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The Structure of Black Carbon

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This paper is concerned with the structure of extremely small crystallites of carbon deposited upon silica by the pyrolysis of methane. Electron diffraction patterns have been obtained from more than 100 carbon films, from some by the reflection method, and from others by transmission after removing the films from their supports with hydrofluoric acid. In some of the specimens the individual crystallites are strongly oriented and reflection patterns obtained from these are approximations to rotation patterns from single crystals. From these patterns we have concluded that the films are made up of pseudo-crystals in each of which the carbon atoms are hexagonally arranged in planes as they are in graphite, but successive parallel atomic layers are displaced so that no regularities exist other than the uniform separation of the planes and the regular arrangement of atoms in each of them.

THE structure of what was formerly called amorphous carbon has been the subject of study by x-ray diffraction for many years, the first pattern from carbon having been obtained by Debye in 1916. Only powder patterns from randomly oriented small crystals have been studied.¹ From these it has been inferred that the structure of black carbon resembles that of graphite with discrepancies which increase with decreasing crystal size until, when the mean linear dimensions of the crystals are of the order of 20A, the pattern consists of only three distinguishable rings and resembles that of an amorphous material.² One can see that the number of measurable parameters is so limited that on the basis of such a pattern alone no deductions as to the arrangement of atoms in the smallest carbon crystallites can be confidently made. Nevertheless, structures have been assigned to the crystallites of such carbons by a sort of extrapolation from the results obtained from other carbons whose structures degenerate progressively from that of graphite.

We have obtained electron diffraction patterns from which the structures of such extremely small crystals can be reliably inferred without reference to any other carbon. In our experiments a marked degree of preferential orientation is observed, and the diffraction patterns are approxi-

mations to those which would be produced by a single crystal rotated about a principal axis. Such patterns yield evidence which is not available in the previously reported patterns from unoriented crystallites.

Representative electron diffraction patterns are reproduced in Figs. 1-3. The three films from which these patterns were obtained were prepared by deposition of carbon upon flat fused silica surfaces in a furnace containing methane and nitrogen³ maintained at about 1000°C. The pattern of Fig. 1 was produced by electrons scattered by reflection from the surface of the deposited carbon. The thin films which gave the other two patterns were first removed by means of hydrofluoric acid from the silica plates on which they were formed, and each was then supported across a narrow slit in such a way that an electron beam could pass directly through it. The pattern of Fig. 2 was produced with the film normal to the electron beam, and that of Fig. 3 with the film rotated from a position normal to the beam by an angle of 45° about a horizontal axis.

On the original plate of the pattern of Fig. 1 one can observe six uniformly spaced diffuse spots or arcs lying along the center line. The best estimate of the separation between these is $s=6.4(0)$ mm, and from this the equivalent crystallographic spacing d can be calculated by

¹ X-ray diffraction patterns from oriented carbon crystallites were, however, obtained by M. Pirani and W. Fehse, *Zeits. f. Elektrochemie* **29**, 168-174 (1923).

² The most thorough investigation is that of V. Hoffman and D. Wilm, *Zeits. f. Elektrochemie* **42**, 504 (1936).

³ The degree of orientation of the crystallites in the surface of the film which gave the pattern of Fig. 1 had been increased by mild oxidation in air, subsequent to the original deposition of the film.

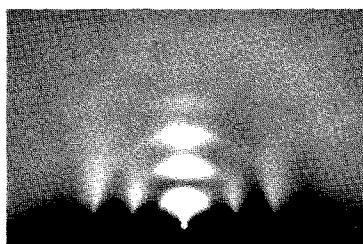


FIG. 1. Electron diffraction pattern obtained by the reflection method from the surface of a film of carbon deposited upon fused silica by the pyrolysis of methane. (Reproduced 0.6 full size, $L\lambda = 2.34 \times 10^{-8} \text{ cm}^2$.)

