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Publication Date
1983-03-01
Materials & Molecular Research Division

Submitted to Philosophical Magazine

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March 1983

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098
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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
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ABSTRACT

The magnetoresistance of glassy carbon heat treated for three hours between 1200 and 2700°C was measured at temperatures from 3 to 100°K in magnetic fields up to 5 tesla.

The magnetoresistance was generally negative and saturated with reciprocal temperature, but still increased as a function of magnetic field. The maximum negative magnetoresistance measured was 2.2% for 2700°C material. Several empirical models based on the idea that negative magnetoresistance is proportional to the square of the magnetic moment were attempted; the best fit was obtained for the simplest model combining Curie and Pauli paramagnetism for heat treatment temperatures greater than 1600°C. The proportionality parameters increased approximately linearly with heat treatment temperature. Positive magnetoresistance was found only in less than 1600°C treated glassy carbon for low measurement temperatures.
§1. INTRODUCTION

Magnetoresistance is the relative change of resistance with magnetic field. Approaches to explain the phenomenon usually emphasize the effect of magnetic field on either the carrier mobility or the number of carriers.

Negative magnetoresistance has always been associated with disorder and crystal defects, chiefly because it is never found in highly ordered nearly defect free materials. It is impossible in single carrier systems, but appears in some amorphous semiconductors, heavily doped semiconductors, and chalogenide glasses (Mott and Davis 1979).

Negative magnetoresistance has been observed in many defective and disordered graphitizable carbons, mostly as a low temperature (liquid helium) phenomenon, and is a complicated function of the magnetic field (Spain 1981, Delhaes 1971, Delhaes, De Kepper, and Ulrich 1974). Magnetoresistance data from single crystal graphite is always positive and has been used extensively to measure the band parameters of the Slonczewski-Weiss band model, mostly through oscillations with magnetic field called the Shubnikov-de Haas effect (Spain 1973).

Glassy carbon is a prototypical nongraphitizable carbon. For a systematic set of heat treatment temperatures (HTT) greater than 1000°C, Yamaguchi (1963) found that its magnetoresistance is negative at 20 K, 77 K, and 300 K. Saxena and Bragg (1977) made measurements of the negative magnetoresistance $-\Delta \rho/\rho$ over a continuous range of temperatures $T$ above 10 K with a maximum magnetic field $H$ of 5 tesla. They
found a "knee" in the curve of $|\Delta \rho/\rho|^{1/2}$ vs $H/T^{1/2}$. The question of whether the negative magnetoresistance reached an asymptotic value or that merely a new smaller slope was established for higher fields and/or lower temperatures was unanswered. This paper better establishes the behavior of the magnetoresistance as a function of $HHT$ between 1000°C and 2700°C at temperatures as low as 3 K.
§2. 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°C 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 ranging from 3 K to 100 K and with magnetic fields up to five tesla.
§3. RESULTS

The magnetoresistance of glassy carbon is usually negative; in this work only at low temperatures for heat treatment temperatures less than 1600°C was positive magnetoresistance observed as also found by Hishiyama, Kaburagi, and Ono (1979) as also shown in Figure 1. The critical temperature at which the magnetoresistance goes from positive to negative is a function of heat treatment temperature, and is approximately 16°K, 10°K, and 8°K for heat treatment temperatures of 1000°C, 1200°C, and 1400°C, respectively. The negative magnetoresistance increases monotonically with increasing magnetic field and higher heat treatment temperatures, as also was observed by Yamaguchi (1963) and Saxena and Bragg (1977), but is observed to saturate with reciprocal measurement temperature (Figures 2 and 3). The largest absolute value measured was -2.2% for 2700°C heat treated glassy carbon with an uncertainty of 0.01%.

The only well worked out theory to describe this phenomenon for many years was Toyozawa's (1962) theory which explained the negative magnetoresistance in dilute metal alloys with ferromagnetic impurities by a spin interaction mechanism. This mechanism predicts that the negative magnetoresistance is proportional to the square of the total magnetic moment. Some moment models have been tested against the data.

