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Technical Report 32-1208

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Abstract

Structure-dependent sources of the variation in diamagnetic susceptibility values and responses to heat treatment among different graphitizing carbons are investigated in pyrolytic carbons Two microstructural parameters, the apparent crystallite layer diameter L_a and the interlayer spacing d, are shown to be important. The total diamagnetic susceptibility χ_T, which is independent of anisotropy, increases with L_a, rapidly in the range below 200 Å and more slowly at higher L_a values. The value χ_T also decreases with decreasing d (increasing layer-stacking order). It is shown that these two types of structure dependence can account, at least qualitatively, for much of the magnetic behavior observed in pyrolytic and other graphitizing carbons Also discussed is the relationship of the electronic structure to the microstructure, which is the source of the observed structure sensitivity. The high susceptibility values of disordered pyrolytic carbons are in excellent agreement with theoretical predictions of the influence of interlayer interactions on the electronic structure. It is concluded that this is the primary source of the observed d dependence. The source of the dependence on L_a is not as well understood.

Structure Dependence of the Diamagnetism of Graphitizing Carbons

I. Introduction

Characteristically, pure carbons are diamagnetic. However, a very broad range of susceptibility values may be observed, and there is great variety in the response of the susceptibility to high-temperature heat treatment, especially among graphitizing carbons of different origins and preparation methods. If the carbons are pure, all of this magnetic behavior must result from influences of the structure of the carbon on its magnetic properties. Graphite, with a hexagonal-layer structure, is the equilibrium crystallographic form of carbon. The small crystallites of disordered graphitizing carbons have a similar structure, except that there is no long-range order in the stacking sequence of the basal-layer planes (turbostratic structure).

It is well known that the diamagnetism of graphite is highly anisotropic and consists essentially of two components. The ion cores contribute an isotropic susceptibility χ_i amounting to about 0.3[1] for any measurement field orientation. The conduction electrons in the basal planes contribute a strongly anisotropic susceptibility χ_e, measured with the field perpendicular to the basal planes, amounting to about 21 in very well-graphitized material. This susceptibility is predominantly of the Landau–Peierls type and depends on the fact that the Fermi level is located in a region of the band where the density of states changes rapidly with energy. Therefore, small changes in band shape or the position of the Fermi level have a strong effect on the anisotropic susceptibility. This is the primary source of the structure sensitivity of the magnetic behavior of graphitizing carbons, which resides almost entirely in the anisotropic component. The ion-core properties would not be expected to be very sensitive to the microstructure of the solid and, in any case, the contribution which they make to the total susceptibility is quite small.

It has been recognized for some time that the magnetic properties of carbons are quite structure-dependent (see Ref. 1). While no claim is made for a definitive bibliography, some representative references may be noted. The importance of the apparent crystallite layer diameter L_a appears to have the longest history of study in pure carbons (Refs. 2–4). More recently, the importance of layer-stacking order and interlayer spacing d have been observed experimentally (Refs. 5–14) and treated theoretically (Refs. 15–19).[2] The interlayer spacing and the degree of layer-stacking order are closely

[1] Susceptibility values are expressed in units of -10^{-6} emu/g throughout this report.

[2] Also in private communication with J. W. McClure

related, d varying continuously from 3.354 to $\geq$ 3.44 Å as the stacking disorder varies from zero for perfect graphite to the completely disordered turbostratic case. The characteristics of the temperature dependence of the diamagnetism also depend on the structure (Refs. 20 and 21). Nevertheless, both experimental evidence for and theoretical interpretation of the interaction between microstructure and magnetic susceptibility are still incomplete.

Most of the recent advances in understanding the structure sensitivity have resulted from studies on pyrolytic carbons. This paper presents additional experimental evidence for the dependence of the diamagnetism of pyrolytic carbons on L_a and d. It will be shown that much of the variety of magnetic behavior observed in graphitizing carbons can be understood in terms of the variation of the diamagnetism with these two structural parameters. The results presented here deal primarily with pyrolytic carbons for two reasons: They offer a range of structural variation not easily realized in more conventional synthetic or natural carbons and graphites, and they are quite pure (Refs. 22 and 23). The latter property is important because impurities can also strongly affect the magnetic behavior. It seems reasonable to expect that the structure sensitivity of other varieties of graphitizing carbons is similar to that in pyrolytic carbons, and some evidence will be offered in support of this assumption. No consideration is given here to the structure sensitivity of the temperature dependence or the anisotropy of the diamagnetism. Only room temperature values of the total susceptibility are reported. The total susceptibility is the trace of the susceptibility tensor and is, therefore, independent of anisotropy. Preliminary accounts of some of these results have been presented elsewhere (Refs. 7, 8, and 23).

