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Magnetic Susceptibility of Carbons and Polycrystalline Graphites. I*

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In this investigation, the relation of susceptibility to the *a* dimension of crystallites was studied over the range from turbostratic carbons with diameters of 50 angstroms, to graphitic crystals with diameters of at least several thousand angstroms. Two series of carbons, one Thermax carbon black in powder form, the other National Carbon baked rods, were prepared in which the crystallite size was varied by heat treatment to different temperatures. A third series consisting of carbon blacks with different particle sizes from 50A to 3000A was prepared by heating to 3000°C, the particle size limiting the crystallite growth. The crystallite diameter was determined from the broadening of the x-ray diffraction lines, 10 (two-dimensional asymmetric diffraction line), and 110. The magnetic susceptibility was measured at room temperature by the Gouy method, and the measurements were made with fields ranging from 2000 to 11 500 oersteds to correct for ferromagnetic impurities. The mass susceptibilities of all carbons plotted against crystallite diameter fall within a narrow band showing that the susceptibility is primarily a function of crystallite size (Fig. 5). Almost all the increase in susceptibility from -0.5×10^{-6}/g for very small crystallites (aromatic molecules) to -7.8×10^{-6}/g for large crystals takes place in the range of diameters from 50A to 150A. The sharp increase in susceptibility is discussed in relation to the changes in the Hall effect and thermoelectric power as a function of heat treatment. It is concluded that this increase is due to an increase in the filling of the π band which brings the Fermi level into a region of higher curvature of the constant energy surfaces.

INTRODUCTION

THE susceptibility of large single crystals of graphite was first measured by Ganguli and Krishnan[1] who found that the difference between the susceptibility parallel to the principal axis and that perpendicular to the principal axis is about -21.5×10^{-6}/g at room temperature. This large anisotropic component of susceptibility has a strong temperature dependence approaching a constant value of -30.0×10^{-6}/g at low temperatures and changing into an approximate linear relation with $1/T$ at high temperatures ($T>300$°K). Several investigators have found that when graphite crystals are ground to a size of one micron and smaller the susceptibility becomes considerably smaller.[2,3] For crystallites containing only a few benzene rings the susceptibility should approach a value between -0.5×10^{-6}/g, the value for a carbon atom, and -0.7×10^{-6}/g, the average susceptibility for a randomly arranged system of benzene rings. Since all the change in susceptibility occurs in the region between very small and very large crystals, this is the region in which the relation of susceptibility to size had to be investigated.

Miwa[4] attempted to check the existence of a relation between susceptibility and size from susceptibility measurements on a number of carbon blacks. The blacks used by him had different crystallite sizes resulting from different methods of preparation. His results indicated that the susceptibility increased roughly linearly with the *c* dimension (thickness of crystallites perpendicular to the graphitic layers). The *c* dimension of his samples varied from about 10A up to 70A. Since the *a* dimension is approximately proportional to the *c* dimension,[5] this would mean that the susceptibility also increases linearly with the *a* dimension. When the size becomes very large, the susceptibility must approach asymptotically the value for single crystals of graphite. Even if Miwa's results were correct, it is clear that the linear relation can hold only over a limited range of crystallite size. It is generally believed that the large susceptibility of graphite is due to motion of electrons in the planes and that the interaction with neighboring planes is very small. Therefore, it seems that it is the *a* dimension which should be considered in studying susceptibility. Recently a considerable amount of information on the electronic behavior of carbons as a function of crystallite size has been obtained,[6] and it seemed important to investigate more extensively the relation between susceptibility and crystallite size from hydrocarbons up to graphite in order to check on the proposed explanation.

After this work was well under way, Wynne-Jones, Blayden, and Iley[7] published a study of the susceptibility of carbons with crystallite diameters ranging from 20A to 90A and also of some natural graphites. The crystallite sizes of the carbons studied by them were in general smaller than those studied here. However, the size ranges overlap sufficiently to permit a comparison of the results of the two investigations (see following).

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* Supported in part by the U. S. Office of Naval Research.

[1] W. Ganguli and K. S. Krishnan, Proc. Roy. Soc. (London) **117**, 168 (1941).

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[3] C. H. Gregory, thesis, California Institute of Technology, 1935 (unpublished).

[4] M. Miwa, Sci. Repts. Tôhoku Univ. **23**, 242 (1934).

[5] R. E. Franklin, Proc. Roy. Soc. (London) **209**, 196 (1951).

