Magnetoresistance of Graphite Fibers
II. Experimental

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Abstract. An experimental study to clarify the theoretical basis of negative magnetoresistance, $-\delta\rho(H)/\rho(0)$, observed in graphite fibers is carried out. The curves of $-\delta\rho(.5T)/\rho(0)$ at 4.2 K and 77 K versus L_a (the crystallite size) both show a maximum for a crystallite size of $\sim$ 900Å. Thus Bright's theoretical prediction that negative magnetoresistance at low magnetic fields H (H <1.4 T) is related to the degree of two–dimensional in-plane ordering is supported by our result.

Introduction

Partially graphitized carbon fibers often exhibit negative magnetoresistance in the liquid helium temperature range.[1] Numerous attempts have been made to explain this phenomenum and a number of theories have been proposed for the negative magnetoresistance.[1,2] The two–dimensional quantized Landau level theory of Bright appears best to account for the observed behavior of negative magnetoresistance at low magnetic fields H (H<1.4T).[1,3]

A brief summary of the Bright theory is given by Sugihara and Dresselhaus.[3] The increase of the density of states and carrier concentration with magnetic field results in negative magnetoresistance.

The parameters of the Bright theory are directly related to the structural parameters of the material under investigation. Consequently, a negative magnetoresistance at low magnetic field should be sensitive to the structure of the fiber and so should provide information about the evolution of the fiber structure from a disordered to the graphitic state as the processing temperature is increased. On the other hand, it is known[4] that for pre–graphitic fibers the ratio of the intensity of the disorder induced Raman line at 1355 cm^{-1} to the Raman allowed line at 1580 cm^{-1}, I(1355)/I(1580) is related to the crystallite size L_a. Values of L_a give the degree of in–plane order in the structure of the fiber. In view of this direct measurement of in–plane order, a way of evaluating Bright's theory is by examining the relation between the negative magnetoresistance and the crystallite size L_a.

Experimental Details

In the work reported here magnetoresistance measurements are made on methane derived fibers using a dc four–probe technique. Contacts were made with silver paint and the fiber was mounted on a mica substrate. A magnetic field up to 9T was generated with a superconducting magnet. Samples were mounted in a Janis cryostat for measurements at 77K and 4.2K.

Raman microprobe spectroscopy measurement was carried out on the same sample as the magnetoresistance measurements. The experimental procedure for the Raman analysis has been described in detail elsewhere.[5] Briefly a Raman microprobe was used in conjunction with an Argon laser (wavelength=4880 Å) and a Tracor TN–1710 diode array detector and signal analyzer to measure Raman lines at 1355.0 cm^{-1} and 1580.0 cm^{-1}. The spectra were analyzed and the relative intensities were measured and compared with the calibration curves of Tuinstra and Koenig.[4]

Results and Discussion

Results for the transverse magnetoresistance at 4.2K and at 77K of carbon fibers heat treated at different temperatures are shown in Fig. 1(a) and (b), respectively. The results show that the negative magnetoresistance effect is most pronounced for fibers heat treated at temperature T_{HT}^c. Below and above T_{HT}^c the negative magnetoresistance decreases. In our samples T_{HT}^c=2200°C and 2067°C when the measurements are carried out at 4.2 K and 77 K, respectively.

This is consistent with Bright's theory which predicts that the negative magnetoresistance is connected to the degree of the two–dimensional in–plane graphitization of the fiber structure. When this two–dimensional ordering is reduced, the negative magnetoresistance decreases, and when interplane correlation and three–dimensional ordering are established the negative magnetoresistance again decreases. On the other hand, as the heat treatment is increased, the fiber structure goes from disordered to two–dimensional in–plane ordering and finally to three–dimensional inter–layer ordering. Therefore for the range of T_{HT} where the fiber structure is developing from disordered to two–dimensional ordering, the negative magnetoresistance will increase. However for the range of T_{HT} where the fiber structure is evolving from two–dimensional to three–dimensional ordering, the negative magnetoresistance will decrease. Consequently the negative magnetoresistance will be a maximum at T_{HT}^c.

