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March 1983

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ABSTRACT

The electrical conductivity and Hall effect of glassy carbon heat treated for three hours between 1200 and 2700°C was measured at temperatures from 3 to 300 K in magnetic fields up to 5 tesla.

The electrical conductivity, of the order of 200 (ohm-cm)^-1 at room temperature, can be empirically written

\[ \sigma = A + B\exp(-CT^{1/4}) - DT^{1/2} \]

where the first term is a strongly scattering metallic component the second term is attributed to variable range hopping, and the third and new term is a negative correction to the metallic conductivity associated with one-dimensionality. All of the constants A, B, and C were insensitive to heat treatment temperature; the constant D decreased with increasing temperature until it disappeared at about 2200°C.

The Hall coefficient was independent of magnetic field, insensitive to temperature, but was a strong function of heat treatment temperature, crossing over from negative to positive at about 1700°C and ranging from -0.048 to 0.126 cm^3/coul.
The idea of one-dimensional filaments in glassy carbon suggested by the electrical conductivity is compatible with the present consensus view of the microstructure constructed through such means as lattice imaging in transmission electron microscopy, and x-ray diffraction and small angle scattering.
Introduction

The electrical conductivity and Hall effect have been measured in a great number of carbons [1]. Carbonaceous materials have a great range of conductivities, but only single crystal graphite can be said to be well understood. In grossly defective graphite, the electrical conductivity increases with temperature as a semiconductor and does not decrease like a semimetal and pure graphite [2].

Glassy carbon is a prototype hard carbon. It can be considered an amorphous material because of its glass-like fracture characteristics and the small apparent crystallite size (15-50 Å) as measured by x-ray diffraction and transmission electron microscopy.

The Hall effect in graphite for small magnetic fields and room temperature is negative, but in general and for soft carbons it is sensitive to local strain, temperature, impurities, and heat treatment temperature, and is a function of magnetic fields [3-17]. Work to explain this phenomenon continues on the modified Slonczewski-Weiss theory along the lines of trigonal warping [18,19,20], wherein the corners of the constant energy Fermi surface become less pointed and more rounded in the presence of a magnetic field.

In the heat treatment range of interest, 1000 to 3000°C, only a few studies have been made of the electrical properties of glassy carbon. Yamaguchi [21], and Tsuzuku and Saito [22] made non-zero magnetic field measurements at 20 and 77 K and room temperature, with a maximum field of 1.4 and 2.2 tesla respectively. Saxena and Bragg [23] did not
make meaningful Hall effect measurements, but took conductivity measurements over a continuous range of temperatures above 10 K. They were the first to put forth an empirical expression for the electrical conductivity.

Thus the objectives of this study were to obtain lower measurement temperatures than the 10 K of Saxena and Bragg, to observe the extended low temperature behavior of the electrical conductivity, and to make a complete set of Hall effect measurements as a function of heat treatment temperatures greater than 1000 °C.

Electrical properties can be extremely sensitive to microstructure, though evidently less so in glassy carbon. Nevertheless, with the achievement of lower measurement temperatures, some conclusions describing the microstructure changes in glassy carbon should be drawn from observations of the electrical conductivity and Hall effect.
Experimental

Glassy carbon was acquired from Polycarbon, Inc., of North Hollywood, CA in plate form after it had been heat treated for one hour at its final heat treatment temperature of 1000°C. It was heat treated further in an Astro graphite furnace for three hours at temperatures ranging from 1200 to 2700°C under inert gas. Specimens were ground and polished to uniform thickness and ultrasonically cut into a four probe bar configuration. Measurements were made under isothermal conditions in a liquid helium cryostat at temperatures from 3 to 300 K and with magnetic fields up to five tesla.
Results

The electrical conductivity of glassy carbon (Figure 1) is of the order of 200 (Ω-cm)$^{-1}$ and is not a strong function of temperature, as the ratio of the conductivities at room temperature and liquid helium temperature is only 12–24%, depending upon heat treatment temperature. For higher temperatures, as Yamaguchi [21], Tsuzuku and Saito [22] and Saxena and Bragg [23] observed, the conductivity increases monotonically with temperature through room temperature, apparently in a manner independent of heat treatment temperature. In high temperature heat treated glassy carbon, the conductivity decreases with decreasing temperature to a plateau. The plateau minimum occurs at decreasing temperatures for decreasing heat treatment temperatures until it no longer remains within the limits of the experiment. For lower heat treatment temperatures than about 2200°C, the conductivity continues to fall off more rapidly with decreasing heat treatment temperature and measurement temperature. The relative precision of the measured electrical conductivity is 0.01% and its absolute accuracy is 3.7%.