II. Experimental Materials and Techniques

Susceptibility measurements were made on a number of pyrolytic carbons obtained from several commercial and private sources. All were deposited essentially isothermally in hot-wall furnaces from methane and most had substrate nucleated microstructures. Deposition temperatures varied from 1600 to 2400°C. This range of deposition temperatures (and variations in other deposition parameters) provided a broad range of initial disordered structures. These structures were progressively changed toward that of graphite by isothermal and isochronal heat treatments at temperatures up to 3200°C in an inert gas atmosphere.

The X-ray structures of the carbons were determined by standard Debye-Scherrer powder diffraction techniques using Cu $K\alpha$ radiation. For all but well-graphitized samples, the diffraction pattern of diamond was superimposed on that of the sample carbon to provide back reflection lines for correction of film dimension changes in processing. The interlayer spacing $d = c/2$ was determined from the position of peak intensity of the (004) diffraction line. Approximate L_a values were calculated from the displacement of the (10) or (11) maxima from the graphite positions by using the formula of Warren (Ref. 24). The films were read visually. For the detailed investigation of the dependence of susceptibility on L_a, a special series of samples was employed.[3] On these samples, accurate L_a values had been determined by a rigorous Fourier analysis technique by Guentert (Ref. 25).

The magnetic susceptibility values were measured at room temperature by the Faraday technique, using apparatus described elsewhere (Refs. 5 and 6). Calibrations by an absolute technique, using a rotating coil gaussmeter and by a comparison technique using pure silver[4] as a standard, gave results in good agreement. The carbon susceptibility samples were cut in the form of cubes approximately 3–4 mm on a side or (for thinner pyrolytic deposits) plates 4–8 mm on a side. Measurements were made with the deposition plane of the deposit oriented perpendicular ($\chi_\perp$) or parallel ($\chi_\parallel$) to the magnetic field. The total susceptibility χ_T is given by the sum of the susceptibility values measured in three orthogonal directions (Ref. 27)

$$\chi_T = \chi_\perp + 2\chi_\parallel = \chi_c + 2\chi_a + \Delta\chi = \chi_c + 3\chi_i + \Delta\chi$$

because pyrolytic carbons are isotropic in the plane of the deposit. The values χ_c and χ_a are the principal susceptibilities of the crystallites measured respectively parallel and normal to the c-axis. The small correction term $\Delta\chi$ (usually negative) is inserted to account for possible contributions by "disorganized" carbon which is not incorporated into the graphitic lattice. Because of the high purity of pyrolytic carbons, there is no reason to expect any field-strength dependence of the diamagnetism, such as results from ferromagnetic impurity.

[3]Provided by O. J. Guentert, Research Division, Raytheon Company.

[4]From the same stock used for calibration by D. E. Soule, C. W. Nezbeda, and A. W. Czandera (Ref. 26) and supplied by Mr. Nezbeda, Parma Technical Center, Union Carbide Corp.

Measurements here (Ref. 6) and elsewhere (Ref. 13) have confirmed this expectation, therefore, no field-strength dependence tests were made in this investigation. All susceptibility measurements were made in a field of approximately 11 kG.

III. Results

The dependence of the total susceptibility χ_T on apparent crystallite layer diameter L_a for pyrolytic carbons is shown in Fig. 1. The open points represent susceptibility values measured in this investigation on samples of known L_a (Ref. 25), the solid points were obtained by Poquet (Ref. 11). The dotted arrows indicate estimated corrections to the plotted points to normalize all of the data to the same interlayer spacing (d = 3.425Å). The numbers by the points indicate the deposition temperature T_d and it is evident that L_a tends to increase with T_d, although other deposition parameters are also known to affect the structure and must be responsible for the scatter in the observed T_d-L_a dependence. The rapid rise of χ_T with L_a in the range $30 \leq L_a \leq 200$ Å is well known from studies of conventional carbons, such as petroleum and pitch cokes (Refs. 2–4). The slower, continued increase of χ_T with $L_a > 200$ Å, however, has only been observed in pyrolytic carbons. For conventional carbons, the susceptibility has generally been found to be independent of L_a above ~250 A, although a maximum is sometimes observed near L_a ~200 A. For example, such a maximum is found for pitch-coke if data on the mean susceptibility $\chi_T/3$ (Ref. 28) and L_a (Ref. 29) as a function of heat treatment for the same material are combined to obtain a plot of susceptibility vs L_a. However, in these materials, it is not easy to separate experimentally the L_a and d dependences. The heat treatment necessary to produce large L_a values also results in significantly decreased d values, which could mask the L_a dependence.

