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An Electron Diffraction Study of Graphitic Oxide

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A structure analysis of graphitic oxide has been made on the basis of 'single-crystal' spot patterns and ring and arc patterns from polycrystalline material. The graphitic oxide was highly disordered, the patterns corresponding to diffraction by individual layers of thickness about 5 Å. These layers are based on puckered carbon sheets, hexagonal in projection, with oxygen atoms and hydroxyl groups attached in a disordered array. A difference Fourier map of the projection of the layer shows fractional oxygen peaks in positions consistent with feasible carbon–oxygen bond configurations.

1. Introduction

Graphitic oxide, also called graphitic acid, is formed as a pale, non-conducting powder by treating a suspension of graphite with strong oxidizing agents. The composition of this material is not well defined, but there seems to be some measure of agreement that the most fully oxidized form approximates to $C_4O(OH)$. Proposals regarding the structure which have been made on the basis of X-ray data and chemical inference are summarized in the review articles of Hennig (1959) and Croft (1960).

From the most prominent but rather diffuse line of the X-ray powder patterns the inter-layer c-spacing is seen to vary with water content but approaches 6·2 Å for the dehydrated form. Two or three weak hk bands have been observed and interpreted as corresponding to a hexagonal layer structure with $a_0 \sim 2{\cdot}45$ Å. From this and the chemical evidence the conclusion is drawn that the material is made up of a highly disordered array of puckered graphite-like sheets of carbon atoms with the oxygen and hydroxyl groups attached on either side in some not very well defined way.

The previous successes of the electron microprobe diffraction techniques, developed in this laboratory, for the study of substances of comparable disorder (Cowley, 1953; Cowley, 1956; Cowley & Ibers, 1956) suggested that further structural information on graphitic oxide could be obtained in this way. From suitable samples we immediately obtained clear, extensive, 'single-crystal', spot patterns. Data from these patterns and also from ring patterns have allowed us to carry out a structure analysis of graphitic oxide, and we have studied the methylated compound in the same way.

2. Experimental procedures

Graphitic oxide was prepared by the method of Hummers & Offeman (1958). The colour of the product varied from a very light to a dark brown, depending on the degree of dispersion. When a drop of a very dilute suspension was evaporated on a carbon supporting film, examination in the electron microscope revealed very thin flakes, lying almost flat on the carbon film, with diameters ranging up to a few microns (*cf.* Beckett & Croft, 1952).

In the electron-diffraction camera, with an electron beam of diameter less than 1μ at the specimen level, the larger crystal flakes give spot patterns such as that shown in Fig. 1. The relative intensities of the spots do not vary appreciably from crystal to crystal and are not affected by tilting of the crystals through small angles.

With electron beams of larger diameter the specimens give ring patterns, as shown in Fig. 2, in which the only rings present are those corresponding to the spots of Fig. 1. The profiles of the rings are asymmetric, falling away slowly on the high-angle side. Tilting of the specimen then gives arc patterns such as Fig. 3 in which the intensity of each arc decreases smoothly away from the zero layer line and shows no sign of the further maxima which would indicate order in the third dimension.

These observations indicate that the patterns are given by particles with only two-dimensional periodicity, *i.e.* by thin layers lying together with no appreciable inter-layer ordering.

From spot and ring patterns given by specimens tilted through large angles a rough indication of the extension of the regions of scattering power around reciprocal lattice points could be obtained, and hence an average layer thickness of 3 to 6 Å could be deduced.

The structure of the layers is seen to have hexagonal symmetry similar to that of a single carbon layer in graphite, with a periodicity $a_0 \sim 2{\cdot}43$ Å (for graphite $a_0 = 2{\cdot}455$ Å). The relative intensities of the spots and rings are close to those which would be expected from single graphite carbon layers, but show some significant differences.