The Hall coefficient for all heat treatments is nearly independent of measurement temperature, as is the Hall mobility. The Hall coefficient is also not a function of magnetic field as is the case in other carbons. However, the Hall coefficient is a strong function of heat treatment temperature (Figure 2) having an absolute minimum at about 1200°C, crossing from negative to positive at about 1700°C and becoming increasingly positive with increasing heat treatment temperature. These results are similar to those of Yamaguchi [21] and
Tsuzuku and Saito [22]. The Hall coefficient observed in this work is small, and lies between \(-0.048 \text{ cm}^3/\text{coul}\) and \(0.126 \text{ cm}^3/\text{coul}\). It is known to within 3.7% with a precision of 0.2%.
Discussion

A. Electrical Conductivity

The most recent comprehensive study of the electrical conductivity of glassy carbon in the high heat treatment temperature (greater than 1000°C) regime was done by R. Saxena and R. H. Bragg [23]. They found that the conductivity $\sigma$ could be empirically written as

$$\sigma = A + B \exp\left(-C T^{-1/4}\right) + \delta(T)$$  \hspace{1cm} (1)

where $A$, $B$, and $C$ are constants and $\delta(T)$ is a term appearing only at low temperatures for low temperature (less than 2000°C) heat treated material. The first and largest term $A$ was attributed to metallic conduction and was thought to be influenced by scattering from "crystal-lite" boundaries. The second term was in the form for Mott scattering or variable range hopping of carriers between localized states. Thus the new contribution to the body of knowledge concerning the electrical conductivity of glassy carbon is the third term of Saxena and Bragg, which was represented as a negative correction term of the Kondo logarithmic form. Because of the extended temperature range of this work, it was found instead that this negative component has a square root inverse temperature dependence, compatible with the recent theory for the low temperature correction for one-dimensional metallic filaments. No explanation is given for the very low temperature
conduction behaviour of high temperature heat treated glassy carbon, though it may be related to increasing apparent crystallite size and dimensionality.

The largest term of the electrical conductivity of glassy carbon has been attributed to strongly scattering metallic conduction between extended states. The conductivity in three dimensions is given as

$$\sigma = S_F e^2 L / 12 \pi^3 h,$$

(2)

where $S_F$ = Fermi surface area and $L$ = mean free path. This formula has been derived in a number of ways. It was derived by Ziman [24,25] in his work with liquid metals, by application of the Kubo-Greenwood formula [26,27,28,29] and also the Boltzman equation [28,29]. If the mean free path $L$ becomes shorter, the conductivity can be legitimately written

$$\sigma = S_F e^2 L_z / 12 \pi^3 h$$

(3)

where $L_z$ is called the Ziman mean free path and is related to the actual mean free path $L$ by $L = L_z / g^2$, where $g$ is the ratio of the density of states at the Fermi level to the density of states at the Fermi level for free electrons. Of course in the limit that $L = a$, the conductivity is given by

$$\sigma = S_F e^2 a g^2 / 12 \pi^3 h$$

(4)
The term A in the present empirical formula appears to be independent of heat treatment temperature (Figure 3). The "apparent crystallite" size of glassy carbon as reported by x-ray diffraction studies increases monotonically with heat treatment temperatures [30,31,32]; therefore if electrical conductivity of glassy carbon depended on crystallite boundary scattering, the conductivity would be dependent on the "apparent crystallite" size. This is apparently not the case. The conductivity formulae given above are also explicitly independent of temperature.

Application of the metallic conductivity formula for three dimensions using a coarse estimation of the parameters would easily make the metallic term approximate the average experimental value of 176 (Ω-cm)^{-1}. For example, if the Fermi surface area is made to be the surface of the reciprocal unit cell of graphite, a is the nearest neighbor distance of 1.42 Å, and g is 0.5, then the minimum conductivity predicted is 19 (Ω-cm)^{-1}. If the mean free path is made larger than the minimum distance a to match the average experimental conductivity, the mean free path becomes 13 Å, or 5 unit cells along the basal planes.