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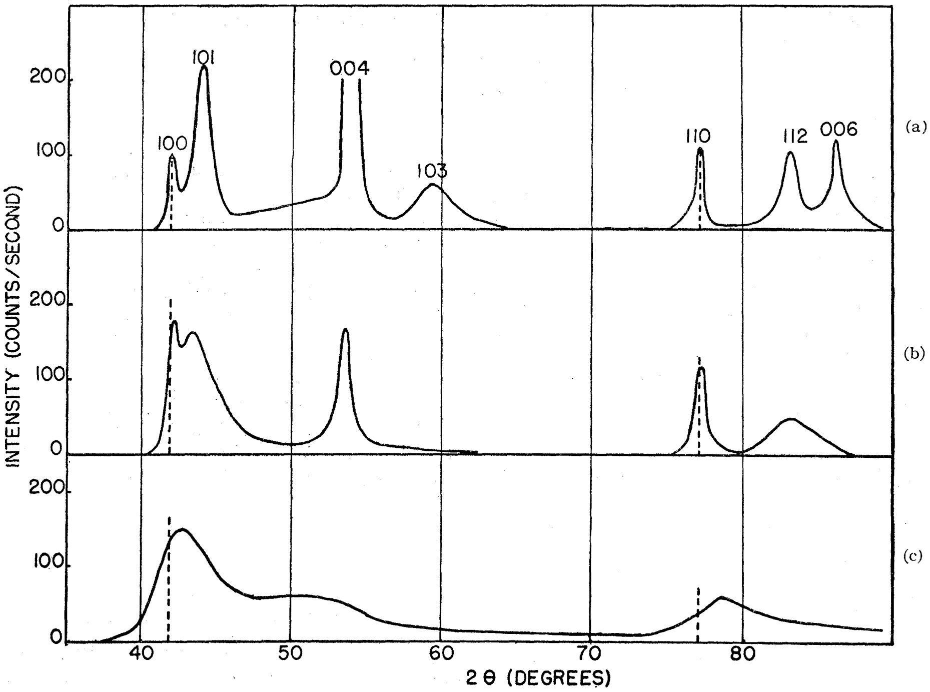

FIG. 1. X-ray patterns of carbons with large graphitic crystals (a), with crystals of intermediate size and layers partially aligned (b), and with small turbostratic crystallites (c).

EXPERIMENTAL AND RESULTS

1. Sample Preparation

Two somewhat different methods were used to obtain various crystallite sizes. The first consisted of heat treating a series of carbon blacks with particle sizes from 50A to 3000A, to a final temperature of 3000°C. It is known from electron microscope studies[8] that in graphitized carbon blacks, the particle size limits the crystallite growth. The series of graphitized carbon blacks, therefore, had different crystallite sizes but all had been heat treated to the same temperature. The second method consisted of heat treating samples to different temperatures to obtain different average crystallite sizes. Two groups of samples were treated in this way, one of commercial baked carbon rods from National Carbon Company, the other a carbon black with a large particle size d (Thermax, $d \sim 3000$A). All the samples were heat treated in a furnace consisting of a graphite tube serving as a resistance element and the temperature was measured with a Leeds and Northrup optical pyrometer. An atmosphere of nitrogen was provided in normal runs, but chlorine was also introduced during some of the runs at temperatures around 1000°C to reduce the amount of ferromagnetic impurity.

2. Measurement of Crystallite Diameters

The crystallite sizes of all the carbons were determined from the broadening of x-ray diffraction lines. In the initial stages of the investigation, the x-ray patterns were recorded photographically by the Debye powder method, and the broadening was measured from microdensitometer traces of the films, while later a North American Philips spectrometer was used. For the Debye powder patterns Cu x-radiation was used with a Ni filter consisting of two foils of 0.005-in. thickness placed around the circumference of the powder camera. Uniform size of samples was insured by extruding them through a 0.5-mm capillary. The characteristics of each film were determined with the aid of a rotating sector disk which gave five exposures each differing by a factor of two. These exposures were adjusted to cover the range of densities on most films and except for densities lower than any background, the density [$\log(I/I_0)$ as measured on a Leeds and Northrup microdensitometer] was linearly related to exposure time. Since the density above the background is directly proportional to the exposure, the half widths of the lines were determined directly from the densitometer trace of the total scattering after the background had been subtracted. For samples investigated with the spectrometer, the lines were measured by a fixed count technique to reduce statistical error in the background.

In order to get the broadening β of the line due to the finite size of the crystallites, the instrument width b was subtracted from the total half-width B. The instrument width was obtained in both the Debye and spectrometer methods from the lines of coke graphitized to 3000°C, and of natural graphite in which the crystallites are so large that the size broadenings are negligible. The x-ray pattern of this coke is shown in Fig. 1, along with patterns of a coke of intermediate size, and one of very small size. The relation between broadening of a line and the crystallite dimensions is: $t = C\lambda/\beta \cos\theta$,

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[8] H. T. Pinnick, J. Chem. Phys. 20, 756 (1952).

