

ELECTRONIC PROPERTIES OF CARBONS AND GRAPHITES*

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This is a review of the experimental data obtained in recent years at the University of Buffalo, the work being undertaken in a concentrated effort to clarify the nature of the electronic processes in carbons and in particular to check the proposed model (S. Mrozowski) of electronic conduction in aromatic solids. Results of studies of electrical resistivity (S. Mrozowski), of infrared absorption and Hall constant (E. A. Kmetko), thermoelectric effect (E. E. Loebner), influence of acceptors on resistivity and thermoelectric effect (E. A. Kmetko), of diamagnetic susceptibility and microcrystalline structure (H. T. Pinnick), and finally of paramagnetic spin resonance absorption (J. G. Castle, Jr.), all as a function of heat treatment temperature (degree of graphitization) are reported and their meaning briefly discussed.

The term "carbon" includes a class of solids which are formed by heating organic compounds in the absence of air or in a reducing atmosphere. As the temperature is increased, polymerization occurs and regardless of whether the starting material was composed of long chain molecules or aromatic molecules, the result of the polymerization is a system of cross-linked planar condensed benzene-ring molecules. At the setting temperature a solid is formed as a result of the formation of C—C bonds between neighboring planes, the planes being stacked parallel in groups like coins in a bag of money. From 400°C to 700°C, these condensed ring systems grow gradually, but all the peripheral carbon atoms are attached by chemical bonds to hydrogen atoms or hydrocarbon groups and therefore these substances are called condensed molecular solids. For the temperature of heat treatment (HT) about in the range of 700°C—

800°C large evolution of gases occurs which is due to the hydrogen and hydrocarbon groups being driven off from the periphery of the condensed ring system leaving small crystallites with a structure similar to graphite. These microcrystals are built from stacks of graphite planes, but the planes, although parallel, lack the directional relationship with one another that is present in graphite single crystals, and this structure is called turbostratic. As HT is increased from 800°C up to 3000°C, the crystallites grow gradually and above 2000°C, the planes begin, one after the other, to align into the regular graphite structure (the rotation occurring when the crystallite diameter exceeds 100 Å¹) until it all becomes polycrystalline graphite for HT greater than 2500°C.

The electronic properties of these various carbons, ranging from molecular solids through turbostratic microcrystallites to polycrystalline graphites, show wide and interesting variations. The electronic properties have been studied quite extensively in recent years at the University of Buffalo, and the results obtained are presented here in a very condensed form. The most obvious property from the point of view of experi-

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¹ H. T. Pinnick, J. Chem. Phys. **20**, 756 (1952).

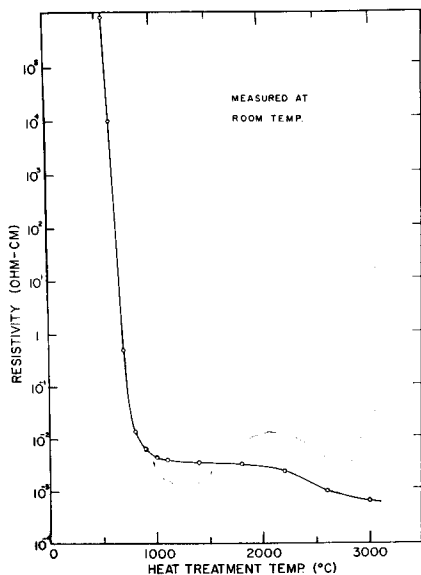


FIG. 1. Electrical resistivity of a soft carbon at room temperature as a function of heat treatment temperature².