The second term of the empirical formula found by Saxena and Bragg [23] for the electrical conductivity of glassy carbon was attributed to variable range hopping or Mott scattering of the form \( \sigma_h = \sigma_p \exp\left(\frac{T_0}{T}\right)^{-1/4} \). This conduction mechanism has been applied to many systems, notably amorphous and degenerate semiconductors and chalcogenide glasses [29].
The prefactor term \( \sigma_p \) has not yet been fully established. A number of forms with varying temperature dependences between \( T^{-1/2} \) and \( T^{5/4} \) have been advanced [33]; all except one do not have a strong temperature dependence. The prefactor evidently depends on the system parameters, such as the distribution density of sites and the density of states as a function of energy [34]. In most cases involving hopping conduction, the conductivity varies over several orders of magnitude, and consequently the temperature dependence of the prefactor is not very important. However, in glassy carbon, the exponential part of the term is markedly smaller than for most other cases, and hence it may not be possible to ignore the temperature dependence of the prefactor. Because competing theories give both direct and inverse temperature proportionalities, a temperature independent prefactor has been used.

Mott scattering is considered a low temperature process; at higher temperatures electrons jump primarily to the nearest available site rather than to some site within a maximum range and thus the conductivity is thermally activated. Up to room temperature, no activated components of the conductivity were ascertained in glassy carbon, though Hishiyama et al. [35] claims to have found two activated components and a hopping component at temperatures less than 4°C for glassy carbon treated at 900°C and 1000°C. Several authors [36-39] have proposed multi-phonon-electron interaction models to extend the range of
exp(-T^{-1/4}) conductivity behavior and as another means of explaining the transition to high temperature activated conductivity.

In many materials where hopping conduction takes place, there is a significant ac component of the conductivity. None was found in glassy carbon in this work.

The exponential part in the hopping term yields a temperature constant

\[ T_\sigma = \frac{16 \gamma^3}{k N(E_F)} = 4.5 \times 10^4 \text{ K.} \]  

(5)

The constant appears to be valid for all heat treatment temperatures. It is considerably less than that measured for amorphous carbon heated below the nonmetal-metal transition temperature and in silicon and germanium (2 x 10^7 K). A reasonable estimate of the density of states puts the localization range, \( \gamma^{-1} \), in the range of 15 Å or so. As shown by Figure 4, the linear hopping term \( B \) is not dependent on heat treatment temperature, and thus the whole hopping term is nearly the same for all heat treatment temperatures.

Kaveh and Mott [40] have reviewed two approaches to a correction of the metallic conductivity. They are the localization approach by Abrahams, Anderson, Licciardello and Ramakrishnan [41] and the electron interaction approach by Altshuler, Aronov, and Lee [42]. In the localization approach, the carrier is allowed to diffuse until an inelastic
scattering even takes place (trapping by a localized state) and thus diffusion of the carriers is limited by the inelastic scattering time. In the electron interaction approach, the effective number of carriers is affected by the correlation between the shift of potential energy and the broadening of the momentum distribution of the carriers themselves as scaled by the physical dimensions. Both mechanisms may be operating simultaneously. The interaction approach has been used to predict a correction in one dimension

\[
\delta \sigma = - \frac{e^2}{h} \left( \frac{2}{\pi} \right)^2 \frac{1}{A} \left( \frac{hD}{kT} \right)^{1/2}
\]  

(6)

where \( D \) is a diffusion coefficient related to the near free path and \( A \) is the cross sectional area. Such a \(-T^{-1/2}\) dependence was found in this work for a component of the electrical conducting inducing the possibility of one-dimensional transport.

The correction term parameter \( D \) becomes progressively smaller as the heat treatment temperature is increased (Figure 5) until the term disappears for heat treatment temperatures greater than 2200°C. Several possible causes are that the diameter of the one-dimensional wires becomes greater or their length becomes shorter, or that there are fewer conducting paths. Because individual filaments are not measured,
but rather the resistivity of a highly interconnected network, individual filament parameters cannot be evaluated. Any effects arising from the junction of filaments or their close proximity have not been taken into account.

Thus the new part to the basic description of the electrical conductivity as advanced by Saxena and Bragg is a one dimensional correction term to the strongly scattering metallic conductivity term, applicable only for glassy carbon heat treated below about 2200°C.

B. Hall Effect

The Hall effect in glassy carbon is insensitive to temperature, and is not a function of magnetic field up to five tesla, but is a strong function of heat treatment temperature.

As mentioned in the introduction, the Hall effect for most carbon materials is sensitive to many variables, among them temperature, magnetic field, strain, impurities, and defect structure. There is no theory that adequately describes the Hall effect in perfect single crystal graphite, and therefore much less so in heavily defective carbons. In the following, the Hall effect for each of the transport mechanisms responsible for electrical conduction are addressed, beginning with the strongly scattering metallic conductivity.