where t is the dimension of the crystal perpendicular to the set of planes giving rise to the line, λ is the wavelength of x-radiation, and C is a constant ordinarily taken to be equal to one. However, small crystallites of carbon have a turbostratic structure with successive planes parallel, but randomly rotated about the direction perpendicular to the planes so that lines corresponding to cross lattice reflections *hkl* of graphite are not present, and only lines corresponding to *hk*0 and 00*l* are observed (Fig. 1c). Warren[9] has shown that the diffuse reflections corresponding to the *hk*0 lines in graphite are the result of two-dimensional diffraction from each plane. He showed that the shape is asymmetric with the intensity falling off more slowly on the large angle side of the peak, and that the constant C in the above relation between broadening and size is equal to 1.85 for two-dimensional diffraction lines. As the crystallite size increases, the layers gradually become oriented in the crystallites in the same manner as they are in the graphitic structure. Franklin[10] has shown that in heat-treated cokes the structure of a crystallite consists of a stack of parallel planes composed of a random mixture of groups of perfectly oriented planes and groups of completely disoriented planes. As the crystallite size increases, the percentage of oriented planes increases and *hkl* lines gradually begin to appear in the x-ray patterns. For example, the 101 line becomes noticeable when it is about $\frac{1}{10}$ as intense as the neighboring 100 line. Experimentally, the beginning of alignment is observed in carbons with quite different histories of temperature treatment in about the same range of sizes, that is, around 150A.[8] Therefore, the orientation of the layers is not caused just by the increased thermal motion at higher temperatures of heat treatment, and probably the orientation process is the result of two competing forces, one tending to align the layers and the other preventing alignment.[8] For crystallites of this order the 101 line shows up on the large angle side of the 100 line in the form of a hump which gives an error of about 20 percent in the determination of crystallite size. Therefore, the 100 line was used only for size measurements of crystallites with diameters less than 150A and above 150A where the alignment gives rise to *hkl* lines, the size was obtained from the half-width of the 110 line which is sufficiently intense at these sizes for accurate half-width determination (Fig. 1b).

3. Magnetic Susceptibilities

The magnetic susceptibility was measured, using a Gouy balance. A regular chainomatic analytical balance was modified so that the sample could be placed in the field of an electromagnet by directly suspending it from the balance arm. The sample and the nylon suspension were enclosed by a glass tube to protect them from air currents. The separation of the pole pieces was approximately 2.0 cm and at this separation the maximum field obtainable was 11 500 oersteds, sufficient to achieve saturation of ferromagnetic impurities. The field intensities were obtained in each case by measuring the current in the coils, the measurement being made with a precision ammeter ($\frac{1}{2}$ percent). A calibration curve of field intensity *vs* current was obtained from fifteen determinations of the field made with a fluxmeter at current settings approximately the same as those used in the susceptibility measurements, and this curve was used to interpolate for fields corresponding to intermediate values of current. A special search coil was used for most of the higher field strengths and it was calibrated with the standard search coil supplied with the instrument. No current regulating device was employed, since the current through the magnet was constant to within 1 percent over the period required for determining the force on the sample, and such a change in current causes an even smaller change in the field.

The susceptibility of a powder sample was measured by placing the powder in the upper part of a special container[11] divided in the center by a flat glass baffle, with the lower half of the container evacuated. The samples which were in the form of rods were suspended so that the lower end of the rod was in the center of the region of uniform field. It was necessary to consider the correction for oxygen in the air displaced by the rod. For the atmospheric concentration of 20 percent this correction has the value $\kappa=+0.03\times10^{-6}$/cc, which was negligible for all samples in this investigation.

The volume susceptibility of all samples, both powders and rods, was measured at room temperature for 15 different field strengths ranging from 2000 oersteds to 11 500 oersteds. The experimental values of the volume susceptibilities were plotted against $1/H$ and this curve extrapolated to $1/H=0$ to correct for ferromagnetic impurities. This procedure does not correct for any paramagnetic impurities, however.

In most instances the correction for ferromagnetic impurities ($\kappa_{5000}-\kappa_{\infty}$) amounted to less than 20 percent. Commercial graphite rods contain relatively large amounts of residual ferromagnetic material from the Fe_2O_3 added to them to inhibit puffing during graphitization and one of these rods was used to check the validity of the procedure. The susceptibility of this rod was measured, and the extrapolated susceptibility obtained was -12.7×10^{-6}/cc, a correction ($\kappa_{5000}-\kappa_{\infty}$) of 100 percent (see curve *a*, Fig. 2). Following LaRosa[12] the rod was purified by heating it in a chlorine atmosphere at 250°C for 30 minutes and the curve of κ *vs* $1/H$ after this treatment is shown in Fig. 2b. Finally, the rod was heated in a chlorine atmosphere at 900°C for 30 minutes and the resulting curve of κ *vs* $1/H$ is shown in Fig. 2c. The larger diamagnetic susceptibility in Fig. 2c at low fields, as well as the smaller value of the

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[9] B. E. Warren, Phys. Rev. **59**, 693 (1941).

[10] R. E. Franklin, Acta Cryst. **4**, 254 (1951).

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[12] M. LaRosa, Nuovo cimento **12**, 284 (1916).