Figure 2 shows the dependence of χ_T on interlayer spacing d for two pyrolytic carbons with L_a values (inferred from χ_T using Fig. 1) of ~350 and ~250 Å. For both carbons, the dependence is approximately linear over the d range from 3.43 to 3.38 Å. For values of $d \leq 3.38$ Å, there is appreciable scatter of the data but,

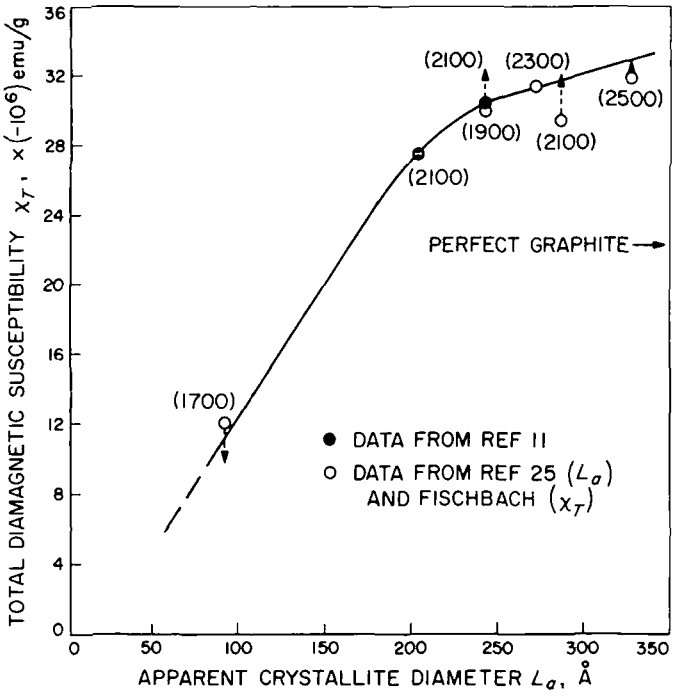

Fig. 1. Dependence of the total diamagnetic susceptibility of pyrolytic carbons on apparent crystallite layer diameter

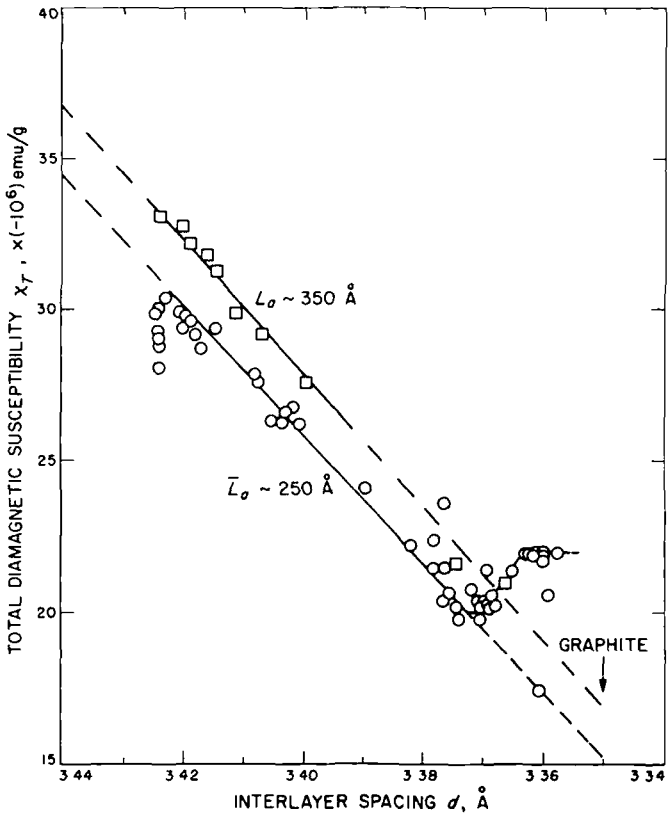

Fig. 2. Dependence of total diamagnetic susceptibility on interlayer spacing for two pyrolytic carbons with different L_a values