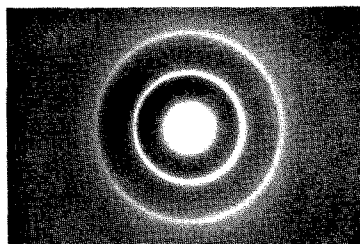


FIG. 2. Pattern by transmission at normal incidence from a carbon film deposited upon silica and subsequently removed with hydrofluoric acid.

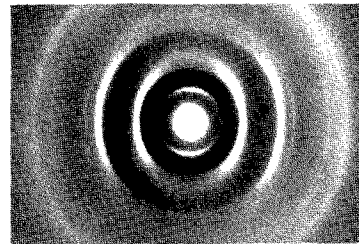


FIG. 3. Pattern from a carbon film inclined 45° to the primary beam, by rotation about a horizontal axis.

means of the relation $d = L\lambda/s$, where L is the distance from specimen to photographic plate and λ is the electron wave-length. Substituting for $L\lambda$ the independently determined value $2.34 \times 10^{-8} \text{ cm}^2$, one obtains $d = 3.6(6) \text{ \AA}$ which is about 9 percent larger than $c_0/2 = 3.35 \text{ \AA}$, the separation between adjacent hexagonal planes in graphite. From the result of this comparison it is natural to infer that the pattern of Fig. 1 was produced by graphite-like crystallites oriented with their hexagonal planes predominantly parallel to the supporting quartz surface. If this inference is correct there must be features in Fig. 1 along a horizontal line through the primary beam position, insofar as the shadow of the specimen permits, which correspond to reflections having Miller indices of the form $(hk0)$, and perhaps also features at other positions corresponding to general indices (hkl) . Crystallographic planes of the hexagonal system for which the third Miller index is zero make up a set having spacings inversely proportional to the square roots of the whole numbers 1, 3, 4, 7, 9, 12, 13... etc., and the radii of electron diffraction rings corresponding to these separations must be directly proportional to these square roots. Actually one can observe in Fig. 1 five features lying approximately along the horizontal line through the primary beam position, and the radii of these, as closely as they can be measured, are proportional to the square roots of the integers 1, 3, 4, 7 and 9. The calculated edge of the hexagonal cell is $a_0 = b_0 = 2.4(6) \text{ \AA}$, which is just the corresponding value for graphite. There are, however, no traces whatsoever of features

other than the $(00l)$ and $(hk0)$ reflections. The diffraction pattern thus gives no evidence of regularities in the structure of the individual crystallites in this specimen of black carbon other than in the arrangement of carbon atoms in the hexagonal planes and in the separation between these planes. The relative intensities of the different $(hk0)$ features correspond furthermore, as closely as we can estimate, to intensities to be expected from parallel but otherwise unrelated planes of carbon atoms, and not to intensities from crystallites having the complete graphite structure; relative to a corresponding pattern from oriented graphite crystals the "arcs" corresponding to the integers 3 and 9 are much too weak, although, of course, much stronger than similar features which would be produced by parallel but otherwise unrelated planes of atoms having a close packed arrangement. The separations and relative intensities of the $(hk0)$ features would have enabled us to deduce directly the arrangement and spacing of atoms in the separate planes, quite independently of knowledge of the graphite structure.

These deductions in regard to the structure of the carbon film are borne out by a more detailed consideration of the diffraction pattern. One can deduce very simply the pattern to be expected from an array of parallel and uniformly spaced but otherwise completely independent planes of carbon atoms. The lattice reciprocal to such a set of cross gratings is made up of the $(00l)$ spots of the graphite reciprocal lattice, and the surfaces of cylinders normal to the hexagonal planes and generated by (hk) lines which pass