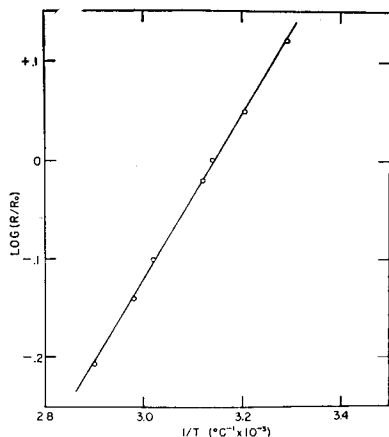


FIG. 2. Typical plot of $\log \rho$ vs $1/T$ for a condensed aromatic molecular solid³.

mental measurement is the electric resistivity ρ at room temperature as a function² of HT . Starting with substances treated to low HT , one finds that molecular solids (HT between 400°C and 700°C) have very high resistivities (See Fig. 1 showing the variation of resistivity with HT for a typical soft coke). Additional information about these sub-

² S. Mrozowski, Phys. Rev. **85**, 609 (1952) and Errata, Phys. Rev. **86**, 1056 (1952).

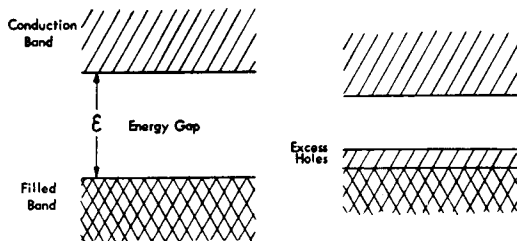


FIG. 3. (a) Band picture for a condensed molecular solid. (b) Band picture for a baked carbon (HT around 1000°C).

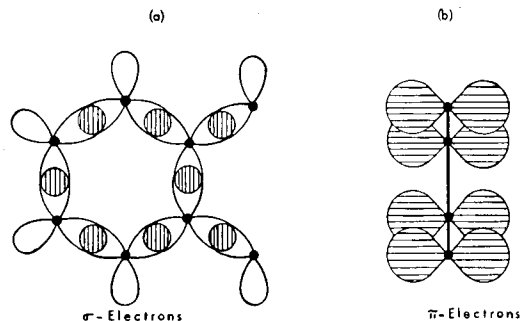


FIG. 4. (a) Schematic of σ -electrons in graphitic plane. (b) Schematic of distribution of π -electrons above and below graphitic planes.

stances can be obtained from a study of the temperature dependence of resistivity. Investigations of this property for molecular solids³ have shown that $\log \rho$ plotted against $1/T$ gives very nearly a straight line (Fig. 2). Such a dependence is characteristic of an intrinsic semi-conductor where the change in resistivity with temperature is due mainly to the change in the number of electronic carriers. The band picture for an intrinsic semi-conductor is shown in Fig. 3a. It is characterized by an energy band which is completely filled with electrons at absolute zero of temperature separated from an empty or conduction band by an energy gap ϵ . Each carbon atom has four valence electrons and in a condensed ring structure, three of these electrons are engaged in forming regular bonds with neighboring carbon atoms as illustrated in Fig. 4a, while the fourth or π -electron, which is responsible for the fractional bond (resonating double bond)

³ E. A. Kmetko, Phys. Rev. **82**, 456 (1951).

TABLE I
Energy Gap in *ev*

Temperature of Treatment (<i>HT</i>)	300°C	350°C	425°C	500°C	540°C	630°C	700°C	800°C
From resistivity vs. temperature.....			.80	.62	.41	.22	.09	.03
From infra-red absorption.....	1.2	.9	.7	.5	.35	.25	.2	

has an average distribution in space as shown in Fig. 4b. These π -electrons are the ones which fill the highest occupied band in these molecular solids. At temperature above absolute zero, because of the statistical distribution in the thermal energy, a number of electrons will have sufficient energy to be lifted into the conduction band and a corresponding number of positive carriers or holes will be left in the lower π -band. Therefore the resistivity will be decreased inversely proportionally to the number of carriers thus created which in turn is proportional to the factor $\exp(-\epsilon/2kT)$. Consequently, the resistivity will be proportional to $\exp(-\epsilon/2kT)$ and $\log \rho$ vs $1/T$ will be a straight line with a slope of $\epsilon/2k$. Not only does this straight line relationship provide information that these molecular solids are intrinsic semi-conductors, but the energy gap ϵ between the filled π -band and the conduction band can be calculated from the slope of the line. Studies³ of the energy gap as a function of *HT* for molecular solids show that the energy gap decreases with increasing *HT*. (Table I.)