in general, χ_T passes through a minimum near $d \sim 3.37$ Å and then recovers to the single-crystal graphite value $\chi_T(G) = 22$ (Refs 13 and 30)[5] for $d \leq 3.36$ Å For some pyrolytic carbons, the initial stages of heat treatment result in an increase of χ_T above the as-deposited value with little or no change in d, as shown in the lower curve in Fig. 2. The present X-ray diffraction measurements (by the Warren peak-displacement technique) were not sufficiently precise to determine if this resulted from an initial small increase in L_a, a decrease in internal strains and lattice distortion, or some other source. X-ray diffraction studies on pyrolytic carbons, such as the two in Fig. 2, show that, in general, L_a remains approximately constant over the d range in which the χ_T-d plot is linear, then increases rapidly to values >500 Å as d decreases below 3 38 Å. This is shown in Fig. 3, where L_a is plotted as a function of d, using data obtained by Poquet (Ref. 11). Similar results have been obtained here (Ref. 23) and by Rouillon (Ref 31). Thus, the linear portion of the Fig 2 plots represents the dependence of χ_T on d at constant L_a, but it is very likely that the upturn of χ_T near $d \sim 3.37$ Å is a manifestation of the dependence on L_a in the range $L_a > 200$ Å. The results of studies on the kinetics and mechanism of graphitization in pyrolytic carbons (Ref 23) are also consistent with this interpretation of Fig. 2. Extrapolation of the linear portions of the curves in Fig. 2 to the completely turbostratic carbon interlayer spacing of 3.44 Å yields values for the total susceptibility of completely disordered two-dimensional graphitic carbon. This value depends on L_a. For the carbon with $L_a \sim 250$ Å, it is about 34.5, while for the carbon with $L_a \sim 350$ Å it is about 37, more than 60% larger than $\chi_T(G) = 22$, the value for perfect three-dimensionally-ordered graphite.

[5]Also in private communication with D E Soule

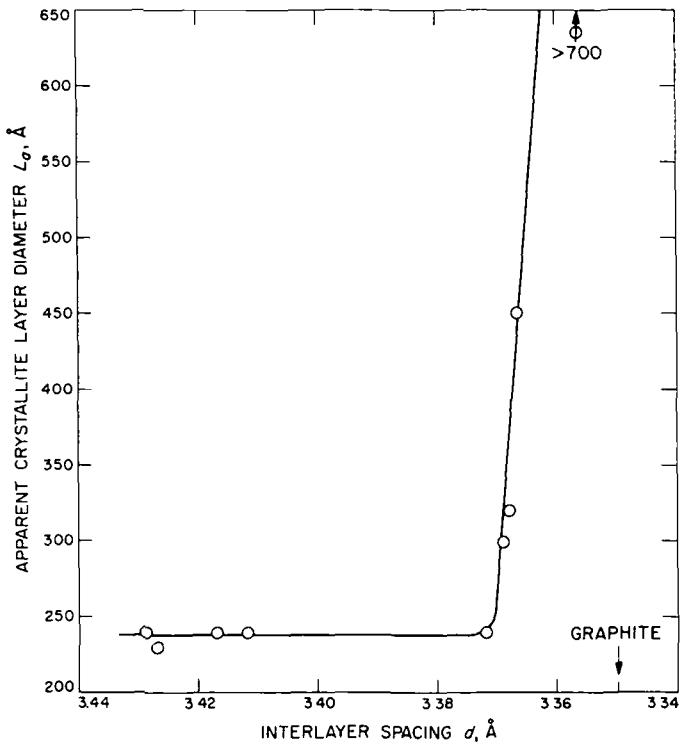

Fig. 3. Apparent crystallite layer diameter as a function of interlayer spacing for a pyrolytic carbon

The preceding results show that the diamagnetic susceptibility of pyrolytic carbons can vary over a range of at least a factor of three as a function of L_a and d, decreasing with decreasing d (increasing layer-stacking order) and increasing with increasing L_a. It is of interest to examine to what extent these two types of structure dependence can account for the range of susceptibility values and heat-treatment responses encountered in graphitizing carbons. The χ_T values of a number of pyrolytic carbons are plotted in Fig. 4 as a function of deposition temperature, T_d. The open points correspond to as-deposited carbons, the solid points correspond to some of the same carbons (circles) after a 1-h heat treatment at 3200°C For the as-deposited carbons, χ_T increases with T_d, passes through a broad maximum in the range from 1900 to 2200°C, then tends to fall off at higher T_d values. Similar results have been reported by Wagoner and Eckstein (Ref 12). Values of d (upper number) and L_a (lower number) are given beside the data points for some representative carbons in Fig. 4. It is evident that the rising branch of the curve ($T_d \leq 2000$°C) is characterized by consistently large d values (disordered, turbostratic stacking) and increasing L_a values. The general increase of χ_T with T_d in this range thus can be attributed to the L_a dependence. The maximum χ_T values correspond to a combination of large L_a and large d. At higher T_d, annealing effects during deposition tend to produce lower d values, causing a decrease in χ_T. Thus, the variation of χ_T with T_d can be rationalized in terms of a combination of the L_a and d dependences. Heat treatment at 3200°C causes L_a to grow and d to decrease to approximately the graphite value and results in χ_T values near the $\chi_T(G)$ value, especially for carbons with large as-deposited L_a. For low T_d carbons, χ_T remains less than 22. This may result from components such as soot particles in which L_a growth is limited.