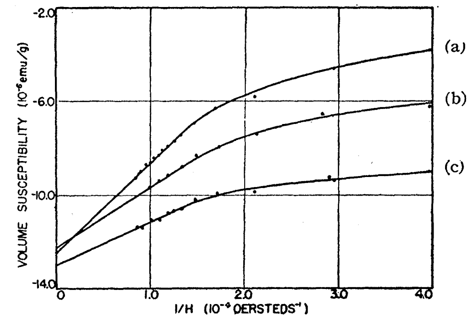

FIG. 2. Volume susceptibility as a function of the reciprocal of the magnetic field intensity for a graphite rod with ferromagnetic impurities removed by successive heat treatments in an atmosphere of chlorine: (a) untreated; (b) treated at 250°C; (c) treated at 900°C. *Correction added in proof:* units are (10^{-6} emu/cc).

slope of κ *vs* $1/H$, shows a considerable reduction of the amount of ferromagnetic material. However, the extrapolated value of κ obtained from the curve, -13.1×10^{-6}/cc, differs from the extrapolated value for the untreated rod by only 2 percent. Since this treatment would probably have removed a large part of any paramagnetic impurities, the very small change shows that the amount of paramagnetic impurities is negligible. It also makes it very probable that the extrapolated values are quite reliable in the other cases where the correction ($\kappa_{5000}-\kappa_\infty$) was only 20 percent or less.

In the measurement of susceptibility of powders by the Gouy method, the uniformity of packing is the main factor limiting the accuracy of the final results. The column of powder in the container described above was about 16 cm long, and to obtain uniform packing the powder was loaded in 10–12 consecutive operations, each one filling about 1.5 cm of the tube. The data obtained for the packing of a typical powder sample (Fig. 3) show that the density of the powder column is constant to within ±2 percent. A further check on the uniformity of packing was made by measuring the susceptibility with the container suspended at one position in the field, and then raising the container by half the average length of one of the sections in which the powder was packed and again measuring the susceptibility. For all samples the results were identical to within ±1 percent.

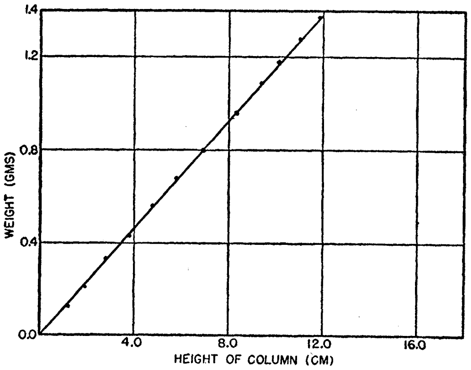

FIG. 3. Density of a carbon black sample as a function of height of column.

4. Results

The results of crystallite size measurements and susceptibility determinations are given in Table I.

There are a number of points in Table I which require an explanation. In the case of powders, the tamping produces orientation with planes perpendicular to the axis of the sample tube and consequently decreases the measured value for the susceptibility since in this direction the susceptibility is -0.5×10^{-6}/g for all sizes. For example, two powder samples of natural graphite were measured without tamping, and the values obtained for the susceptibility were about -6×10^{-6}/g. For these samples the holder was tapped to pack the powders, and even without tamping the plate like structure of the particles with the c axis of the crystals perpendicular to the plates resulted in a preferred orientation of crystal planes perpendicular to the axis of the sample tube. From electron micrographs of shadowed replicas of graphitized Thermax, it has been established[13] that the structure of these carbon blacks changes during graphitization from spherical into polyhedra with the crystallite planes parallel to the faces of the polyhedra. Therefore, when the carbon blacks are tamped, no preferred orientation should occur and

TABLE I. Summary of results of determinations of the *a* dimension of crystallites and corresponding diamagnetic mass susceptibilities.

Sample	Heat treatment (°C)	Particle size (A)	*a* dimension (A)	Mass susceptibility (g^{-1})
Carbolac	3000	50[a]	90	-5.1×10^{-6}
Voltex	3000	100–200[b]	100	−5.2
Kosmobile 77	3000	300–330[b]	115	−6.7
Statex A	3000	360[b]	130	−7.2
Acetylene black	3000	430[b]	110	−6.7
Lampblack	3000	1000–2000[b]	150	−7.8
P-33	3000	1500–2000[b]	350	−6.8
Thermax	3000	2500–5000[b]	500	−7.4
Thermax	2600	2500–5000[b]	340	−7.0
Thermax	2200	2500–5000[b]	180	−7.1
Thermax	1900	2500–5000[b]	90	−4.0
Thermax	1800	2500–5000[b]	80	−1.7
Thermax	1400	2500–5000[b]	40	−1.9
Petroleum coke	3000	10 000	500	−7.8
N.C. carbon rod	1200	...	50	−1.8
N.C. carbon rod	1450	...	70	−1.9
N.C. carbon rod	1500	...	72[c]	−2.5
N.C. carbon rod	1600	...	76[c]	−2.4
N.C. carbon rod	1700	...	83[c]	−3.7
N.C. carbon rod	1800	...	90	−5.4
N.C. carbon rod	1850	...	100	−6.0
N.C. carbon rod	2200	...	180	−7.4
N.C. carbon rod	2450	...	440	−7.4
N.C. graphite rod	...	...	500	−7.8

[a] R. P. Rossman and W. R. Smith, Ind. Eng. Chem. **35**, 972 (1943).
[b] *Carbon Black Manual* (Witco Chemical Company, New York, 1945).
[c] Interpolated from curve of *a* dimension *vs* heat treatment.