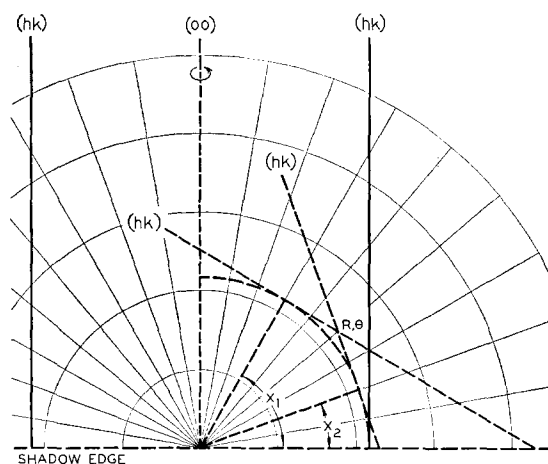


FIG. 4. Diagram illustrating the production of an (hk) diffraction feature of Fig. 1 by preferentially oriented cross gratings of carbon atoms.

through the points $(hk0)$ of the graphite reciprocal lattice. For the case of hexagonal planes parallel to the surface and to the primary beam, the sphere of reflection, which is approximately a plane, intersects these cylinders in straight lines normal to the shadow edge. If the various pseudocrystallites are imperfectly aligned, with the hexagonal planes of many of them making small angles with the general surface, then the resulting diffraction lines will be distributed over an angular range about the normal to the shadow edge. The superposition of many such lines will be expected to give to each of the (hk) diffraction features the shape of a fountain, or narrow fan, appearing to diverge approximately from its intersection with the horizontal line through the primary beam position; one observes just this shape for those $(hk0)$ features of Fig. 1 whose form can be clearly made out.

It is not difficult to calculate roughly the distribution of scattering intensity to be expected in one of the (hk) features of the pattern of Fig. 1. This distribution is quite approximately the same as it would be if the carbon planes were completely unrelated, and the calculation is carried out on that basis. Let χ represent the angle between the general plane of the surface and the planes of a set of parallel cross gratings, and assume that the number of gratings having normals lying in the element of solid angle $d\omega$ is proportional to $f(\chi)d\omega$. In Fig. 4 the plane of the paper is chosen to represent the sphere of

reflection and the horizontal line through the origin its intersection with the plane of the specimen surface. The lattice reciprocal to each cross grating is the set of (hk) lines described earlier, and the reciprocal lattices of many planes parallel to each other form coaxial (hk) cylinders. The reciprocal lattice cylinders of those sets of parallel planes, which are parallel to the primary beam, will intersect the plane of Fig. 4 in straight lines. The broken reciprocal lattice lines (hk) correspond to the two orientations χ for which sets of cross gratings parallel to the primary beam contribute to the intensity at the point R, θ . The total intensity at R, θ is made up of increments from all sets of cross gratings whose normals are parallel to the tangents drawn from R, θ to the sphere of radius $R_0 = L\lambda/d$, where d is the spacing between the cross-grating lines which correspond to the feature under consideration. By assuming for the distribution function $f(\chi) = \exp(b \cos^2 \chi)$ and integrating over all values of χ corresponding to gratings whose normals are parallel to these tangents, one finds that the number of gratings contributing to the intensity at R, θ is proportional to

$$(1 - R_0^2/R^2)^{\frac{1}{2}} \int_{-1}^{+1} \exp[bB(x+A)^2] dx / (1-x^2)^{\frac{1}{2}}, \quad (1)$$

where

$$A = (R^2 - R_0^2)^{\frac{1}{2}} (\tan \theta) / R_0 \text{ and } B = R_0^2 (\cos^2 \theta) / R^2.$$

One represents random orientation of cross gratings by setting $b=0$, and the number of gratings contributing to the intensity at R, θ for this case is proportional to $(1 - R_0^2/R^2)^{\frac{1}{2}}$ as one sees by evaluating the integral. One can expect that the actual intensity at R, θ for $b \neq 0$ will be given by the ratio of these two quantities multiplied into the intensity at R, θ for random orientation. The latter as calculated by v. Laue⁴ is $E^2/R(R^2 - R_0^2)^{\frac{1}{2}}$. Here E , the atomic form factor, can be replaced⁵ by $(Z-f)/R^2$ which, in the range with which we are concerned, is approximately proportional to $1/R$. In this way one finds that the intensity at R, θ will be approxi-

⁴ M. v. Laue, *Zeits. f. Krist.* **82**, 133 (1932). This expression is infinite at $R=R_0$, due to the assumed unlimited extent of each grating. We understand that Dr. B. E. Warren has carried through the v. Laue calculation for the case of randomly oriented gratings of limited extent.