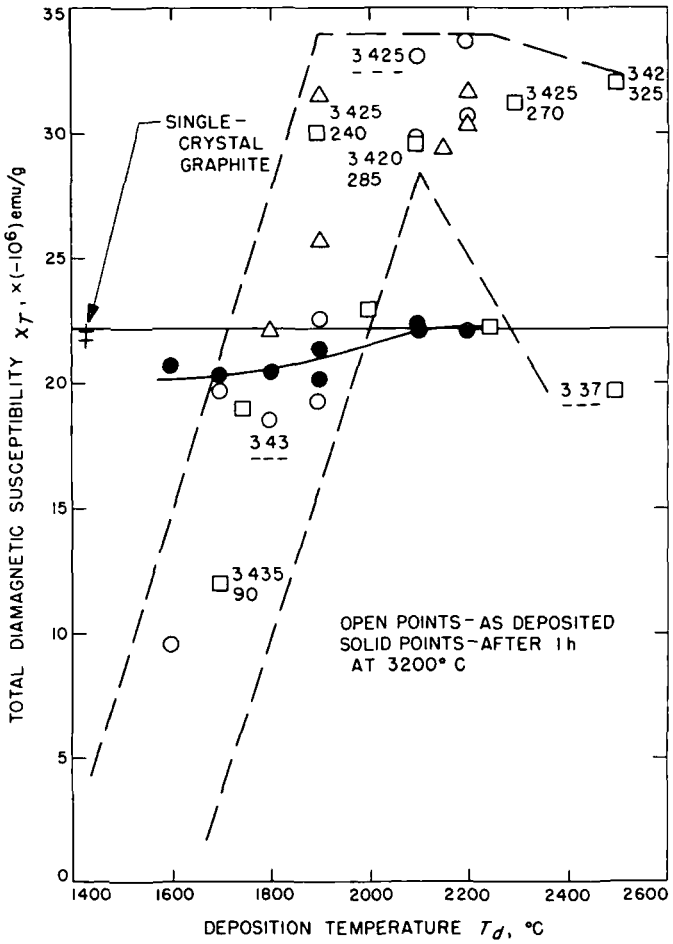

Fig. 4. Total diamagnetic susceptibilities of pyrolytic carbons as a function of deposition temperature

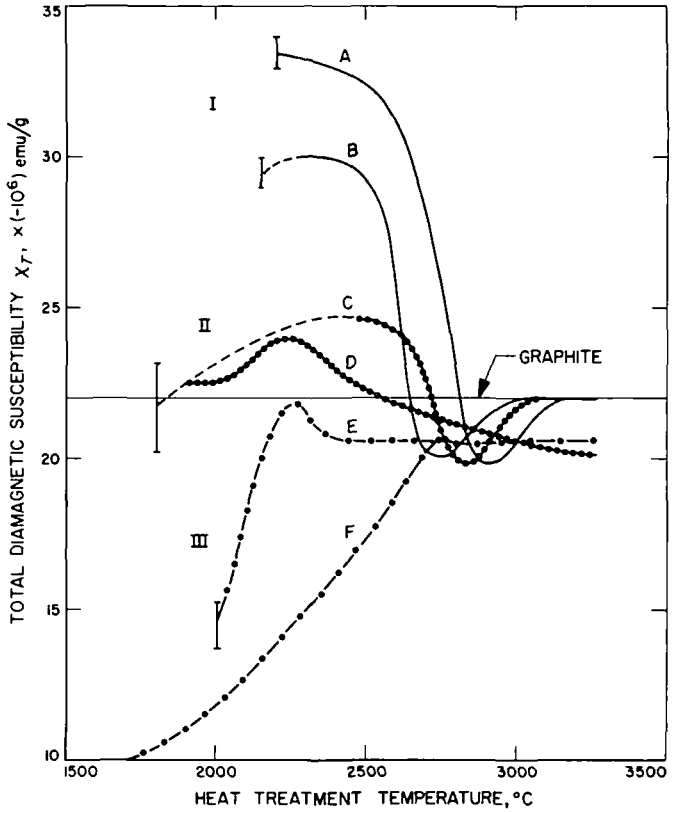

Fig. 5. Total diamagnetic susceptibility of several pyrolytic (A–D and F) and coke-pitch (E) carbons as a function of isochronal treatment temperature