The first model tried in an attempt to explain these data was a paramagnetic moment model based on the fact that glassy carbon contains both localized and extended states which would be expected to have
Curie and Pauli moments respectively. Thus the square root of the absolute value of the magnetoresistance has been fitted to a term proportional to a Brillouin function with spin 1/2 and a term independent of temperature and linear in magnetic field. These proportionality parameters are plotted as a function of heat treatment temperature in Figures 4 and 5. They are roughly described as linearly increasing with this parameter. The model fits well at the highest heat treatment temperatures, but less well at intermediate values (Figure 6 and 7).

There are some questions concerning the validity of this analysis. Firstly, even though the effective number of Bohr magnetons remains the same for heat treatment temperatures greater than 1600°C, the lower limit of the model, this number is much too large (6.2±0.1) for single carbon atoms. This result is similar to that found in other studies using this idea, such as in doped Ge, InAs, and GaAs (Hedgcock 1967). Large moments such as these have also been found in dilute ferromagnetic impurities in palladium determined through electron paramagnetic resonance (EPR) (Shaltiel, Wernich, Williams, and Peter 1964) and cold neutron scattering (Low and Holden 1966) and have been interpreted as long range polarization or localization of the palladium atoms surrounding the impurity.

Another problem with the Curie/Pauli model is that graphite and most carbons have temperature dependent diamagnetic magnetic susceptibilities. Diamagnetism in graphite is anisotropic (Ganguli and Krishnan 1941); in fact the degree of anisotropy in carbon materials
has been used as a reliable measure of graphitization (Pacault 1974, Pacault and Marchand 1957). Simply put, the diamagnetism of graphite consists of two components; a small ($= -0.4 \times 10^{-6}$ emu/g) isotropic part due to the ion cores: and a c-axis part inversely proportional to temperature and sensitive to crystallite sizes less than about 150 Å. This latter part is attributed to London diamagnetism associated with the ring structure of graphite and free electron Peierls diamagnetism (Fischbach 1961). The theory of diamagnetism in bulk single crystal graphite has been addressed by McClure (1960, 1956). Recent developments have produced a theory applicable to both sheet (Volpilhac and Hoarau 1978, Hoarau and Volpilhac 1976) and corrugated ribbons of graphite (McClure and Hickam 1982) which make up the microstructure of carbon fibers. Though the geometrical model assumptions may be adjusted to better match the microstructure of glassy carbon, the exact calculations themselves are not trivial. However, because the negative magnetoresistance is so well behaved, a moment model proportional to the square of the theoretical diamagnetic moment could be anticipated to compare about as well as do the experimental ribbon and sheet diamagnetic moments to theory.

The only reported magnetic susceptibility measurements of glassy carbon heat treated in the range of interest were done by Fischbach (1967) and were used as a measure of the degree of preferential alignment of the laths after high temperature (1600-2900°C) tensile tests. He reported the diamagnetic susceptibility of his starting
materials as $\chi_T = -9 \times 10^{-6}$ emu/g for a heat treatment temperature of 2000°C and $\chi_T = -16 \times 10^{-6}$ emu/g for 3000°C, where $\chi_T$ is one third of the trace of the magnetic susceptibility tensor. He implied linear interpolation of the magnetic susceptibility between these two extremes.

Paramagnetic moments have been measured in a glassy carbon precursor (Omori and Yajima 1979) heat treated at temperatures less than 800°C. The effective number of Bohr magnetons measured was 6.6, comparable to the number derived from the present magnetoresistance measurements, but it is unknown whether this is due to impurities (iron) intentionally introduced in solution in the carbon matrix or to the carbon itself. Paramagnetic moments have been found in a number of carbons (Smith and Sarachik 1980, Carmona, Delhaes, Thalence and Lasjolias 1977, Szczurek 1977), but usually in those heat treated at temperatures less than 1500°C, leading to the conclusion or at least strong implication that paramagnetism due to unpaired electrons, free organic radicals, and other defects is annealed out at higher temperatures.