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[13] E. A. Kmetko, Phys. Rev. **86**, 651 (1952).

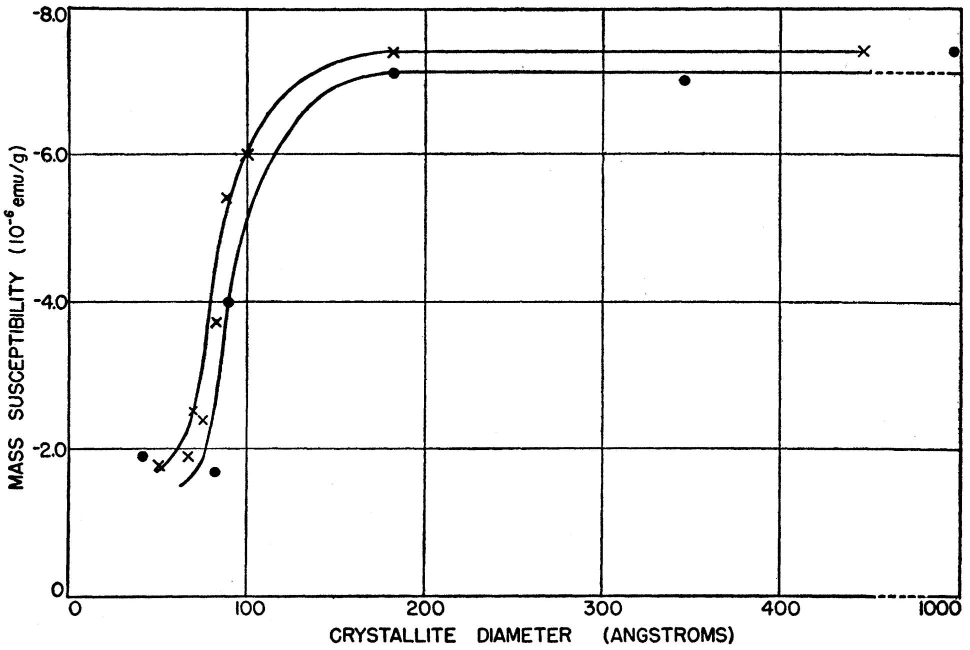

FIG. 4. Mass susceptibilities at room temperature of National Carbon rods (×) and Thermax carbon black powder (o) heat treated to different temperatures.

no correction for orientation is necessary to the values of Table I.

The value of the *a* dimension for Carbolac found in this work is larger than the average particle size as specified by the manufacturer. The 002 line of the x-ray pattern of graphitized Carbolac consists of a broad line with a sharp peak superimposed on it showing that it is a mixture of two very different size distributions. These large crystallites give a relatively larger contribution to the x-ray scattering since the contribution to the x-ray scattering is proportional to their mass. The average particle size is generally determined from average diameter so that the x-ray size measurement weights the larger sizes more heavily. In addition, Carbolac is manufactured by an oxidation of larger particles so there is a greater probability for graphitized Carbolac particles to consist of a single crystallite than for other carbon blacks where the average crystallite size is about $\frac{1}{3}$ to $\frac{1}{4}$ of the particle size.

In Fig. 4, the susceptibilities at room temperature of the series of National Carbon rods and the series of Thermax carbon blacks heated to different temperatures, are plotted as a function of the crystallite diameter. The two curves have similar shapes but reach slightly different values at larger crystallite sizes where the susceptibility is almost constant with increasing size. In the process of extrusion of carbon rods, the coke particles become aligned and there is consequently a preferential orientation of the crystallites relative to the axis of the rod. The preferred orientation will be with the crystallite planes parallel to the axis of the rod but randomly oriented about this axis. The partial alignment occurring in extrusion might explain why slightly higher values are obtained for commercial graphite rods than for carbon blacks and polycrystalline graphites with no preferential alignment.

There is also a small difference in the size range at which the rapid increase of susceptibility occurs. This might be due to the two series of samples having a somewhat different distribution of sizes, so that the averaging in the x-ray size determination would give the same average crystallite diameter, but the averaging in the susceptibility because of its different statistical weighting of the sizes would give a little different average value for susceptibility. The very similar behavior of these two series of samples suggests, however, that the susceptibility is primarily a function of crystallite size with possibly small differences arising from variations in structure due to the origin of the carbons. In Fig. 5, the susceptibilities of all the carbons investigated regardless of origin are plotted against crystallite diameter and they all fall in a narrow band which lends further support to the view that the susceptibility is in some unknown way depending on crystallite size.