Similar patterns were obtained from methylated

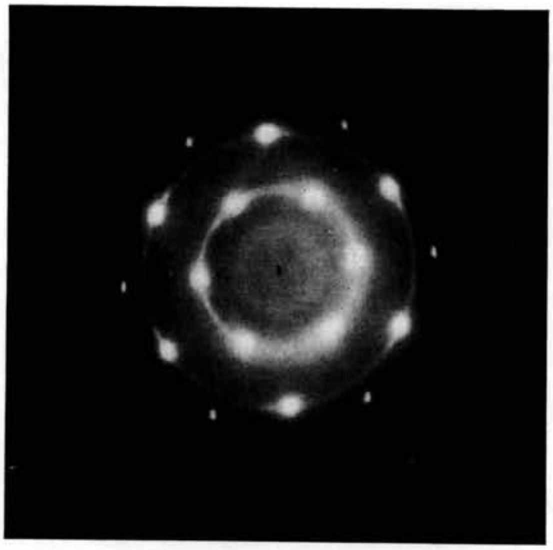

Fig. 1. Spot pattern from a graphitic oxide flake obtained by the electron micro-probe method.

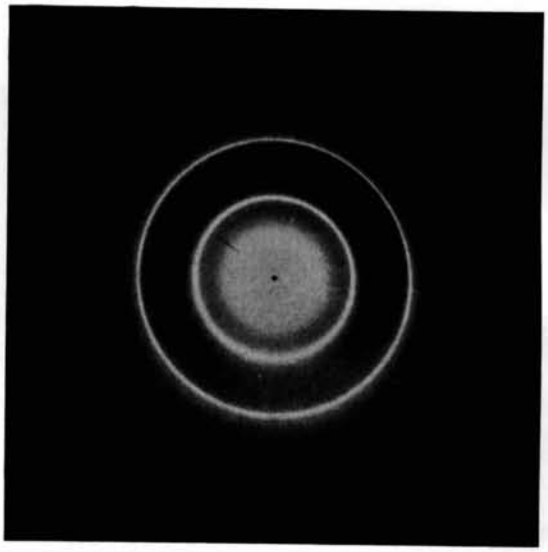

Fig. 2. Ring pattern from oriented polycrystalline graphitic oxide.

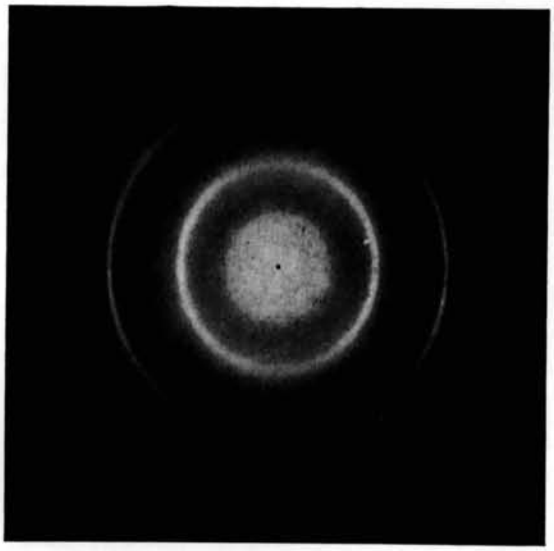

Fig. 3. Pattern from tilted specimen of oriented polycrystalline graphitic oxide.

graphitic oxide, formed by reaction of graphitic oxide with diazomethane. The diazomethane was prepared by the method of de Boer & Backer (1954). Graphitic oxide was treated with a solution of diazomethane in ether for about two weeks with occasional stirring, and then dried in vacuum. In the compound so formed, the hydrogen of the hydroxyl groups was replaced by methyl groups. The c-spacing determined by X-ray diffraction was correspondingly increased by 4 Å.

The methylated compound could be dispersed in water for specimen preparation by agitation with an ultrasonic generator. A redetermination of the c-spacing after such a dispersion was dried out confirmed that the dispersion in water caused no decomposition.

3. Intensity measurement

The relative intensities of the spots in the spot patterns were estimated visually using several series of plates taken with exposure times increasing progressively in a fixed ratio (*e.g.*, 2 to 1 or 3 to 1). The intensities in ring patterns were obtained by microphotometering similar series of plates, and also, independently, by the electronic method, based on a phosphor and photomultiplier, developed by Goodman (1962).