Figure 5 shows some of the variety of susceptibility responses observed for isochronal heat treatment of pyrolytic and conventional carbons. Similar results can be obtained with isothermal treatments as a function of time at temperature. Carbons A through D and F are pyrolytic, carbon E is a petroleum coke-coal tar pitch composite (pretreated at 2000°C for 15 min). Three general types of behavior may be distinguished. This categorization is only for convenience of discussion and is not meant to imply that only these types of response may be observed. In fact, a continuous range of behavior, of which the three types shown are representative, would be expected to be possible. Type I (curves A and B) is characterized by a high initial χ_T, which decreases to a minimum and finally recovers to the graphite value with increasing heat treatment. It is typical of pyrolytic carbons isothermally deposited at from 1900 to 2300°C and has already been shown in Fig. 2. Type II (curves C and D), starting from a value near that of graphite, shows an initial increase to a maximum, then a decrease to a minimum which may or may not be followed by recovery to the graphite value, this has been observed for pyrolytic carbons isothermally deposited at temperatures from 1700 to 2000°C. For type III (curves E and F) the susceptibility is initially quite low and increases to a saturation value less than $\chi_T(G)$, sometimes passing through a maximum on the way. Similar maxima observed as a function of isothermal treatment time for pitch coke have been reported by Mazza et al. (Refs. 28 and 32) and by Gasparoux (Ref. 33). The pyrolytic carbon F was deposited at 1600°C.

Significant simplification of the plot in Fig. 5 results when χ_T is plotted against d, instead of treatment temperature, as shown in Fig. 6. The data for type I, including a number of carbons in addition to A and B, now fall within a fairly narrow band. The data for type II fall within another narrow band. The remaining scatter, maxima, minima, etc., can be largely rationalized in terms of the L_a dependence. Type I behavior is observed for initially turbostratic pyrolytics with $L_a > 200$ Å. As

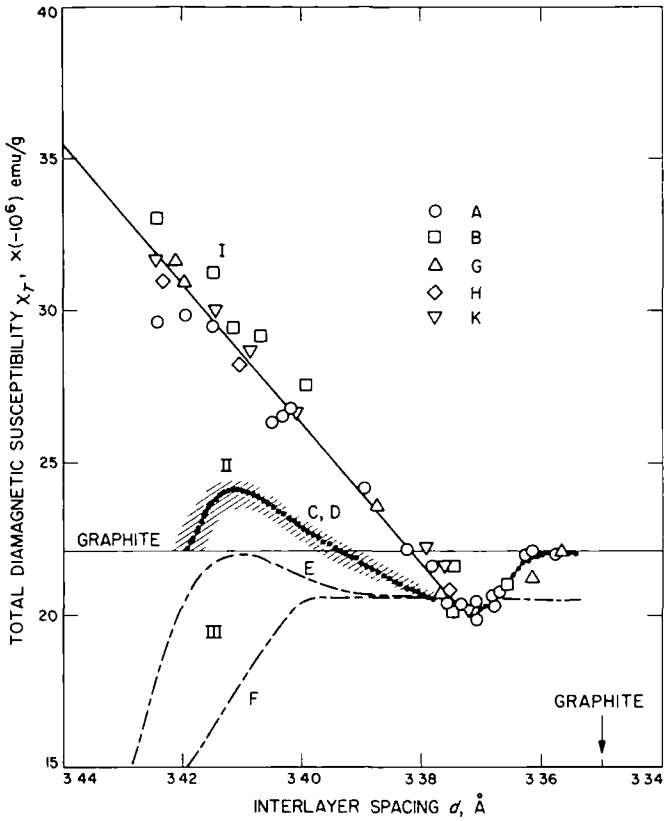

Fig. 6. Total diamagnetic susceptibility of several carbons (data from Fig. 5) as a function of interlayer spacing. Additional data for type I carbons G, H, and K have been included