DISCUSSION

As can be seen from Fig. 5, where the mass susceptibilities at room temperature of all the carbons investigated are plotted as a function of crystallite diameter, almost all the change in susceptibility from the value for very small crystallites to that for very large crystals occurs in the relatively small range of crystallite diameters from 50A–150A. This is in disagreement with the work of Rao[2] and of Gregory[3] who found that susceptibility of large crystals of natural graphite already starts decreasing when they are reduced to a size of one micron by grinding. They also found a decrease in the susceptibility of Bi ground to a similar size. It was

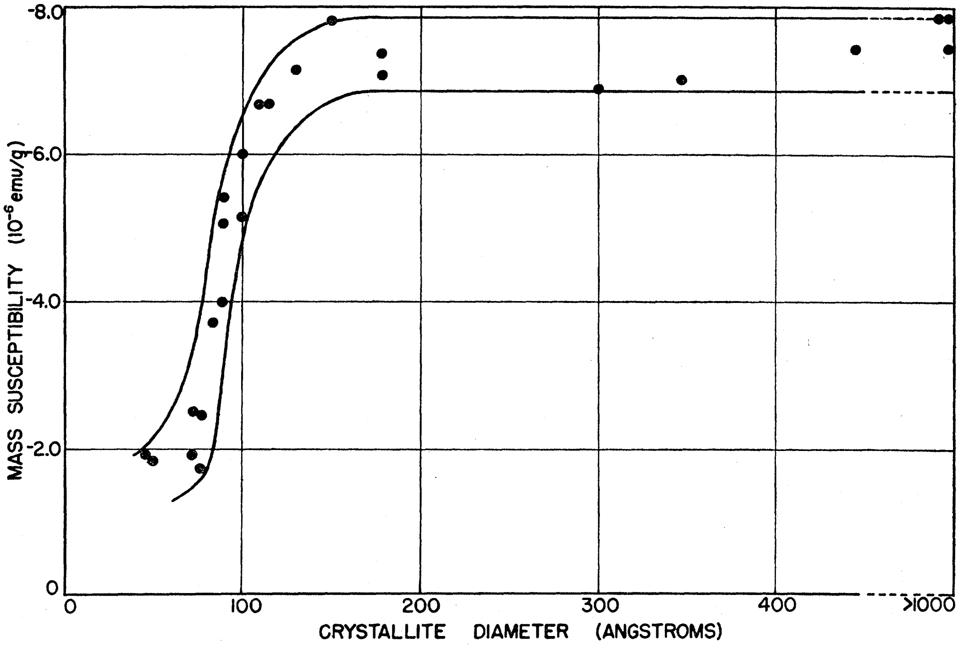

FIG. 5. Mass susceptibilities at room temperature of all carbons investigated.

shown later that the decrease of susceptibility of Bi was due to surface films of oxides and other impurities introduced by the grinding process.[14] Since it is known that oxide surface films are formed on carbon when it is ground in air,[15] it seems likely that such surface films were responsible for the decrease of susceptibility of small crystals of graphite in their experiments. The dependence of susceptibility on size found in the present investigation also disagrees with Miwa[4] who found a linear increase of susceptibility with size up to 70A (c dimension). His results, however, can only be considered as qualitative since he did not determine the crystallite size for the carbons whose susceptibility he investigated, but used the values quoted by other investigators for carbons of the same type but probably of different origin.

The recent work of Wynne-Jones, Blayden, and Iley,[7] on the other hand, is in general agreement with the results reported here in the size range from 50A–100A, with several noteworthy differences however. They found that for carbons produced by coking cellulose, dibenzathrone, and a pitch extract, the susceptibility increases slowly with size from -0.5×10^{-6}/g at 20A up to about -1.0×10^{-6}/g at 40A, then more and more rapidly for diameters in the range from 40A–100A. The susceptibilities of these three particular carbons are somewhat lower at small sizes than the carbons investigated in the present work. The susceptibility at such small sizes, however, depends strongly on the percentage of the carbon which is in the form of condensed molecules. In the coking of the particular organic materials which they used, the aromatization process is probably less rapid due to the formation of cross links between rings which hamper the growth of larger condensed ring molecules. Furthermore, the region of crystallite sizes where they found the fast increase of susceptibility is shifted towards somewhat small sizes relative to those found in this work. They did not observe the leveling off of the susceptibility at values about 150A since their crystallite size range extended only to 100A. Their curves for the three types of carbons do not overlap but are shifted somewhat relative to one another along the horizontal axis and this led them to conclude that there is no general relationship between susceptibility and crystallite size. Such small differences between carbons with different structures are certainly to be expected and a study of them might present an interesting field for further investigation. However, the existence of such a general dependence on size as given in Fig. 5 is very significant and requires an explanation.

The anisotropic component of susceptibility of condensed aromatic systems seems to be well understood at present. Pauling[16] was the first to propose an explanation of this large anisotropy. He assumed that in setting up the magnetic field, circulating currents are induced around the aromatic rings in addition to the regular induced currents within atoms responsible for ordinary atomic diamagnetism. The induced currents represent something like a Larmor precession of the π electrons and the calculated magnetic moment increases very rapidly with size. This semiclassical model gives a value more than 50 percent too large in the case of four condensed rings (pyrene) and a value equal to that of graphite already for a molecular diameter of about 40A.

