods as a function of heat-treatment temperature T_{ht}. These curves were obtained from Fig. 4 after using the data for absolute power of pure platinum and slightly adjusting the absolute level according to the Hall coefficient crossover.

which are thermally activated into the upper band. It is clearly seen that, following the energy-band model, the thermoelectric power will go through a positive maximum in the transition region ($1900<T_{ht}<2250$). With increasing parameter T_{ht}, the energy difference between the top of the π band and the Fermi level steadily diminishes while the energy difference between the bottom of the conduction level and the Fermi level decreases maybe even more rapidly, becoming of the order of kT, the thermal energy, in the transition region. Thus, considerable numbers of electrons are lifted from the Fermi level into the conduction band by thermal agitation. The maximum has to occur at a particular heat treatment where the decrease of the thermoelectric power, due to the increasing number of activated electrons and holes, outweighs the increase of Θ due to the decreasing number of excess holes. If this explanation is correct, then for lower T the position of the maximum should shift to higher values of the parameter T_{ht} as observed. Moreover, this temperature shift of the maximum in Θ shows that the existence of a maximum cannot be due to driving out of impurities by heat treatment, even irrespective of the fact that chlorination of the samples does not affect the shape of the curves.

With conduction taking place in two bands, the thermoelectric power of graphitized carbons and polycrystalline graphite resembles somewhat the situation in germanium discussed by Johnson and Lark-Horowitz,[27] when both bands have unequal numbers of carriers and both contribute to the generation of the Seebeck voltage. However, a quantitative treatment of the thermoelectric power of carbons and graphite is currently hampered by a number of considerable difficulties. Throughout most of the regions I and II one deals with a considerable degree of Fermi degeneracy. Moreover, the conventional metal or semiconductor models are inapplicable as the E *vs* $\mathbf{k}$ surfaces are not parabolic.[28] The only thing that can be said without detailed theoretical study is that negative values of the Hall constant and of the thermoelectric power Θ found in highly graphitized samples indicate a larger mobility for electrons than for holes.

In general, the results of the thermoelectric power determination in carbons and graphite are consistent with Mrozowski's model.[6] Because of the insufficient theoretical information available on the shape of energy surfaces within the Brillouin zones of the carbon and graphite structures, qualitative agreement is all that can be obtained at present.

Figure 10 reveals that for highly graphitized soft carbons (large values of T_{ht}) a large numerical increase in the absolute thermoelectric power occurs at low temperatures, which is in agreement with observations reported by Tyler and Wilson.[10] The conventional theory does not predict such an anomalous rise in the values of the thermoelectric power at low temperatures. However, some time ago Gurevich[29] showed that such deviations can result from the influence of phonon currents on the charge-carrier distribution. Recently, Fredrikse,[30] Herring,[31] and Klemens,[32] independently of Gurevich, have proposed a similar explanation for the anomalous behavior of germanium and of some metals at low temperatures. Fredrikse describes the effect as an additional emf contributed by a "phonon drag" of electrons, and Herring gives a detailed discussion of this effect for various models of semiconductors. Herring has shown that the "phonon drag" emf is developed only when little boundary scattering is present. Thus, this effect should be prominent for highly graphitized carbons only and in fact this is the behavior which can be inferred from Fig. 10.

In the preceding discussion, the influence of the disorganized carbon phase and the presence of potential barriers on the observed values of the thermoelectric power were neglected. The theory of thermoelectric power in nonhomogeneous semiconductors and across potential barriers was recently developed by Tauc.[33] His treatment shows that the thermoelectric contribution of the barriers can be completely neglected in our case.[34]

The explanation of resistivity in carbons was given in some detail by Mrozowski several years ago.[6] The existence of the observed resistance plateau was

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[27] V. A. Johnson and K. Lark-Horowitz, Phys. Rev. **92**, 226 (1953).

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

[29] L. Gurevich, J. Phys. (U.S.S.R.) **9**, 477 (1945); **10**, 67 (1946); J. Exptl. Theoret. Phys. (U.S.S.R.) **16**, 193 (1946).

[30] H. P. R. Fredrikse, Phys. Rev. **91**, 491 (1953); **92**, 248 (1953); T. H. Geballe, Phys. Rev. **92**, 857 (1953); T. H. Geballe and G. W. Hull, Phys. Rev. **94**, 1134 (1954).

[31] C. Herring, Phys. Rev. **92**, 857 (1953); **96**, 1163 (1954).