The dependence of the size of the energy gap on *HT* was also checked by studies of infrared absorption³. If infrared radiation of frequency ν such that $h\nu > \epsilon$ is incident on a thin film of one of these molecular solids, the photons will be absorbed by lifting electrons out of the π -band into the conduction band. However, when the frequency ν is such that $h\nu < \epsilon$, the photons can no longer be absorbed and the film should therefore be transparent to radiation with frequencies lower than $\nu = \epsilon/h$. This effect is demonstrated in Fig. 5, which shows the shift of absorption edge in pyrolyzed cellophane as

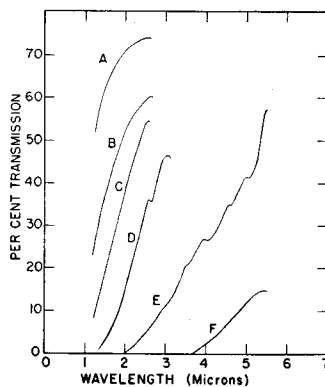


FIG. 5. Absorption edge for pyrolyzed cellophane films of different heat treatment³ A, 300°C; B, 350°C; C, 425°C; D, 630°C; E, 700°C.

HT is increased. For higher *HT* the gap is smaller and consequently the frequency at which the film becomes transparent, given by $\nu = \epsilon/h$ is smaller or the wavelength λ is longer. Since the absorption of radiation results in some electrons being lifted into the conduction band, these molecular solids should become more conducting under illumination and might be used as detectors for radiation of wave-lengths up to the absorption limit. This prediction has been checked and it has been shown that condensed aromatic solids can be used as radiation detectors⁴.

Returning to a consideration of the resistance at room temperature as a function of *HT*, a plot of ρ against *HT* is shown in Fig. 1 for a typical soft carbon, that is, one made from a starting material such as petroleum coke or coal tar pitch which remains fluid up to approximately 450°C (most of the remainder of the discussion will be limited to such

⁴ B. D. McMichael, E. A. Kmetko and S. Mrozowski, J. Optical Soc. Am. **44**, 26 (1954).

soft carbons). Over the range of HT from 500°C to 800°C , coinciding with the range where the large evolution of gases occurs, the resistivity decreases from $10^7 \text{ ohm}\cdot\text{cm}$ to $10^{-2} \text{ ohm}\cdot\text{cm}$. The following explanation has been given for this rapid decrease in resistivity². When the hydrogens and hydrocarbons are driven off from the peripheries of a condensed ring system, some of the σ -electrons from the peripheral carbon atoms which formed a valence bond with the hydrogen or hydrocarbons are left unpaired (some carbon atoms become bonded to neighboring crystallites); a π -electron can now jump from the π -band into the σ -state, forming a spin pair. The effect of this is to remove an electron from the π -band and to create a hole at the top of the filled band. Consequently, a large number of holes or positive charge carriers are created and this accounts for the very great drop in resistivity. The band picture for carbons of this type is illustrated in Fig. 3b. There is still an energy gap present, but the number of excess holes is so large that the number of electrons excited thermally into the upper band is negligible in comparison, and therefore the existence of the gap does not affect the electronic properties of carbons with an HT of from 800°C up to 2000°C (why this is not true above 2000°C will be clear later).