From arc patterns, such as Fig. 3, and from spot patterns from tilted specimens it is obvious that, for the 'single crystal' unit of the structure, the distributions of scattering power around the $hk0$ reciprocal-lattice points are very much elongated in a direction perpendicular to the crystal flakes. This elongation is presumably partly due to the very limited thickness of the flakes, and partly due to tilting or bending of the flakes. The types of elongation corresponding to these effects acting separately are illustrated in Figs. 4(*a*) and (*b*).

If I_{hk} represents the integrated scattering power around the hk reciprocal-lattice peak, the intensity per unit length of a ring, I^R_{hk}, will be proportional to I_{hk}/r for case 4(*a*) or I_{hk}/r^2 for case 4(*b*). For a combination of the two effects we may write

$$I^R_{hk} = c_1 p_{hk} \,.\, I_{hk}/r^b, \tag{1}$$

where $1 \le b \le 2$.

Here p_{hk} is the multiplicity factor, r is the radius of the ring and c_1 is a constant.

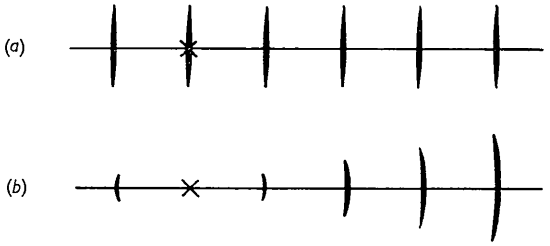

Fig. 4. Elongation of regions of scattering power around reciprocal lattice points due to (*a*) shape transform only and (*b*) tilting of crystallites only.

The intensity of the hk spot given by the intersection of the Ewald sphere, assumed planar, with the regions of scattering power, is given by $I^S_{hk} \propto I_{hk}$ for the pure crystal size effect, Fig. 4(*a*), but for the tilt effect, Fig. 4(*b*) is given by $I^S_{hk} \propto I_{hk}/r$. When both effects are present, not necessarily in the same proportions as for the ring patterns, we assume that

$$I^S_{hk} = c_2 I_{hk} r^a / r^b \quad \text{with} \quad 0 \le b - a \le 1 \,, \tag{2}$$

so that

$$I^S_{hk} = c_2 r^a I^R_{hk} c_1 p_{hk} \,. \tag{3}$$

The value of the exponent, a, is then chosen so that $p_{hk} I^S_{hk}/r^a \,.\, I^R_{hk}$ is a constant, independent of r. The exponent best fitting the graphitic oxide data was found in this way to be $a = 0{\cdot}6$.

Table 1. *Comparison of observed and calculated structure amplitudes for graphitic oxide*

h, k	$\lvert\Phi_o\rvert$	$\lvert\Phi_c\rvert$	$\lvert\Phi_c\rvert$ (Carbon only)
10	114	118	111
11	100	100	92
20	33	34	41
21	23	21	21
30	36	36	32
22	20	24	23
31	12	10	10
40	8	8	8
32	6	6	6
41	12	12	12
33	9	9	9

All intensities were expressed in terms of the intensity of the second ring of the pattern, arbitrarily put equal to 100. For the inner five rings the intensities measured from the ring patterns were taken since their accuracy was considered higher than for the estimates of spot intensities. For the outer reflections measurement of the ring intensities was not feasible, and the estimated spot intensities were used. The observed structure amplitudes, corresponding to $(I_{hk})^{\frac{1}{2}}$, are listed in Table 1. The value $b = 1{\cdot}20$ used in equation (1) was found, together with the temperature factor, by plotting the logarithm of (I_o/I_c) against $(\sin^2 \theta)/\lambda^2$.

In deriving the structure amplitudes in this way it is assumed that the variation in orientation within the regions giving spot patterns was great enough to permit the Ewald sphere to be approximated by a plane. This assumption seems to be justified. The assumption that the intensities may be expressed in the form (1) or (2) should likewise not introduce any serious error, since small errors in a or b, or deviations from a power-law relationship, may be compensated for by slight adjustments of the temperature factor.