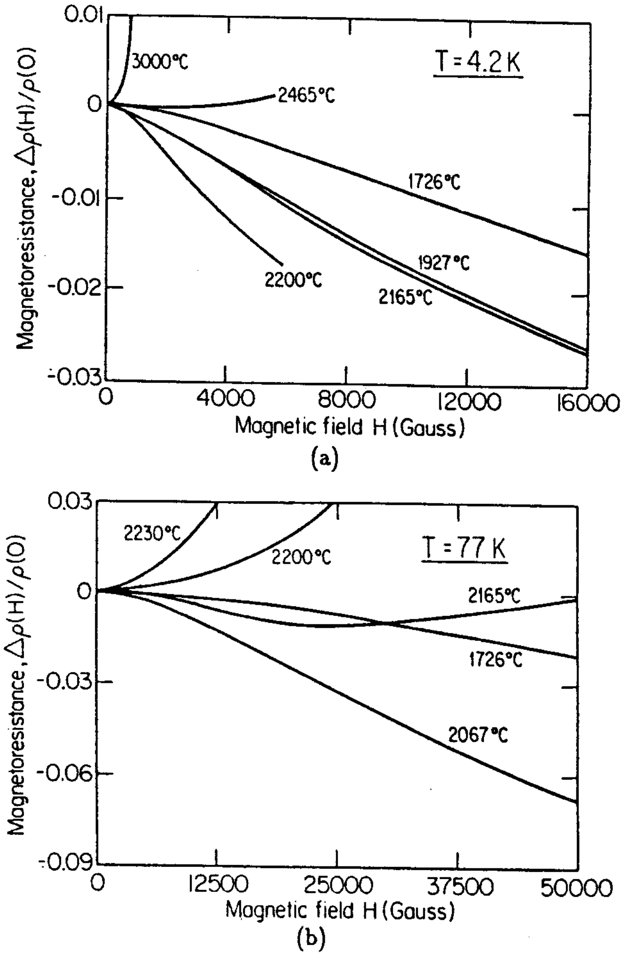

Figure 1: Magnetoresistance, $\Delta\rho(H)/\rho(0)$ vs. H, measured at (a) 4.2 K and (b) 77 K for carbon fibers with various heat treatments.

To demonstrate that as T_{HT} is increased the fiber structure develops increasing degrees of order, Raman spectroscopy measurements are done on the individual fibers with the Raman microprobe. The results of an analysis of these data are summarized in Table 1.

Table 1: In-plane crystallite sizes as determined from Raman Microprobe studies.

Heat treatment T_{HT} (°C)	Crystallite size L_a(Å)
1726	110
1927	310
2067	380
2165	930
2200	950
2465	1270
3000	>2000

In Fig. 2 L_a is plotted versus magnetoresistance at a fixed magnetic field H of 0.5 T. At both measurement temperatures of 77 K and 4.2 K the curves show a peak confirming the prediction of the Bright theory. Note that T_{HT}^c depends on the temperature at which the magnetoresistance measurement is carried out. This means that the temperature of the fiber also affects the optimal conditions for negative magnetoresistance. In addition, note that

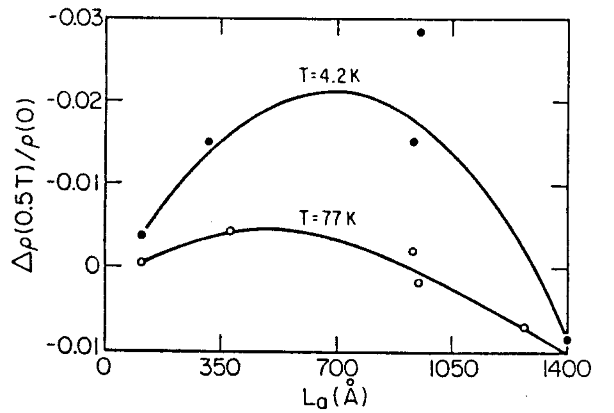

Figure 2: Magnetoresistance, $\Delta\rho(H)/\rho(0)$, measured at H = 0.5 T vs. crystallite size L_a for carbon fibers. The curves are given as a guide to the eye.

for the same T_{HT}, the negative magnetoresistance is greater at 4.2 K. Both these observations are in accordance with Bright's theory.

It is interesting that our results at 77 K as shown in Fig. 1(b) reveal a large negative magnetoresistance even at high magnetic fields ($H \sim 5$ T). Usually the pre-graphitic carbons show a negative magnetoresistance in the weak field region H < 1.4 T, and with further increase of the field intensity, the magnetoresistance becomes positive.[6] On the basis of the Bright theory the high field (5 T) result can be explained as follows. If an average relaxation time at 77K is $\sim 10^{-14}$ sec., a condition of $(\omega_c\tau)^2 < 1$ is realized for H = 5 T, when $m^* = 0.04m_0$ is inserted. An excess density of states N_0 for the $n = 0$ Landau level of 5×10^{18} to $2 \times 10^{19}/cm^{-3}$ occurs due to a small three-dimensional ordering. The density of states in each two-dimensional Landau level is given by $g=4s/\pi c_0$, where $s = eH/\hbar c$ and c_0=3.354Å. Inserting H = 5 T into g, we obtain $g = 5.62\times10^{19}/cm^{-3}$ which is larger than the value of N_0 employed by Bright.[1] Accordingly, in the 5 T range an increase of electron and hole concentration with H is more pronounced than in the weak magnetic field region.

In conclusion, our magnetoresistance data confirms the prediction of Bright's theory that negative magnetoresistance for H<1.4T is related to the degree of two-dimensional in-plane ordering.

Acknowledgments

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