So far only the effect of the number of carriers on the resistivity has been considered, since the change of number of carriers was so great that small changes in scattering were unimportant for low HT . It becomes necessary, however, to include the scattering of the carriers in order to explain the rest of the ρ vs HT curve. In general, any deviation from perfect periodicity in the lattice of atoms will scatter electrons and thus increase the resistivity. One source of departures from perfect periodicity is the thermal motion of the atoms, and the thermal scattering causes an increase in resistance with increasing temperature. For example, in metals, where the number of carriers is independent

of temperature, the entire change of resistance is due to an increase in thermal scattering. In carbons, there is an additional scattering at the boundaries of crystallites and at the intercrystalline contacts. For very small crystallites this scattering overshadows thermal scattering and the resistance is due almost entirely to boundary and intercrystalline contact scattering. In Fig. 6 the resistivity as a function of temperature is shown for a number of different HT . For carbons treated to 1000°C – 1100°C , the temperature coefficient of ρ is negative, which shows that the intercrystalline scattering decreases with increasing temperatures since the number of carriers does not change appreciably with temperature. The curves for polycrystalline graphites with different HT and the curve for a single crystal are also shown in Fig. 6.

Having discussed scattering, it is advantageous to consider two other electronic properties which measure more directly the

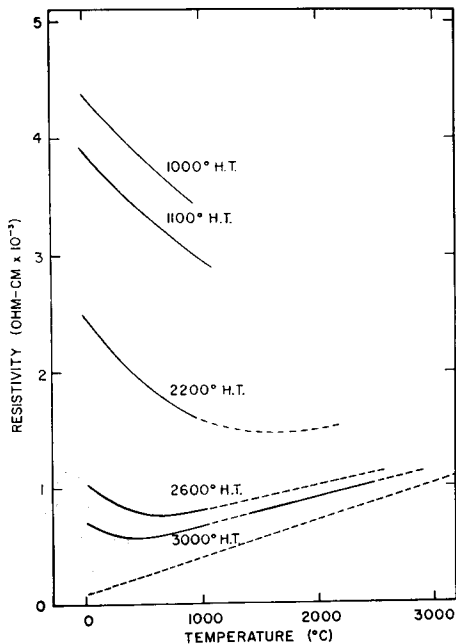


FIG. 6. Resistivity vs temperature for carbons of different heat treatment².

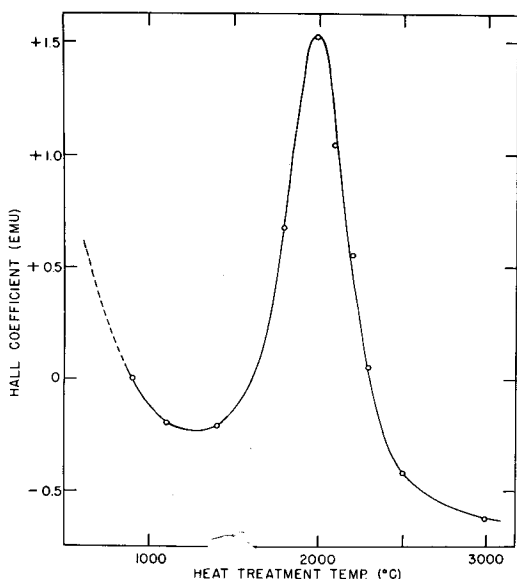


FIG. 7. Hall coefficient for a soft carbon as a function of heat-treatment temperature⁶.

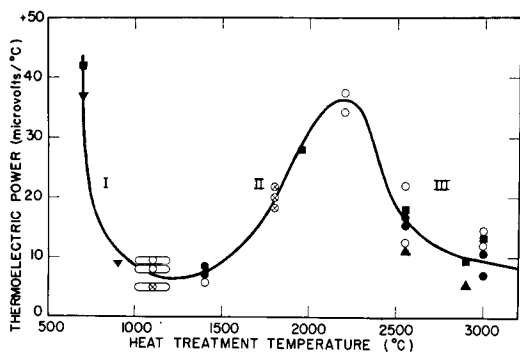


FIG. 8. Thermoelectric power *vs* platinum for soft carbons as a function of heat-treatment temperature⁶.

number of carriers in a solid. The Hall effect and thermoelectric power both depend on the reciprocal of the number of carriers so that when the number of carriers is small their magnitude is large. Their sign also gives information about the type of carriers, whether they are electrons or holes. If the sign of the Hall coefficient and thermoelectric power is negative, the predominant carriers are electrons, while if it is positive, the predominant carriers are holes. The Hall

coefficient⁵ and thermoelectric power⁶ for carbons at room temperature as a function of *HT* are plotted in Fig. 7 and 8. Both graphs show a decrease in magnitude in the region of *HT* from 500°C–1200°C, indicating an increase in the number of carriers. This increase in the number of carriers is due to the hydrogens and hydrocarbons being driven off from the peripheral carbon atoms and the increase continues until all the peripheries are almost bare, which occurs for an *HT* of approximately 1200°C.