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[14] Bhatnagar, Varma, and Anwar Al-Hag, Kolloid-Z. **78**, 9 (1937).

[15] R. H. Savage and C. Brown, J. Am. Chem. Soc. **70**, 2362 (1948).

[16] L. Pauling, J. Chem. Phys. **4**, 673 (1935).

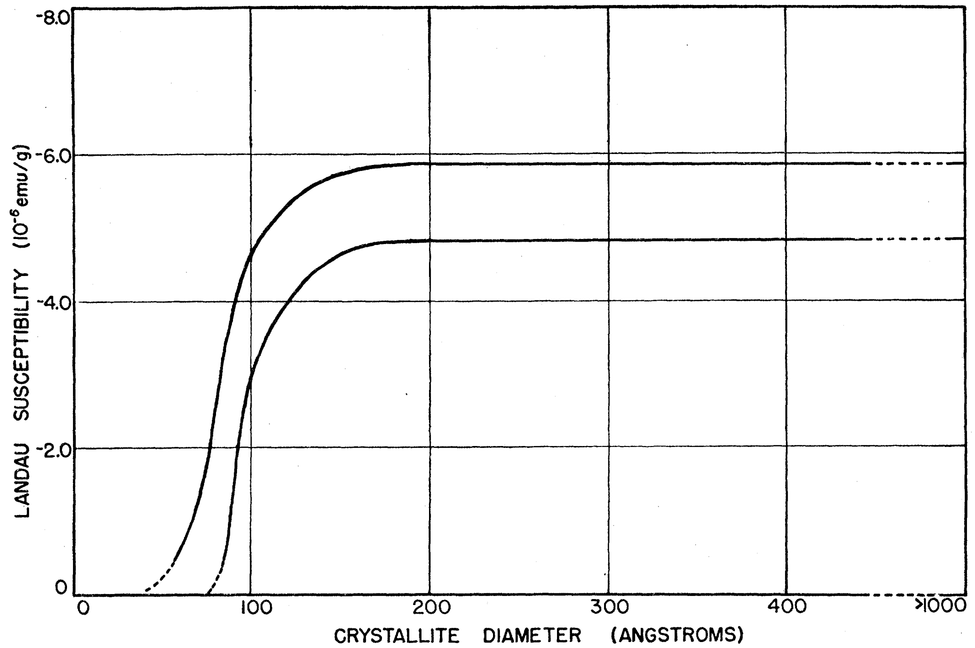

FIG. 6. Landau diamagnetism obtained by subtracting closed-shell diamagnetism from susceptibility curve, Fig. 5.

London[17] and Brooks[18] made quantum-mechanical calculations for aromatic systems and London, for example, obtained values in good agreement with experiment for systems containing up to four rings. These calculations show that the anisotropic component of susceptibility is very nearly proportional to the number of benzene rings with small deviations due to differences in arrangement of the rings. Experimentally, the proportionality to the number of benzene rings holds up to a ten-ring system (ovalence[19]). It has been pointed out[6] that this is just what one would expect since the resonance electrons in these aromatic molecules just fill a Brillouin zone and for a full zone the diamagnetism should be proportional to the molecular volume or in this case to the number of benzene rings. Assuming that this result can be extrapolated to larger systems, it is found that the average susceptibility of the π electrons plus the atomic susceptibility for randomly arranged planes of 15A diameter is -1.6×10^{-6}/g, for planes 25A in diameter, -1.8×10^{-6}/g, and for the limiting case of very large crystals (two carbon atoms per ring), -2.0×10^{-6}/g. The planes in crystallites of carbon are not all of the same size and shape. Furthermore, some of the carbon is in the form of a disorganized phase dispersed in the intercrystalline regions. Therefore, these extrapolated values will represent an upper limit for the total closed shell diamagnetism at a given size, the lower limit being -0.5×10^{-6}/g, the value for completely disorganized carbon atoms. The relative amount of carbon in the disorganized form will undoubtedly depend on the starting material so that for crystallite sizes up to 50A, the susceptibility will fall somewhere between these two limits; in fact, this is what is always observed in experiments.

