Diamagnetic Susceptibility of Pyrolytic Graphite*

D. B. FISCHBACH

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

The diamagnetic susceptibilities of some pyrolytic graphites deposited at 2100–2300°C have been measured at room temperature. As-deposited samples had significantly larger susceptibilities than that of well-graphitized carbons or single-crystal graphite. Heat treatment at temperatures above 2300°C caused the total susceptibility to decrease to a minimum value, then rise and level out at a value characteristic of graphite, as a function of treatment temperature. The relationship of the susceptibility behavior to the structure of the pyrolytic graphite is discussed.

THE magnetic susceptibility of graphite is large, diamagnetic, and very anisotropic. Diamagnetism is a property of the benzene-ring structure of carbon atoms and the anisotropy is consistent with the crystal structure, but the magnitude of the susceptibility has, until recently, posed a theoretical problem.[1] It is the purpose of this note to report on some new measurements which show: (1) that the diamagnetic susceptibility of certain oriented carbons (pyrolytic graphites) is significantly larger than that of single-crystal graphite, and (2) that the susceptibility of these carbons goes through a minimum as a function of heat-treatment temperature and finally approaches that of graphite.

Measurements were made by the Faraday method calibrated against platinum as a standard. Correction for ferromagnetic impurities was made by the Owen-Honda method, using field strengths of 6000 to 15 000 oe. The absolute values of the susceptibilities are believed to be accurate to ±3%, but the relative precision is better than that. All values are reported in units of (-10^{-6}) cgs units per gram. The measurements were made at room temperature on samples from three slabs of pyrolytic carbon obtained from two sources. This material was made by decomposition of a dilute hydrocarbon gas on a graphite substrate heated to 2100–2300°C. Heat treatments were carried out in graphite furnaces in an inert-gas atmosphere. The susceptibility was measured perpendicular $(X_\perp)$ and parallel $(X_\parallel)$ to the plane of the deposit. Within experimental error, $X_\parallel$ was isotropic in this plane. Because the pyrolytic carbon has a high degree of preferred orientation, $X_\perp$ and $X_\parallel$ correspond approximately to measurements perpendicular and parallel, respectively, to the (0001) crystallographic planes. The total susceptibility,[2] $X_T = X_\perp + 2X_\parallel$ (the spur of the tensor) has also been computed from these data.

The room temperature susceptibility values for the three carbons (A, B, and C) after various heat treatments are given in Table I. The values for natural single crystals reported by Krishnan and Ganguli[3] and Poquet *et al.*[4] are also shown. With heat treatment, no change occurs until the temperature exceeds 2300°C. Then both X_T and $X_\perp$ decrease to a minimum value near 2900°C and level out again at temperatures above about 3200°C. The results for X_T are shown in Fig. 1. $X_\parallel$ decreases monotonically in the same temperature range and approaches the single-crystal value after treatment at temperatures of 3200°C and above. It is interesting to note that despite appreciable differences in anisotropy, which persist throughout the heat treatment, and despite probable differences in manufacturing technique the values for materials A and B fall on the same curve in Fig. 1. The as-deposited and 3400°C values for material C also fall on this curve, but the minimum (not shown) for C occurs about 200°C lower than that for A and B.

The total susceptibility of the as-deposited carbons is appreciably larger than the value for single crystal graphite or well-graphitized petroleum carbons (20.5–21.2).[2] It is well known that the susceptibility of
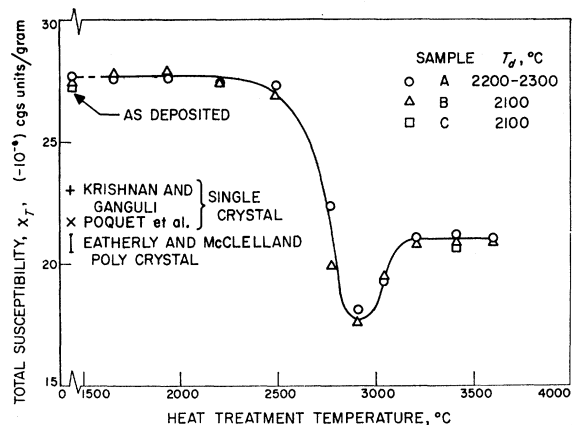

FIG. 1. The total diamagnetic susceptibility (at room temperature) of three pyrolytic carbons (A, B and C), deposited at temperatures T_d, as a function of heat treatment temperature. Values for single-crystal and polycrystalline graphites are also shown for comparison.