It will be noted that the change of sign of the Hall coefficient (and of the absolute thermoelectric power) from + to - takes place during the process of creating excess holes. If the carriers are holes, how can the sign be negative? The positive carriers, or holes, are really electrons near the top of the band which go in the opposite direction to that which we ordinarily expect when accelerated by an electric field. At the bottom of the band the electrons behave normally, so somewhere in the band they have to change from electron-like to hole-like behavior. For *HT* of about 800°C, so many electrons are removed from the π -band that the level below which holes start behaving like electrons is reached.

Both Hall coefficient and thermoelectric power increase throughout the range of *HT* 1200°C–2100°C, showing a steady decrease in the number of carriers. Since all the foreign atoms have been driven off from the peripheries already at *HT* 1300°C, no more excess holes can be created, but the crystallite size is gradually increasing and therefore, the relative number of peripheral σ -traps which depends on the ratio of the diameter of the crystallites to their area decreases and so does the number of holes in the filled band. Somewhere around *HT* 1700°C the sign changes back to + again, when the

⁵ E. A. Kmetko, J. Chem. Phys. **21**, 2152 (1953).

⁶ E. E. Loebner, Phys. Rev. **84**, 153 (1951) and Errata, Phys. Rev. **86**, 1056 (1952).

band becomes filled above the previously mentioned critical level.

The plateau in the ρ vs HT curve in the region from 1200°C–2000°C can now be understood. The number of carriers is continually decreasing due to the gradual growth of crystallites, but the scattering which is primarily due to crystallite boundaries and intercrystalline contacts decreases also because of the growth of crystallites. The net result of the change in these two factors is that the resistivity remains almost constant.²

Going back to the curves of Hall coefficient and thermoelectric power, after the positive peak is reached at 2100°C, they both begin to decrease and eventually change sign again. The decrease for HT beyond the peak shows that the effective number of carriers is again increasing. This is due to the fact that the energy gap which was decreasing steadily becomes so small for HT greater than 2100°C that the activation energy is of the order of kT at room temperature and a great number of electrons are raised by thermal motion into the upper or conduction band². For this region of HT , the resistivity also begins to decrease, mainly due to the decrease in scattering and also due to the possible net increase in the effective number of carriers or decrease in their effective masses and consequently increased mobility. The energy gap decreases progressively until, for large crystals, it becomes zero or even slightly negative (overlap of bands)⁷. The fact that the Hall coefficient and thermoelectric power are negative for graphite indicates that when the numbers of electrons and holes are about equal, the electrons are the predominant carriers due to smaller effective mass. Fig. 9 summarizes the changes in the band structure throughout the range of HT from 400°C to 3000°C. This band model is a refinement of the model originally proposed⁸ and later modified² and

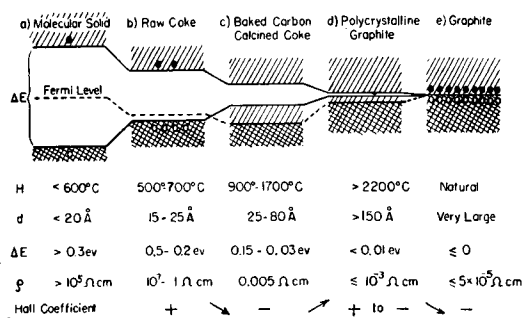


FIG. 9. Energy band scheme for carbons of different heat treatment⁴.