Friedman [43,44,45] has worked out the Hall coefficient and Hall mobility for a random phase model (RPM). This model applies for conductivity by extended states where the scattering length approaches the lattice or nearest neighbor spacing. He writes the Hall coefficient
the Hall mobility $\mu_H$

$$
\mu_H = 4\pi \frac{e a^2}{h} \left( a^3 J N(E_F) \right) (\eta \bar{z}/z)
$$

and the ratio of the Hall mobility to the drift mobility is

$$
\frac{\mu_H}{\mu_D} = \frac{6kT}{J} (\eta \bar{z}/z)
$$

where $W$ is the bandwidth,

$z$ is the number of nearest neighbors

$\bar{z}$ is the number of closed loops about a site

$N(E_F)$ is the density of states/ev at the Fermi level and

$\eta$ is a constant less than unity and

$J$ is the transfer energy integral between sites.

It should be noted that $R_H$ is inversely proportional to $N(E_F)$; for

a judicious choice of constants it is given as

$$
R_H = \frac{C}{\eta e c g}
$$

where $g = N(E_F)/N(E_F)$ free electrons and $C = 0.7$. Similar results

have been found by Kaneyoshi [46], Ziman [47], and Straub et al. [48].

The Hall mobility and coefficient for hopping conduction are not

well known [49,50]. Proposed forms for the mobility range from con-

stant [51,52] to weakly activated as the hopping conductivity [53,54]
proportionality constant \( \exp(-T^{-1/4}) \), to thermally activated [55]. However, in most cases, the Hall coefficient and mobility are small, and are expected to be minor components in the present case.

The Hall coefficient for the low temperature one dimensional wire correction has not been predicted, but is expected to be small especially if the dominant mechanism is localization diffusion.

The Hall effect cannot in general be used to predict the density of carriers or even whether the majority carriers are electrons or holes. This sign anomaly is dependent not only on the number of nearest neighbor sites, but also on the transfer integral or bonding between sites [49,50,51,56,57,58]. A number of authors have commented on the anomaly of carrier sign between the Hall coefficient and thermopower in chalcogenide glasses, and amorphous germanium and silicon [29].

As Figure 2 shows, the Hall coefficient in glassy carbon is a strong function of heat treatment temperature, having a minimum at about 1200°C and crossing over from negative to positive with increasing temperature at about 1700°C. This is an indication that there is a change in the microstructure occurring with increasing heat treatment temperature, but due to the ambiguities cited above, the exact nature of the microstructural transformation cannot be deduced from the Hall coefficient. The Hall effect is not a function of the magnetic field up to 5 tesla; Jirmanus et al. [59] detected no magnetic field dependence up to 15 tesla in the Hall measurements that they made.
If it is assumed that the measured Hall coefficient is due entirely to the contribution from the random phase metallic model and the formula \( R_H = \frac{C}{n e c g} \) holds, then for glassy carbon heated at 2700°C, which shows the largest Hall coefficient for material in this study and for which the model assumption should be most justified, the predicted number of carriers is \( 7 \times 10^{19} / \text{cm}^3 \). Through electron spin resonance Orzeszko and Yang [60] measured \( 5 \times 10^{18} \) spins/cm³ in their high heat treatment temperature glassy carbon.

The microstructure of glassy carbon is essentially the skeleton of its polymer precursors at low heat treatment temperatures. This material does not readily give lattice images in the transmission electron microscope; also, the positive deviation from the Porod Law in small angle x-ray scattering shows that electron density fluctuations occur in at least some of the carbon matrix [61,62]. As the heat treatment temperature is increased to about 2000°C, ribbons or laths are imaged in the transmission electron microscope, and the Porod law deviation is no longer apparent in small angle x-ray scattering. In wide angle x-ray diffraction, the interplanar spacing associated with the first diffraction maximum remains constant at 3.44 Å, characteristically the spacing associated with the (002) plane in turbostratic carbons, up to a heat treatment temperature of about 2200°C [32,63]. The interplanar spacing slowly decreases with higher heat treatment temperature. The weight loss during heat treatment also saturates at about this temperature [64]. The Hall effect becomes positive at about 1700°C,
also about the lower limit for our negative magnetoresistance models [65]. While the magnitude of the conductivity does not change greatly, the form is slightly altered in that a low temperature correction term characteristic of a one dimensional filamentary skeleton network appears for heat treatment temperatures less than about 2200°C. The two linear conductivity parameters appear to be independent of heat treatment temperature. The range of localization and the mean free path are of the order of 15 Å; they cannot be correlated to either an apparent crystallite size or a pore size which increase monotonically with heat treatment temperature. There does appear to be some inhomogeneities in the material which may be responsible for some of the scatter in the parameters.