⁵ N. F. Mott, *Proc. Roy. Soc. A* **127**, 658 (1930).

mately, $J = \text{Expression (1)} / R^2(R^2 - R_0^2)$. In order to determine the value of the constant b we have estimated that, for the (10) feature, the intensity in Fig. 1 is about one-tenth as great at $R = R_0$, $\theta = 30^\circ$, as at $R = R_0$, $\theta = 0^\circ$, and by numerical integration we have found that $b = 8$ corresponds to a value of this intensity ratio of 9.4. Using this value ($b = 8$) the intensity has been calculated⁶ at various points within the (10) feature, and the values obtained are plotted as a contour diagram in Fig. 5. (The numbers on the contour lines of Fig. 5 are J multiplied by 50.) Except for the region close to $R = R_0$, where the assumption of unlimited extension of each grating introduces serious error, the calculated intensity distribution of Fig. 5 is similar to that which is apparent in Fig. 1. This seems to us to confirm the assumption that the various cross gratings of which each crystallite is composed are unrelated except for their parallelism and uniform separation. (One cannot, however, determine from the experiments whether or not successive atomic layers are merely displaced laterally in random fashion from their positions in the graphite lattice, or are both displaced and rotated.)

We believe that the considerable vertical breadths of the (00 l) features in Fig. 1 arise from poor resolving power of the individual crystallites due to small dimensions parallel to their c axes. Some of the breadth of these features might, conceivably, be attributed to non-uniform separation of atomic planes, but this would result in progressive increase in breadth with increasing order of reflection. As closely as we can estimate the breadths at half-maximum of the various orders are about the same, and we therefore conclude that the planes in each crystallite are uniformly spaced and that the spacing is the same in different crystallites. From the vertical breadths we estimate that the mean dimension in the direction parallel to the c axes is 8A, indicating that on the average the crystallites are made up of only three planes of carbon atoms. With this fact in mind the striking contrast between the character of the (00 l) and the (hk) reflections is especially significant, as it

offers further confirming evidence that there is no regularity in the way the uniformly spaced planes of atoms lie upon each other in each crystallite, even as regards one plane and its next neighbor.

This conclusion is supported by diffraction patterns obtained by the transmission method. Measurements of the features of the patterns of Figs. 2 and 3 indicate that all of them, as in Fig. 1, have indices of the form ($hk0$) or (00 l).

The rings in the pattern obtained at normal incidence (Fig. 2) have radii proportional to the square roots of the whole numbers 1, 3, 4, 7, 9 and 12 and thus correspond to cross-grating reflections of the form (hk). There are no traces of (00 l) reflections, and we know therefore that the cross gratings in this film are strongly oriented, as is the case in the film which produced the pattern of Fig. 1. Microphotometer curves obtained from the (10), (11) and (20) rings of Fig. 2 are reproduced as Fig. 6, the ordinates being the differences between the logarithms of the light intensity I transmitted through the photographic plate and the logarithms of the intensity I_B corresponding to the estimated background curve. These microphotometer curves are more satisfactory than similar curves previously obtained from x-ray diffraction patterns of black carbon, because strong (00 l) diffraction rings are