Recently a magnetic moment model having the same characteristics as the square root absolute magnetoresistance data was published by Kobayashi, Fukagawa, Ikehata and Sasaki (1978). It was developed to describe the magnetization of silicon atoms in heavily phosphorus doped silicon. The total magnetization moment is given as follows:

$$M = \frac{N(0) \mu_B \sinh X}{\beta Z} \ln \left( \frac{\cosh X + Z}{\cosh X - Z} \right)$$

(1)
where $X = \beta g \mu_B H$

$\beta = (kT)^{-1}, \ T = \text{temperature}, \ k = \text{Boltzman's Constant}$

$\mu_B = \text{Bohr magneton}$

$g = \text{effective moment Bohr magnetons}$

$H = \text{magnetic field induction}$

$Z = (\cosh^2 X - p)^{1/2}$

$p = e^{-U/T}$

$U = \text{intra-state correlation energy}/k$

This moment model behaves very similarly to the Curie-Pauli model. If the intra-state correlation energy is zero, the moment magnetism behaves like Pauli paramagnetism. If the intra-state correlation energy is nonzero, at high magnetic fields the moment shows Curie-like behaviour, saturating with inverse temperature. The model was fitted to the present data; the proportionality parameter $Q$ and intra-state correlation energy $U$ are plotted in Figures 8 and 9 as functions of heat treatment temperature where

$$Q = \frac{N(O) \mu_B \sinh X}{\beta Z} \ ; \ M = Q \ln \left( \frac{\cosh X + Z}{\cosh X - Z} \right) \quad (2)$$

and where $g$ has been found to be independent of heat treatment temperature and nearly the same as in the Curie-Pauli model. The linear parameter $Q$ increases with heat treatment temperature as did the other linear parameters in the Curie-Weiss model above. However, $U$ increases with heat treatment temperature until $2200^\circ C$ where it appears to reach
a plateau. The fit of this model compared with the Curie-Pauli model is only slightly inferior, and, as with the Curie-Pauli model, is worse at intermediate heat treatment temperatures.

Saxena and Bragg (1977) found that the square root of the absolute value of the negative magneto resistance is linear with the magnetic field divided by the square root of the temperature for lower values for this parameter. Bright (1979) has used this data in this way to support his model of overlapping localized and extended states for negative magneto resistance in pregraphitic carbons. He assumes that the broadening of the Landau levels is Gaussian, and that the standard deviation of the broadening distribution is proportional to the zero-field carrier drift mobility. This model predicts that near equilibrium (low fields less than 1.5 tesla), the negative magneto resistance is proportional to \( \mu^4 H^2 \), where \( \mu \) is the drift mobility and \( H \) is magnetic field, and thus that the drift mobility is proportional to the inverse fourth root of temperature. The proportionality constant is plotted as a function of heat treatment temperature in Figure 10. It increases roughly linearly with temperature. This model, as with the previous models introduced, fits increasingly worse for decreasing temperatures (Figures 11 and 12). Furthermore, the Hall mobility (Baker and Bragg 1983), while not necessarily the carrier mobility, is nearly independent of measurement temperature and does not have a definite inverse fourth root temperature dependence.
Other theories of negative magnetoresistance exist. One approach is that the magnetic field aligns the spins of a disordered material, eliminating scattering centers and thus increasing the effective mobility (Movaghar and Schweitzer 1977). Another approach is that localized carriers with low mobilities are induced from an impurity band into the conduction band where the mobility is higher, thus effectively increasing the number of carriers and the conductivity (Giovannini and Hedgcock 1972, Fukuyama and Yosida 1979, Kawabata 1980). Most of these theories have been developed for application to specific materials (semiconductors) and for limiting cases of low fields. None seem to fit the present data as well as the moment models.

Positive magnetoresistance was observed for heat treatment temperatures less than 1600°C and for temperatures less than 20 K in glassy carbon. The temperature at which the magnetoresistance goes from negative to positive decreases as the heat treatment temperature increases.

The classical case of positive magnetoresistance (Wilson 1953) is applicable to metals, semiconductors, and other materials where a band model has been used to successfully describe the electronic structure. The magnetoresistance is given by

\[
\frac{\Delta \rho}{\rho} = \frac{a}{b} \left( \frac{b + 1}{a + b} \right)^2 \frac{\nu_h^2}{\nu_h^2} \frac{H^2}{1 + \left( \frac{a - b}{a + b} \right)^2 \nu_h^2 H^2} = c' H^2
\]
for small fields such that $\nu_h^2 H^2 \ll 1$.

\[ a = \frac{n_e}{n_h}, \text{ the ratio of carrier concentrations} \]
\[ b = \frac{\nu_h}{\nu_e}, \text{ the ratio of carrier inabilities} \]

Considering that the negative magnetoresistance dominates at high temperatures, the positive magnetoresistance must disappear with increasing temperature, which implies that the mobility is inversely proportional to temperature. A positive component was added to the present empirical Curie/Pauli model describing the negative magnetoresistance in high temperature glassy carbon in an attempt to produce an empirical model for the whole range of heat treatment temperatures. This was unsuccessful.