noted earlier, for these carbons L_a initially remains constant while d decreases, taking χ_T down to the minimum value Thereafter, the further decrease in d is associated with a marked growth of L_a, which causes χ_T to increase and approach $\chi_T(G)$ Characteristically, type II carbons have initial L_a values in the range 125–200 Å, while for type III, L_a is initially less than 125 Å. X-ray diffraction studies indicate that for these carbons L_a increases and d decreases occur simultaneously as a result of heat treatment Graphitization studies have shown that there is a relationship between L_a and the minimum d value that can be obtained Very little decrease in d occurs for $L_a < 150$ Å, but for larger crystallite sizes there is a relationship of the form $-\Delta d \propto /1L_a$ (Refs. 23 and 34) Initially, therefore, the susceptibility behavior in type II and III carbons is dominated by the L_a dependence and increases as L_a grows with heat treatment. As L_a increases above approximately 150 Å, both L_a and d change with heat treatment, but the d dependence dominates and causes χ_T to decrease Finally, as d approaches the limiting graphite value, the L_a dependence dominates again, as in type I. The reason for the occurrence of susceptibility maxima in some cases, but not in others, for type III carbons is not clear. It may be related to the distribution of L_a values in the carbon. The low final χ_T value is not well understood. It could be accounted for by the presence of nongraphitizing components (disorganized carbon or stable small L_a components). For example, a χ_T value of 20 would be produced by the presence of less than 10% of a component with $\chi_T \sim 1$. If this nongraphitic component consisted of sufficiently small atom groups, its contribution to the X-ray diffraction pattern would be so broadened that it would be lost in the background scattering and would not affect the d values determined from peak intensity measurements.

IV. Discussion

It has been shown in the previous section that much of the room temperature diamagnetic behavior observed for pyrolytic and conventional coke-pitch carbons can be understood, at least qualitatively, in terms of the dependence of the susceptibility on the apparent crystallite-layer diameter L_a and the interlayer spacing d. In principle, it should be possible to construct a three-dimensional surface representing the diamagnetism of pure graphitizing carbons as a function of both L_a and d. The changes associated with structural changes, such as those produced by heat treatment, could be then described in terms of paths on this surface. The utility of such a construction is doubtful, however. For carbons in general, both L_a and d represent average values of distributions of some sort It seems likely that the detailed character of the distributions would depend on the origin and method of preparation of the carbon, and would change with treatment Thus, an infinite family of surfaces, or a solid, would be required to represent the detailed structure sensitivity of all graphitizing carbons.

It is of interest to consider the physical bases for the strong structure sensitivity of the diamagnetism of carbons. The L_a dependence is the most poorly understood in this regard Although there is extensive evidence that L_a is an important parameter in the electronic properties and graphitization process of carbons, there is considerable uncertainty about the meaning of L_a. The parameter L_a is determined experimentally from the width, peak intensity position or shape (Fourier analysis) of the (hkO) X-ray diffraction peaks In the absence of appreciable lattice distortion, any of these techniques should give a value equal to, or at least proportional to, the

actual average crystallite layer plane diameter in turbostratic carbons. The measurement is more difficult in partially graphitized carbons and graphite. In general, however, there is appreciable distortion broadening of the diffraction peaks, as indicated by the fact that analysis of the (100) and (110) peaks generally yield different values for L_a, and the X-ray L_a values are often much smaller than the crystallite dimensions observed by electron microscopy (Ref. 35) Correction for distortion effects, while possible in principle, is difficult. Therefore, L_a is most generally considered to be some sort of mean X-ray coherent scattering length related to both the crystallite size and lattice distortion. Mering and Maire (Ref 36) have suggested that L_a may be a measure of the curvature of the basal layers Ruland has emphasized[6] the influence of structural defects, such as large holes in the layers, layers linked together by small bridges, and layer bending in producing L_a values smaller than the actual extent of the layer structure. These considerations show the difficulty in assigning any absolute significance to the dimension L_a and help to explain the wide variations in the details of the χ_T vs L_a relationship reported by different workers for different carbons. In the determination of L_a on the pyrolytic carbons used here, Guentert (Ref. 25) employed a rigorous Fourier analysis technique. He found little evidence of distortion effects, so that L_a may be a true measure of crystallite size in these materials In any case, it appears reasonable to interpret L_a as a parameter related to the size of relatively perfect layer regions.

Why, then, should the magnetic susceptibility depend on the size or perfection of the layer planes? It has been suggested (Refs 17 and 37) that the region of strong dependence, $L_a < 200$ Å represents the transition from molecular behavior in which all of the π electrons contribute to the susceptibility to solid-state collective electron band behavior in which the susceptibility arises only from electrons near the Fermi level. The continued, but less pronounced, dependence on $L_a \geq 200$ Å may result from limitation of the effective electronic ring current radius by crystallite boundaries or other strongly scattering layer plane defects (Ref 17)[7] Although both of these explanations seem reasonable, both lack detailed confirmation and must be considered tentative.