It is evident that the closed-shell diamagnetism can account for only about a quarter of the total susceptibility of randomly arranged large crystals of graphite. Therefore, the remaining three-quarters must have a different origin. Ganguli and Krishnan[1] assumed that the anomalous susceptibility of graphite is due to a Landau-Peierls diamagnetism of the π electrons which form a two-dimensional gas with a low temperature of degeneracy. In order to fit the theoretical curve with the experimental data, they further assumed that electrons have effective masses equal to the electronic mass for directions of motion in the plane, but a very large effective mass in the direction perpendicular to the plane. However, their theory raised some serious objections in regard to specific heat and paramagnetism. A modification of the Ganguli-Krishnan theory which considers the Landau diamagnetism of holes and excited electrons removes these difficulties and gives a reasonable agreement with the experimental data.[6]

As mentioned above, for sizes below 50A the measured susceptibilities are always below the limiting value for the closed-shell diamagnetism of aromatic molecules and it seems probable, therefore, that in this region the Landau diamagnetism is zero or at least very small. For sizes of 75A and above, the disorganized carbon phase is not present, having been used up in the growth of turbostratic crystallites. This is shown by the disappearance of the strong diffuse scattering occurring in the x-ray patterns of all baked carbons which has been observed by Franklin[9] and in our laboratory. Therefore, above 75A the Landau diamagnetism of excited

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[17] F. London, J. phys. radium **B**, 397 (1937).

[18] H. Brooks, J. Chem. Phys. **8**, 939 (1940) and **9**, 463 (1941).

[19] Akamatu, Inokuchi, and Handa, Nature **168**, 520 (1951).

electrons and holes is obtained by subtracting the closed shell diamagnetism from the total susceptibility. This difference is roughly plotted as a function of crystallite size in Fig. 6. The increase of the Landau diamagnetism from zero to its maximum value over the range of diameters 75A–150A is very sudden, and it is interesting to inquire as to which factor is mainly responsible for such a behavior.

One might be inclined to attribute the appearance of the Landau diamagnetism to the additional order introduced by the change from the turbostratic structure of small crystallites into the three-dimensional ordered structure of large graphite crystals. For example, the anomalously large diamagnetism of Bi disappears when its crystalline order is destroyed upon melting.[20] However, this additional ordering in carbons takes place over quite a wide range of crystallite sizes and only about 25 percent of the planes are ordered[9] at the sizes when the Landau diamagnetism has already reached its maximum value.

The energy gap between the π band and the conduction band decreases with increasing crystallite size. The gap is very large for small crystals and is zero, or might even be negative (slight overlap of bands)[21] for large crystals of graphite. One might ask if the steep rise in Landau diamagnetism is not directly connected with thermal activation of electrons into the conduction band. In order to examine this explanation, the behavior of the Hall effect[22] and thermoelectric power[23] as a function of crystallite size has to be considered. For carbons with crystallite size of 50A the Hall coefficient and thermoelectric power are both negative, since so many π electrons are trapped in surface states that the Fermi level is depressed below the inflection curve on the energy surface. As the crystallite size is increased the number of surface traps becomes smaller, and the electrons released from these traps return to the π band thus raising the Fermi level. At crystallite sizes of approximately 75A, the Fermi surface is located close to the inflection curve and in this range the Hall coefficient and the thermoelectric power change sign. For larger sizes the filling of the π band increases steadily. As a result, the effective number of carriers decreases, and the Hall coefficient and thermoelectric power increase up to a positive maximum at sizes of about 125A. For sizes larger than 125A, the Hall coefficient and thermoelectric power start decreasing since the activation energy becomes progressively smaller and consequently more and more electrons are thermally excited into the conduction band. It is evident that the increase in the number of carriers by thermal excitation cannot be the reason for the steep increase in Landau diamagnetism since both the Hall coefficient and thermoelectric power show there is no appreciable excitation of electrons at room temperature for sizes less than 125A, and for this size the Landau diamagnetism has already increased considerably. In fact, the effective number of carriers is actually decreasing slightly through the range 75A–125A.[6]

As the energy gap decreases with increasing size, the curvature of constant energy curves might increase near the zone corners.[6] For a given filling of the zone, the susceptibility which is proportional to $\alpha_1\alpha_2$ will thus increase. Furthermore, at the same time as the Fermi level is raised by the return of trapped electrons into the π band with increasing size, the Fermi surface will also be nearer to the corner of the zone where the curvature of the energy surfaces is greater; thus the susceptibility might again increase in spite of the decrease in the effective number of carriers.

At present it seems most probable to the author that the sudden increase in Landau diamagnetism with crystallite size in the range of sizes 75A–150A is due to the combined influence of these two factors, that is of the increase of curvature of the energy surfaces near the zone corners and the raising of the Fermi level into regions of higher curvature. An investigation of the susceptibilities of residue compounds of carbons with bisulfate ions and of the temperature dependence of susceptibility of carbons with different crystallite sizes is currently being performed and it is hoped that it will furnish some information as to the relative importance of these two factors.

It seems very significant, however, that the susceptibility reaches almost its maximum value at 150A and stays approximately constant from there on over such a wide range of crystallite sizes, a range in which the Hall effect, thermoelectric effect, and electric resistivity vary so strongly. Of course, due to a lack of knowledge of the exact shape of the energy surfaces, the whole discussion can be only qualitative and the explanation of all details is at present impossible. On the other hand, it appears possible that the whole approach to the theoretical explanation will have to be strongly modified in the light of the results of the recent work on Landau-Peierls diamagnetism as reported by Dingle,[24] Adams,[25] and others.

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