[32] P. G. Klemens, Australian J. Phys. **7**, 520 (1954). Klemens discusses the deviations for the Thomson coefficient.

[33] J. Tauc, Czechoslov. J. Phys. **3**, 282 (1953).

[34] H. K. Henisch and M. Francois (reference 23) showed that although the conductivity is very sensitive to the presence of intercrystalline barriers for selenium, the thermoelectric power can be considered a true property of the bulkof the crystallites.

explained to be due to a compensation between the decreasing number of excess carriers and the decreasing amount of electronic scattering at the crystallite boundaries. The subsequent knee and decrease in resistance with heat treatment results from the transition to a two-carrier conduction with electrons having a higher mobility than the holes. The position of the knee should, by such reasoning as above, shift to higher values of T_{ht} in a manner similar to the shift of the thermoelectric maxima. The fact that the position of the knee following the plateau shifts correspondingly with the position of the maximum of the thermoelectric power, indicates that the assumed mechanisms of conduction in carbons is essentially correct.

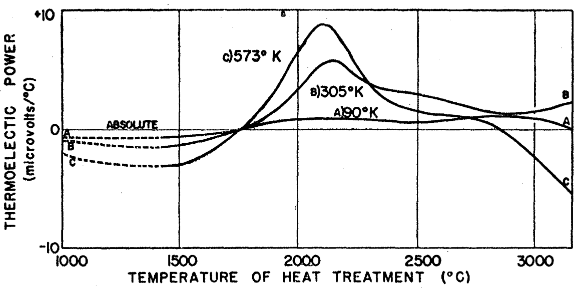

FIG. 11. The absolute thermoelectric power Θ of hard carbon rods 5 through 8 as a function of heat-treatment temperature T_{ht}. These curves were obtained from Fig. 6 after adjusting the absolute level similarly as in Fig. 10.

B. Hard Carbons

The structure of hard carbons is known to differ considerably from that of soft carbons: the diameter of the graphite layers, stacked to form turbostratic crystallites, is very much smaller after the same heat treatment, and the amount of disorganized carbon is much greater. This is probably due to a large amount of criss-cross linkage and the absence of preferred alignment of crystallites, which inhibit crystallite growth.[6]

The present x-ray investigation of phenol-benzaldehyde carbon, a particular kind of hard carbon, brought to light an extreme case of two-phase graphitization. Two-phase and three-phase graphitization was originally reported by Franklin,[16] who found that it was exhibited to a greater or lesser degree by almost all hard carbons. From the data given in the previous section, it is quite evident that about 13% of the crystalline phase of the substance graphitizes around 2200°C and constitutes a softer carbon phase. It is interesting to find a carbon which exhibits this phenomenon to a higher degree than any of those reported by Franklin.[16] Because of the higher percentage of the softer phase present in PB-carbon it was possible to establish that the appearance of the soft phase is not quite sudden, as reported by Franklin, but occurs gradually between 1400°C and 2300°C. Moreover, an ultimate conversion of the hard phase into the soft one was found to begin after treatments to temperatures above 2800°C. After heat treatment to the highest temperature used during this investigation, 3100°C, more than one-half of the conversion has been accomplished.

These two stages of graphitization are reflected in the dependence of the resistance of PB-carbon on heat treatment, since two plateaus are observed. Each plateau is similar to the single plateau of soft carbons, and presumably the explanation in terms of the band model Fig. 9 is also similar. The over-all resistance decrease in hard carbons is still somewhat smaller than the decrease observed for soft carbons, showing that, in accordance with the x-ray studies, the softening of the hard phase is not complete at 3100°C.

The absolute thermoelectric power Θ of a PB-carbon is plotted in Fig. 11. It has been again obtained by bringing each of the curves of Fig. 6 to a crossing with the zero axis at $T_{ht}=1750°C$. The shifts necessary to bring each of the curves to a common crossing at 1750°C are about the same as the ones used in plotting Fig. 10—this agreement strengthens our belief as to the approximate correctness of the procedure also in this case in spite of the fact that the exact location of the Hall crossover is not known for this type of carbon.

The explanation of the thermoelectric maxima and their shift with temperature T toward higher T_{ht} is probably the same as in the case of soft carbons. The prominence of the Θ maxima in PB-carbon is, however, somewhat surprising, since around 2300°C only one-eighth of the crystalline substance undergoes graphitization. The higher electrical conductivity of the softer phase might be responsible for this higher Θ contribution as well as for the apparent absence of the second maximum (except at the lowest temperature).

ACKNOWLEDGMENTS

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