A much firmer theoretical basis exists for the dependence of the diamagnetism on the interlayer spacing. McClure (Ref 15)[7] has shown that interlayer interactions have a strong influence on the electronic susceptibility of graphite When the susceptibility is calculated using a three-dimensional model which takes interlayer interactions into account, the theoretical value agrees with the experimentally observed value for single-crystal graphite $\chi_T(G) = 22$ at room temperature (Refs. 16 and 17). However, using a two-dimensional model (no interlayer interactions) a room temperature total susceptibility in the range 35–39 is obtained theoretically, depending largely on the value taken for the intralayer interaction parameter $\gamma_0 = 2.60$–2.80 (Refs. 15 and 18).[7] According to the theory, the value of γ_0 can be determined from the experimentally observed temperature dependence of the susceptibility at high temperatures, and analysis of the single-crystal data of Krishnan and Ganguli (Ref. 38) and of Poquet, et al. (Ref. 30) gives values in the range quoted above.

The present experimental susceptibility values for turbostratic pyrolytic carbons, 34 5–37 for $L_a = 250$–350 Å, respectively (Fig. 2), agree very well with the theoretical calculations for two-dimensional graphite The experimental values appear to increase with L_a so that a limiting susceptibility of ≥ 39 seems reasonable for very large layer diameters, suggesting that $\gamma_0 \geq 2.80$. According to the theory, second-neighbor-layer plane interactions have the largest influence on the susceptibility.

In disordered, turbostratic graphitizing carbons, the interlayer interactions (especially for second and higher neighbors) may be expected to be very much less than in ordered graphite for two reasons. The average interlayer spacing is larger, by about 2%, than in graphite, and successive parallel layers are believed to be randomly rotated about the c-axis and translated normal to it so that there is no correlation in the stacking sequence of the layers The lack of stacking orders appears to be the most fundamental influence acting to destroy the layer interactions, and it is generally considered also to be the cause of the increased d spacing. The behavior of the metastable rhombohedral modification of graphite, which has an ABCABC stacking sequence instead of the ABABAB sequence of the normal stable, hexagonal graphite form, lends strong support to this conclusion. McClure (Ref. 18) has calculated theoretically that the susceptibility of rhombohedral graphite should be about 35, and this has been confirmed experimentally by Pacault and Gasparoux (Refs. 14 and 39). Although the stacking order in rhombohedral graphite differs appreciably from that of hexagonal graphite, the interlayer spacing differs

[6] In a private communication

[7] Also in a private communication with J W McClure

very little. No evidence of any rhombohedral phase was found in the pyrolytic carbons studied here.

No explicit theoretical expression appears to have been developed for the variation of the diamagnetism with layer ordering in partially graphitized carbons. Marchand (Ref 19) has treated the case where d varies without change in the degree of stacking order. This approach appears to be reasonable for explaining the contribution of thermal expansion to the temperature dependence of the susceptibility, but seems inadequate to handle the changes produced by graphitization for reasons discussed previously Experimentally, the present data (such as those in Fig 2) exhibit too much scatter to determine whether the susceptibility actually varies linearly with d or has some more complex dependence This question has relevance to the mechanism of graphitization because the detailed manner in which layer-stacking order develops must be involved. Nevertheless, it can be stated with confidence that the high-susceptibility values observed in as-deposited pyrolytic carbons with large L_a values result from the reduced interlayer electronic interactions in the turbostratic structure, and that the dependence of the susceptibility on interlayer spacing results largely from the evolution of such interactions as layer ordering develops

V. Conclusions

The diamagnetism of pyrolytic carbons has been shown experimentally to depend strongly on both the apparent crystallite-layer diameter L_a and the interlayer spacing d. The L_a dependence may reflect the evolution of the electronic structure from a molecular to a band type and, perhaps, the influence of electron-scattering defects, such as crystallite boundaries. The d dependence can be attributed to the influence of the layer-stacking order on the interlayer electronic interactions. Very good agreement is obtained between the experimental and theoretical susceptibility values for turbostratic carbon, but the detailed dependence of $\chi_\parallel$ on the layer-stacking order in partially graphitized carbons has not been solved theoretically These two types of structure dependence can account, at least qualitatively, for much of the variety of diamagnetic behavior observed in pyrolytic and other graphitizing carbons.

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