4. Structure analysis

The dimensions ($a_0 = 2{\cdot}43$ Å) and intensities of the spot and ring patterns are close to those of a single carbon layer of the normal graphite structure. From the chemical evidence it is clear that the aromatic resonance structure of graphite cannot be present to any appreciable extent. The hexagonal net of these dimensions must represent the projection of a puckered layer in which the carbon–carbon bonds are in roughly tetrahedral configurations. Since there was no evidence of superlattice spots, either sharp or diffuse, it was concluded that there was no appreciable ordering of the oxygen positions, so that the basic hexagonal unit cell containing two carbon atoms should have approximately $\frac{1}{2}$O and $\frac{1}{2}$OH averaged over symmetrically equivalent positions. A Fourier map based on the amplitudes listed in Table 1 showed clearly the hexagonal carbon array with no other features except a suggestion of a bridging between the carbon peaks.

A difference Fourier map was calculated by subtracting calculated contributions from the hexagonal carbon array, assuming a temperature factor, $B=0{\cdot}47$. The phases of the reflections were dominated by the carbon contributions to the extent that no ambiguities arose in the assignment of signs to the $||\Phi_o|-|\Phi_c||$ values.

Since intensities were measured on a relative, rather than an absolute basis, and the exact composition of the graphitic oxide was not known, the contribution of the carbon atoms to be subtracted was uncertain to the extent of a constant multiplier. It became evident that the peaks due to oxygen atoms would be considerably broader and more diffuse than those corresponding to carbon atoms. The criterion was therefore used that at the carbon positions no sharp positive or negative peaks should remain in the difference map. This led to the assumption of a composition such that only about two-thirds of the oxygen atoms corresponding to the formula $C_4O(OH)$ were present. The resulting difference Fourier map is shown in Fig. 5.

It is seen that peaks corresponding to possible oxygen positions appear around the carbon positions and also around the mid-point of the carbon–carbon bonds. In addition a broad diffuse peak appears around the centre of the carbon hexagon.

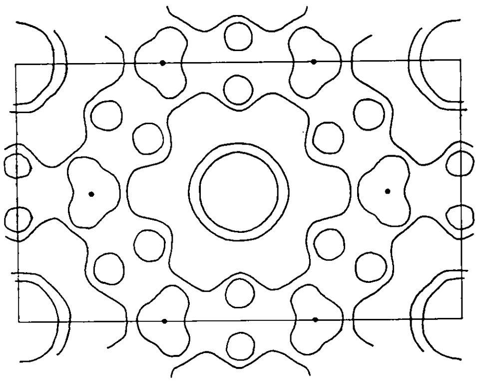

Fig. 5. Difference Fourier map for graphitic oxide. Carbon atoms have been subtracted from the positions indicated by dots.

Fractional oxygen atoms were assumed to lie at the origin of the hexagonal cell, at the carbon positions $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$, and at the positions $(0{\cdot}40, 0)$, $(0{\cdot}60, 0)$ and other symmetrically equivalent positions. The relative weights given to these different types of position were in the ratio 1:2:1, and a high value for the temperature factor ($B \approx 2{\cdot}3$) was assumed. Then the structure amplitudes $|\Phi_c|$ given in Table 1 were obtained when the total oxygen content of the unit cell was taken to be about 0·8 oxygen atom. The agreement with observed amplitudes is very good, with a reliability factor $R=0{\cdot}035$. However this should not be taken to indicate that the positions or relative weights of the fractional oxygen atoms have been determined with any degree of accuracy since the value of R is not a sensitive function of these variables. It is merely an indication that the sort of oxygen distribution deduced from the difference synthesis is probably correct in its general form although possibly not in detail.

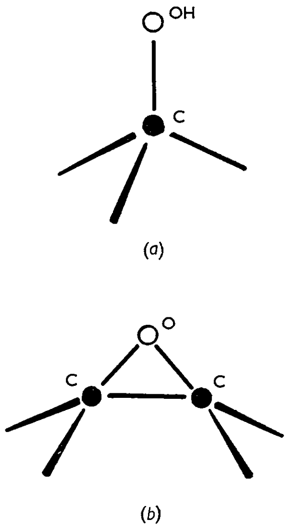

Fig. 6(*a*) and (*b*). The two types of oxygen bonding deduced from Fig. 5.