[1] J. W. McClure, Phys. Rev. **119**, 606 (1960); *Proceedings of the Fourth Conference on Carbon, 1959* (Pergamon Press, New York, 1960), p. 177.

[2] W. P. Eatherly and J. D. McClelland, Phys. Rev. **89**, 661 (1953).

[3] K. S. Krishnan and N. Ganguli, Nature **139**, 155 (1937); Z. Krist. **A100**, 530 (1939).

[4] E. Poquet, N. Lumbroso, J. Hoarau, A. Marchand, A. Pacault, and D. E. Soule, J. chim. phys. **57**, 866 (1960).

TABLE I. Room-temperature magnetic susceptibility values for pyrolytic carbons
and single-crystal graphites in units of (-10^{-6}) cgs units/gram.

Sample	Total χ_T	Perpendicular to deposit $\chi_\perp$	Parallel to deposit $\chi_{\parallel}$	Anisotropy ratio $\chi_\perp/\chi_{\parallel}$
As-deposited:				
A (deposited at 2200–2300°C)	27.6	23.4	2.1	11
B (deposited at 2100°C)	27.6	21.8	2.9	7
C (deposited at 2100°C)	27.3	21.6	2.8	8
After heating to 2900°C:				
A	18.1	16.2	0.9	17
B	18.3	15.7	1.3	11
C	20.0	17.8	1.1	16
After heating to 3400°C:				
A	21.2	20.2	0.5	40
B	21.0	19.0	1.0	19
C	20.7	19.0	0.8	24
Natural single-crystal graphite				
Krishnan and Ganguli[3]	23.0	22.0	0.5	44
Poquet et al.[4]	21.7	21.0	0.3	65

partially graphitized carbons increases with the crystallite layer plane diameter up to sizes of 100–150 A and is constant thereafter.[5,6] Generally, the proportion of material in which the stacking sequence is correct also increases with crystallite size. Available evidence (our own[7] and others[8,9]) indicates that the crystallite size of as-deposited pyrolytic carbons similar to those used here is greater than 100 A, but the density of stacking faults is very high (i.e., it is turbostratic). This combination of conditions is believed responsible for the large susceptibility of these materials. Both the larger interlayer spacing and the changed interlayer interactions in the turbostratic material may be expected to alter the band structure.

On heat treatment in the range 2400–3400°C, pyrolytic carbon "recrystallizes" with extensive changes in many physical properties. X-ray diffraction analysis indicates that stacking faults are largely eliminated and the degree of preferred orientation increased during this process. The increase of preferred orientation is evident in the decrease of $\chi_{\parallel}$ and the increase in $\chi_\perp/\chi_{\parallel}$. The susceptibility minimum is apparently associated only with the elimination of stacking faults since it is not sensitive to preferred orientation differences. The

minimum could result either from changes in band structure or from electron trapping during the transition from highly faulted to nearly perfect graphite. The susceptibility of the well-graphitized pyrolytic carbon (after heating to 3200–3600°C) is in general agreement with the recent results of Poquet et al. on purified natural single crystals. The higher values obtained by Krishnan and Ganguli might have resulted from impurities or damage to their crystals either during formation or extraction.

The results discussed above apply in detail only to pyrolytic carbons deposited at 2100–2300°C. There is abundant evidence[8–10] that the as-deposited structure of pyrolytic carbons and their response to heat treatment depends strongly on deposition temperature. Preliminary results on materials deposited at 1900–2000°C indicate χ_T values in the range 19.3–20.7 and the minimum is either small or absent, in general agreement with results of Soule.[11]

[5] H. T. Pinnick, Phys. Rev. 94, 319 (1954).
[6] A. F. Adamson and H. E. Blayden, Industrial Carbon and Graphite (Society of Chemical Industry, London, 1958), p. 28.
[7] W. V. Kotlensky (unpublished).
[8] A. R. G. Brown and W. Watt, Industrial Carbon and Graphite (Society of Chemical Industry, London, 1958), p. 86.
[9] O. J. Guentert and C. T. Prewitt, Bull. Am. Phys. Soc. 5, 187 (1960) and private communication.
[10] E. G. Steward and B. P. Cook, Z. Krist. 114, 245 (1960).
[11] David E. Soule (private communication).