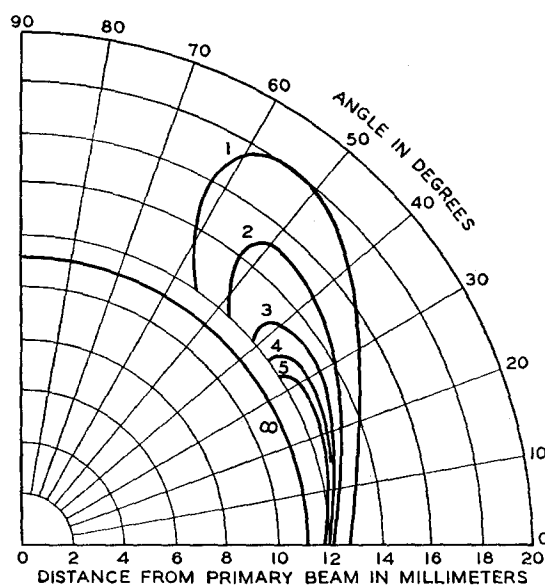


FIG. 5. Calculated intensity distribution in a (10) diffraction feature of Fig. 1, plotted as a contour diagram.

⁶ We are indebted to Dr. L. A. MacColl for advice and assistance in the numerical integrations.

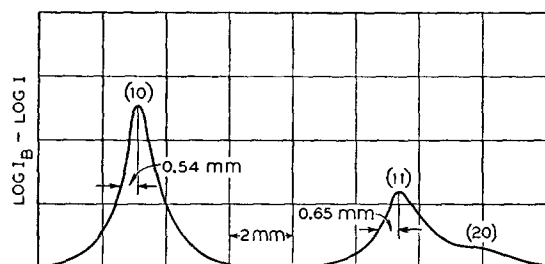


FIG. 6. Microphotometer curves of the (10), (11) and (20) diffraction rings of the pattern of Fig. 2.

present in the latter and overlap the (hk) reflections. The maxima of Fig. 6 are asymmetrical in the manner to be expected from imperfectly oriented cross gratings,⁴ and we cannot calculate the mean breadth of the cross gratings directly from the widths of the curves at half-maximum. A fair estimate can, however, be obtained by substituting, for the ring broadening in the Scherrer formula for crystal size, twice the difference between the radius of a particular ring at maximum intensity and that at half-maximum on the inner side. This will not yield exactly the mean linear dimension but the error will not be important. Estimated in this way, the widths at half-maximum, ΔR , of the (10) and (11) peaks of Fig. 6 are $2(0.54)$ mm and $2(0.65)$ mm. These correspond to average linear dimensions, ϵ , of the cross gratings of 22A and 18A, respectively, as calculated from the Scherrer formula in the form $\epsilon = \lambda/\Delta R$. The reason for the discrepancy between these estimates is not clear; similar disagreement has been observed in x-ray determinations.² Microphotometer curves were taken upon another pattern through the (10), (11), (21) and (30) rings, and an attempt was made to account in some simple fashion for the variation in half-breadth which was observed. In this we have been unsuccessful.

The diffraction features which appear on the pattern of Fig. 3 are (002), (004) and the (hk) reflections corresponding to the whole numbers 1, 3, 4, 7, 9 and 12. The (00 l) reflections are those which appear most strongly along the vertical center line, and the (hk) reflections along the horizontal. The fact that even along the horizontal line the (002) reflection appears weakly, whereas this reflection is entirely absent in the pattern of Fig. 2, is evidence that the crystallites in the film which produced the

pattern of Fig. 3 were less sharply oriented than those in the film which gave the latter pattern. Except for this quantitative difference the orientation was, however, the same in the two films. The difference between the character of the (00 l) and the (hk) reflections is brought out almost as clearly in Fig. 3 as in Fig. 1. One observes in Fig. 3 that the locus of (002) reflections is a circle, whereas the (10) and the (11) features are not true circular arcs but flare outward above and below the center line. The contour diagram of Fig. 5 can be used to estimate very crudely the intensity distribution to be expected within these features. To accomplish this one imagines this diagram reflected through the line $\theta = 0^\circ$ and both parts then rotated through 360° about $\theta = 90^\circ$ as an axis, resulting in an appropriate volume density distribution in reciprocal space. Intensities in the pattern of Fig. 3 are then represented by the intersection of this solid with a plane normal to the plane of the paper and inclined 45° to $\theta = 0$. The horizontal radial distribution through an (hk) feature of Fig. 3 will be represented by the contour lines at $\theta = 0$ in Fig. 5, and the vertical radial distribution approximately by the contour lines at $\theta = 45^\circ$ in the same diagram. One should realize, of course, that the diagram of Fig. 5 was calculated by assuming cross gratings of infinite extent, whereas the gratings are actually only about 20A wide; furthermore, the diagram corresponds to more strongly oriented crystallites than was the case in the film which gave the pattern of Fig. 3.