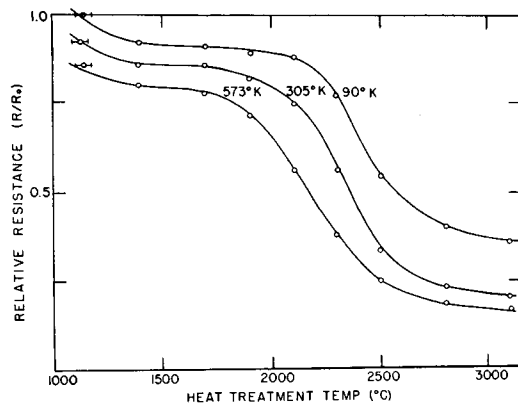


FIG. 10. Relative electrical resistance of a soft carbon as a function of heat treatment for three ambient temperatures⁹. (a) 90°K; (b) 305°K; (c) 573°K.

seems to give a rough but satisfactory explanation of all the electronic properties of carbons here reported except the paramagnetic resonance.

Recently a study has been made of the thermoelectric power and resistivity as a function of HT for three different temperatures⁹. The results of this study are shown in Figs. 10 and 11. The resistivity plateau extends to higher HT at the lower temperature since the resistivity does not begin to decrease until kT is of the same order as the activation energy, and a smaller activation energy corresponds to a carbon treated to a higher temperature. When kT is large, the resistivity starts decreasing for a large activation energy, or for a carbon treated at a lower temperature.

⁷ S. Mrozowski, J. Chem. Phys. **21**, 492 (1953) and Phys. Rev. **92**, 1320 (1953).

⁸ S. Mrozowski, Phys. Rev. **77**, 838 (1950).

⁹ E. E. Loebner, Phys. Rev., April (1956).

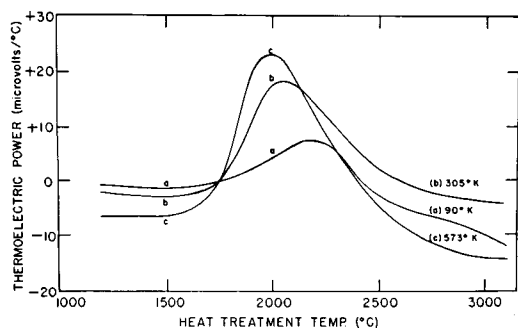


FIG. 11. Absolute thermoelectric power for a soft carbon as a function of heat treatment for three ambient temperatures⁹.

In a similar manner, the thermoelectric power at a high temperature starts decreasing for lower *HT*, that is, for a larger activation energy, whereas the peak at low temperature occurs in carbons with a smaller activation energy or larger *HT*. For *HT* below 2100°C, the thermoelectric power is proportional to the temperature, showing that baked carbons have a semi-metallic behavior, the number of carriers being almost independent of temperature.

Another experimental method for studying the electronic processes in carbons is by the introduction of HSO_4^- ions between the graphite layers. In this case a corresponding number of electrons is driven out from the π -band by electrostatic repulsion and the number of carriers is changed without changing the crystallite size and the energy gaps. The first experiments with sulfuric ions were performed at Argonne Laboratory on graphite¹⁰, and later investigations were made at the University of Buffalo in which a number of carbons were studied.⁵ Fig. 12 shows the change in relative resistance as a function of the number of holes created in the π -band. The 3000°C carbon, which when untreated has a nearly filled π -band, shows a large decrease in relative resistance since the relative change in the number of carriers is quite large. The relative resistance of the 2200°C carbon changes somewhat less rapidly than that of the 3000°C carbon, but

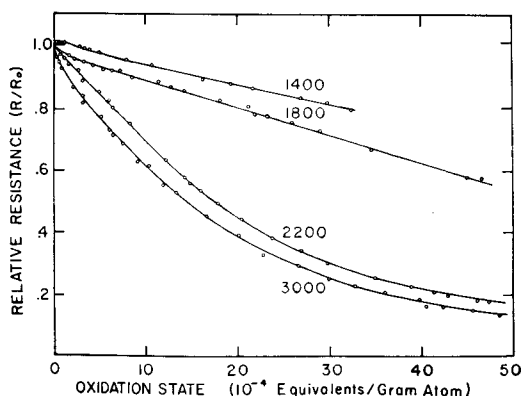


FIG. 12. Relative resistance as a function of oxidation state for carbon with different heat treatments⁵.