One of the components of the electrical conductivity of glassy carbon is variable range hopping (Baker and Bragg 1983, Saxena and Bragg 1978a). Magnetoresistance for hopping conduction between localized states without interaction with extended states is positive and highly sensitive to magnetic field (Shklovskii and Lien 1978) at least for low fields as

\[ \frac{\Delta \rho}{\rho} \propto \exp H^2 \]  \tag{4}

Hishiyama et al (1979) considers this mechanism as responsible for positive magnetoresistance observed at low temperatures for low temperature heat treated glassy carbon. Examination of Figure 1 shows that the above is not an adequate description of the experimental behaviour of the positive magnetoresistance observed in glassy carbon.
Of the models discussed above, the moment models for negative magnetoresistance fit the full range of data for high temperature heat treated glassy carbon best. Unfortunately they are also the most ambiguous in that the proportionality constant linking the negative magnetoresistance to the square of the moment is unknown but is expected to be a function of the density of states. Even the sign of the magnetic moment remains ambiguous. Any positive component of the magnetoresistance in these high heat treatment temperature glassy carbons is small and not easily separable, and was ignored.

Consider that negative magnetoresistance is due to the interaction of localized and extended states as influenced by a magnetic field and that the positive magnetoresistance observed is due to interaction between only localized states. It appears then that the interaction of localized states decreases with heat treatment temperature, most likely due to the annealing out of localized states. At high heat treatment temperature, the interaction increases as the heat treatment temperature is raised.

This view is supported by the electron spin resonance data of Orzeszko and Yang (1974) except in the transition range where the Hall effect changes signs. Apparently, negative magnetoresistance is inversely proportional in some way to the density of states, even though the moment model predicts that it should also be proportional to the square of the number of spins.
Recently, Hishiyama, Kaburagi, Ono, Inagaki, and Kamiya (1980) made the observation that negative magnetoresistance is characteristic of turbostratic carbon as opposed to positive magnetoresistance in graphitic carbon, and that this negative magnetoresistance is proportional to apparent crystallite size along the c-axis or [002] direction, an idea used earlier by Kawamura and Tsuzuku (1974) in their study of porosity and graphitization of glassy carbons. Saxena and Bragg (1978b) have measured an activation of energy of 215 40 kcal/mole for the coarsening of the turbostratic laths in glassy carbon by means of x-ray diffraction. This activation energy compares favorably with the activation energy for graphitization in other carbons (Fischbach 1971). Thus for a systematic set of heat treatment times at high temperatures, glassy carbon magnetoresistance data should yield a similar activation energy.
§4. CONCLUSIONS

We conclude that negative magnetoresistance in high temperature heat treated glassy carbon saturates with reciprocal temperature but not with magnetic field for fields less than five tesla. Several models based on an interpretation in terms of temperature dependent magnetic susceptibility provide plausible explanations for this behavior but none could be confirmed as correct. Positive magnetoresistance found at low observation temperature in low temperature heat treated glassy carbon remains unexplained.
ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.
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Figure 1

HTT1200-3

MAGNETORESISTANCE

A: T = 3.4 K  E: T = 20. K
B: T = 4.6 K  F: T = 50. K
C: T = 6.4 K  G: T = 100. K
D: T = 10.2 K

H**2 (TESLA)**2

XBL 829-11525
Figure 2
Figure 3
Glassy Carbon

$\left| \frac{\Delta \rho}{\rho} \right|^{1/2} = X H + \frac{\Gamma}{H} \tanh \left( \alpha_0 \frac{H}{T} \right)$

Figure 4
Glassy Carbon

\[ |\Delta \rho / \rho|^{1/2} = X H + \Gamma \tanh(\alpha H / T) \]

Figure 5
Figure 6
Figure 7
\[ \left| - \frac{\Delta \rho}{\rho} \right|^{1/2} = \beta \frac{H}{T^{1/2}} \]
Figure 11
Figure 12
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