It has been pointed out that the degree of preferential orientation is different in different films (for example, those which produced the patterns of Figs. 2 and 3). More than a hundred films have been investigated and it has been discovered that the degree of orientation is considerable in some and slight in others. The patterns chosen for consideration here have been selected from those showing a high degree of orientation.

SUMMARY

We have shown that these films of pyrolytically deposited carbon consist of pseudo-crystals each made up of 3 or 4 parallel and uniformly spaced but otherwise randomly disposed atomic

planes in each of which the carbon atoms are hexagonally arranged as in graphite. This structure is just that inferred from x-ray studies⁷ of

⁷ For example, V. Hoffman and D. Wilm, reference 2; H. L. Riley, *Sci. J. Roy. Coll. Sci.* **10**, 10-20 (1940).

similar carbons, but in our experiments evidence is obtained which is not available in the previously reported patterns from unoriented crystallites and the deductions are made without reference to any other carbon.

JULY, 1941

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Spectroscopic Studies of the Simpler Porphyrins

III. The Absorption Spectra of *ms*-Tetraphenylporphine and a Series of Its Metal Complex Salts

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(Received April 14, 1941)

The molecular absorption coefficients of *ms*-tetraphenylporphine and the Cu, Ag₂, Mg, Zn, Cd, Hg, SnCl₂, Pb, MnCl, FeCl, Co and Ni complex salts have been measured over the visible region of the spectrum. The curves representing the absorption coefficients as a function of the wave-length are shown. The variations in the spectra of the metal salts of this one *ms*-tetrasubstituted porphine are much greater than those which have been found in the spectra of the different *ms*-tetrasubstituted porphines which so far have been studied.

INTRODUCTION

THE two previous publications in this series have been concerned with absorption spectra of synthetic porphines which were not metal complex salts. The first¹ was a study of the spectra of porphine and four *ms*-tetrasubstituted porphines, of which *ms*-tetraphenylporphine was one. The second² was a study of the spectra of the two isomeric forms of those porphines for which the two isomers were available. At the time of the first investigation the *ms*-tetraphenylporphine was the most difficult of the series to prepare and not enough of the substance was available to perform a separation of the isomers, consequently the material used in that investigation of the spectrum of *ms*-tetraphenylporphine contained a mixture of the two isomers. Since that time, a procedure for the synthesis of this porphine has

been discovered³ which yields quantitatively only the isomer of HCl number 13.5.* This is a

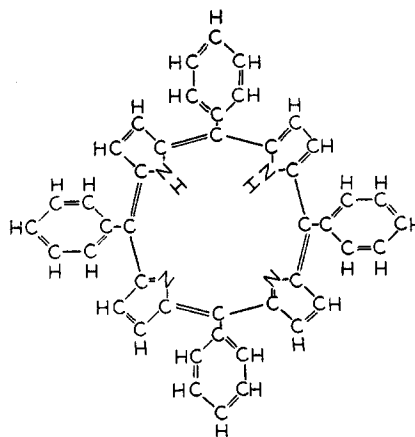


FIG. 1. Structural formula of *ms*-tetraphenylporphine.

¹ V. M. Albers and H. V. Knorr, *J. Chem. Phys.* **4**, 422-425 (1936).

² H. V. Knorr and V. M. Albers, *J. Chem. Phys.* **9**, 197-203 (1941).

³ Rothmund and Menotti, *J. Am. Chem. Soc.* **63**, 267-270 (1941).

* The HCl number of a porphyrin is defined as the concentration of HCl which will extract two-thirds of the porphyrin from an equal volume of ether solution on thorough shaking.