The oxygen peaks at the carbon positions presumably correspond to OH groups attached to single carbon atoms with the C–OH bond almost perpendicular to the layer as in Fig. 6(*a*). The peaks midway between carbon atoms must represent oxygen atoms bonded to adjacent carbon atoms in the epoxy-type linkage shown in Fig. 6(*b*). The peaks at the centre of the carbon hexagons could represent adsorbed water molecules: they could also arise from a small degree of short-range ordering between adjacent layers.

5. Discussion

Since the observed structure amplitudes do not differ a great deal from those calculated for a carbon layer alone, as shown by the last column of Table 1, the deduction of even approximate oxygen positions is justified only because we can be confident of both the accuracy of the intensity data and of the validity of the conversion to structure amplitudes. The intensity measurements are estimated to be accurate to within 5%, at least for the inner reflections which are significant in this respect. The conversion to structure amplitudes was made assuming the single-scattering approximation to be valid, and in the case of this material with light atoms and an effective crystal thickness of about 5 Å there can be little doubt of this. Nor is there sufficient inter-layer ordering present to modify the intensities in any significant fashion.

No very definite evidence either for or against the oxygen configurations of Fig. 6 can be derived from the many investigations which have been made using chemical, spectroscopic or X-ray diffraction methods. In the structure proposed for graphitic acid by Ruess (1947) and its modification proposed by Clauss, Pless, Boehm & Hofmann (1957), both based principally on chemical evidence, the oxygen bridges are formed not between adjacent, but between alternate carbon atoms. For such oxygen positions peaks would be expected in the difference Fourier map, Fig. 5, at positions between alternate carbon peaks where, in fact, the calculated function has its lowest point. The proportion of such ether linkages must therefore be very small.

Figs. 6(*a*) and (*b*) represent ideal symmetrical cases of the configurations deduced. All the bonds in equivalent positions relative to the oxygen atom make the same angle with the plane of the layer. This will not necessarily be so in practice. Since there is no ordering of the oxygen-atom positions, the arrangement and type of bonding of the oxygen neighbours will not be the same around each oxygen atom. The inclination of the C–C bonds, and so also of the C–O bonds, to the plane of the layer will vary. This has the effect of spreading out the oxygen peaks along preferred directions and introducing for them a very high effective temperature factor.

6. The structure of methylated graphitic oxide

The spot and ring patterns obtained from methylated graphitic oxide samples appeared to be identical with those given by graphitic oxide except that the innermost ring and corresponding spots were appreciably weaker. Relative to the second ring, taken as 100, all other intensities remained the same but the amplitude of the first was measured as 81, or considerably less than the value 114 for graphitic oxide. The corresponding change in the difference Fourier map is that the weak broad maximum at the centre of the carbon hexagon becomes very much stronger. The inference is that when the C–OH side chain is replaced by $C\text{–}O\text{–}CH_3$, the CH_3 group tends to take up a position above or below the centre of the carbon ring. This position is consistent with reasonable values for the bond lengths and bond angles of the side chain and seems reasonable from geometric and chemical considerations. The magnitude of the change in intensity of the first ring is consistent with the addition of rather less than half a CH_3 group per unit cell.

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References

BECKETT, R. J. & CROFT, R. C. (1952). *J. Phys. Chem.* **56**, 929.

BOER, TH. J. DE, & BACKER, H. J. (1954). *Recueil Trav. Chim. Pay-Bas*, **73**, 229.

CLAUSS, A., PLASS, R., BOEHM, H. P. & HOFMANN, U. (1957). *Z. anorg. Chem.* **291**, 205.

COWLEY, J. M. (1953). *Acta Cryst.* **6**, 522.

COWLEY, J. M. (1956). *Acta Cryst.* **9**, 391.

COWLEY, J. M. & IBERS, J. A. (1956). *Acta Cryst.* **9**, 421.

CROFT, R. C. (1960). *Quart. Rev. Chem. Soc. London*, **XIV**, 1.

GOODMAN, P. (1962). *J. Phys. Soc. Japan.* **17**, 294.

HENNIG, G. R. (1959). *Prog. Inorg. Chem.* **1**, 129.

HUMMERS, W. S. & OFFEMAN, R. E. (1958). *J. Amer. Chem. Soc.* **80**, 1339.

RUESS, G. (1947). *Monatsh. Chem.* **76**, 381.