The idea of two-phase graphitization of hard carbons is not new. Franklin [66] advanced the idea of two- and three-phase graphitization from detailed x-ray diffraction measurements. Loebner [67] also cited a two phase graphitization scheme, using not only x-ray diffraction data, but electrical resistivity and thermoelectric power data also.

The most important implication that the electrical measurements have on the general view of the microstructure of glassy carbon is that glassy carbon heated at temperatures less than 2200°C has a one dimensional metallic component, as shown by the inverse square root dependence of the low temperature correction term. This view is also supported by evidence from transmission electron microscopy, small angle x-ray scattering, and a saturation of the weight loss during heat
treatment. The disappearance of this one-dimensional component of the microstructure is also demonstrated by the sharp change in the Hall effect and a less marked change in the magnetoresistance.
Conclusions

The following conclusions have been made:

The electrical conductivity of glassy carbon in the heat treatment temperature range 1000 to 2700°C was found to have three empirical components:

- a temperature independent component attributed to the conductivity or transport between extended states and fitting the description for a metal with strong scattering.
- a variable range hopping component, for which the exponential term \( \exp(-\left(\frac{T_0}{T}\right)^{1/4}) \) is constant for all heat treatment temperatures. The power of the temperature in this exponential argument indicates transport in three dimensions.
- a low temperature term that for heat treatment temperatures conduction correction for metallic thin wires or filaments. For higher temperatures, the conductivity decreases to a shallow minimum as the temperature decreases. The nature of the conductivity for temperatures below the minimum remains to be explored.

The Hall effect is temperature insensitive. The results are comparable to other literature values. The Hall coefficient changes signs from negative to positive with increasing heat treatment temperature at about 1700°C and shows a negative maximum at about 1200°C.

The microstructure of glassy carbon has a one dimensional component at low heat treatment temperatures as supported by evidence from the electrical conductivity and also from the transmission electron
microscope and small angle x-ray scattering. The transition from one-dimensional behavior is marked by a change in the sign of the Hall coefficient, and the disappearance of the one dimensional metallic conductivity correction term. The nature of the transition remains unknown as to whether it is simply a coarsening of the filaments or whether a true phase transformation takes place. At higher heat treatments, the "apparent" crystallite size of the turbostratic laths increases, and the increase in negative magnetoresistance is thought to be due to this. This view of the microstructure of glassy carbon as a function of heat treatment temperature is consistent with the consensus literature model.

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44. L. Friedman, Phil. Mag. 38 467-476 (1978).
45. L. Friedman, Phil. Mag. 41 347-50 (1980).


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Figure 1: Electrical conductivity of glassy carbon representative of high A) 2550 and low B) 1200°C heat treatments. The solid lines are calculated by least squares from the empirical equation
\[ \sigma = A + B \exp(CT^{-1/4}) - DT^{-1/2} \]  
(XBL 831-7609)

Figure 2: Hall coefficient of glassy carbon as a function of heat treatment temperature  
(XBL 816-5907A)

Figure 3: The strongly scattering metallic component A of the electrical conductivity of glassy carbon plotted as a function of heat treatment temperature  
(XBL 828-6434)

Figure 4: The prefactor B of the variable range hopping component of the electrical conductivity of glassy carbon as a function of heat treatment temperature  
(XBL 929-6535)

Figure 5: The parameter D of the one dimensional correction to the metallic electrical conductivity component of glassy carbon plotted as a function of heat treatment temperature  
(XBL 828-6436)
Figure 1
Figure 2

HTT = 3 hr

HTT 1000°C as rec'd

Total range for T = 2.8 - 100°C

RH

(cm³ / (Coul.))

1000

2000

3000

XBL816-5907A
Glassy Carbon

\[ \sigma = A + B \exp(-C_0 T^{-1/4} - DT^{-1/2}) \]

Figure 3
Figure 4

Glassy Carbon

\[ \sigma = A + B \exp(-C/T^{1/4}) - DT^{-1/2} \]
Glossy Carbon

\[ \sigma = A + B \exp(-C_0 T^{1/4} - DT^{1/2}) \]

Figure 5
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