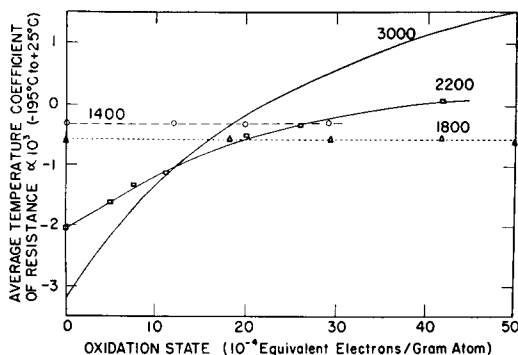


FIG. 13. Temperature coefficient of resistance as a function of oxidation state for carbons with different heat treatments⁵.

the 1800°C carbon, which already has quite a large number of excess holes in the π -band, shows a small change in resistance since the relative change in the number of carriers is small. Finally, the 1400°C carbon shows still less change in resistance for the same reason.

In Fig. 13, the temperature coefficient of resistance is plotted as a function of the number of holes introduced into the π -band by such an oxidation for carbons of different *HT*⁵. There is no change for 1400°C and 1800°C carbons, but for the 3000°C carbon the removal of a small number of electrons makes a large relative change in the number of carriers and, consequently, the temperature coefficient of resistance changes mark-

¹⁰ G. R. Hennig, J. Chem. Phys. **20**, 1438 (1952).

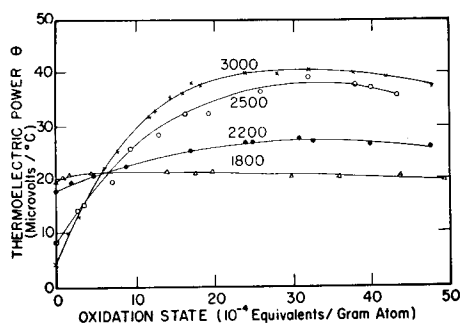


FIG. 14. Thermoelectric power vs platinum as a function of oxidation state for carbons with different heat treatments⁵.

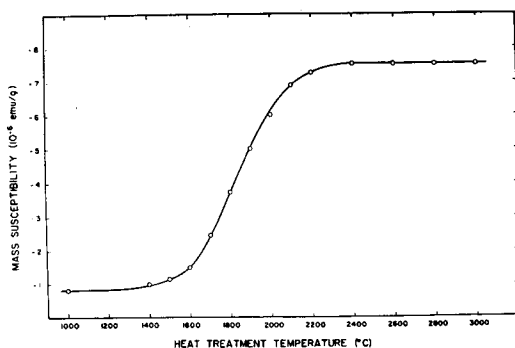


FIG. 15. Mass susceptibility of carbons as a function of the heat treatment temperature¹¹.

edly with oxidation. The results for thermoelectric power are plotted in Fig. 14 and the general trend is very much the same⁵. There is little effect on the 1800°C carbon, where the number of excess holes is large, but for 3000°C carbon, where the relative change in number of carriers is large, the thermoelectric power changes very strongly.

Magnetic properties furnish still another method of studying the electronic processes in carbons and in some respect should give more direct information since they like the Hall effect for a single carrier are independent of scattering. The diamagnetic susceptibility of carbons at room temperature has been investigated¹¹ as a function of *HT* and the results are shown in Fig. 15. The susceptibility increases from the value -0.5×10^{-6} per gram, which is the susceptibility

for individual carbon atoms, to -7.5×10^{-6} per gram, the value for a disordered array of large crystals, mainly over a small range of *HT* (from 1600°C to 2100°C) and remains constant for larger sizes. The diamagnetism for *HT* less than 1600°C is of a molecular nature (closed shell diamagnetism²) but it changes into a free electron diamagnetism for *HT* above 2100°C. It is rather difficult to understand why the susceptibility should remain constant through the range 2100°C–3000°C where the Hall coefficient and thermoelectric power show that the number of carriers is undergoing a radical change¹¹. The steep increase in susceptibility occurs for crystallite sizes too small for the change to be ascribed to the rotational ordering of planes in crystallites. The results show that the theory of diamagnetism is not in a very satisfactory state at present and must be improved before a complete interpretation of the diamagnetism of carbons will be possible.

The study of paramagnetic resonance in carbon provides a way of studying the behavior of individual electrons. Each electron behaves like a tiny magnet due to its spin and when placed in a magnetic field can be oriented either parallel or anti-parallel to the field. The difference in energy between these two positions depends mainly on the magnetic moment of the electron, the magnetic field, and slightly on the interaction of the electron with the surrounding medium. If a radio-frequency field of frequency ν such that $h\nu$ is equal to the energy difference between the two orientations of the spin is applied, the rf energy is absorbed by a resonance effect, resulting in a flipping over of the electron spins. Since the magnetic field and ν can be measured, the magnetic moment of the electrons can be determined and this gives information as to how "free" in the given medium the electronic spins are. The amount of rf energy absorbed gives information about the number of carriers, and the amount by which one can vary the magnetic

¹¹ H. T. Pinnick, Phys. Rev. **94**, 319 (1954).

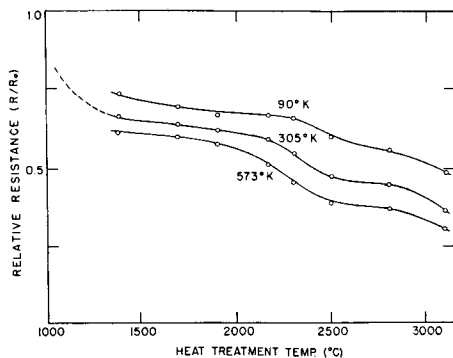


FIG. 16. Relative electrical resistance of a hard carbon as a function of heat treatment temperature for three ambient temperatures⁹.

field for a given ν and still get absorption supplies information about the local field acting on the electrons. Recently the paramagnetic resonance absorption has been found in various types of carbons and graphites using microwaves¹² and this technique promises to become another useful tool for studies of carbons.

All the above discussion referred to soft carbons or easily graphitizable carbons. There is another class of carbons made from

¹² J. G. Castle, Jr., Phys. Rev. **92**, 1063 (1953). Paramagnetic spin resonance in graphite was found independently by G. R. Hennig and B. Smaller; see G. R. Hennig, B. Smaller and E. L. Yasaitis, Phys. Rev. **95**, 1088 (1954).

starting materials which solidify at much lower temperatures and thus possess a more disordered structure. The abundance of cross-links hinder the graphitization process and the ρ vs. HT curve, for example, differs from soft carbons in that the plateau extends to higher HT . The graphitization also proceeds somewhat differently, as shown by the existence of another plateau at higher HT (Fig. 16)⁹. A similar situation exists with the thermoelectric power of hard carbons as a function of HT where a second small maximum is possibly present at an HT of around 3000°C⁹. These differences between hard and soft carbons are probably connected with the two-phase graphitization occurring in hard carbons¹³.

The study of the various electronic properties of carbons: electric resistivity, temperature coefficient of resistivity, Hall coefficient and thermoelectric power, as a function of HT and for interstitial compounds has made possible a fairly complete, although at present somewhat qualitative, picture of the electronic processes occurring in carbons. Further studies are being carried out which promise to give more information with which the picture can be extended and refined.

¹³ Two- and three-phase graphitization was discovered by R. Franklin, Proc. Roy. Soc. (London) **209**, 196 (1951).