5. Proposed and possible developments

It is intended to produce the half-tone masks for pairs of indices such that $h^2+k^2 \leqslant 64$. Masks with higher indices would have narrow bands and a photocell would be averaging the illumination over too great a fraction of a band to give accurate results.

The machine used for durene was only of a temporary nature. The final machine will be equipped with 80 photocell–potentiometer combinations and, since the machine deals only with centro-symmetrical structures, it should be possible to include up to 160 atoms per unit cell by considering only one-half of the cell.

For the purpose for which the Huggins masks were originally made, i.e. photographic Fourier synthesis, a half-tone image would be quite unsuitable. However, the half-tone masks have been tested when thrown out of focus just sufficiently to produce a continuous gradation of intensity, and it was found that the transmission properties were scarcely affected. Used in this way, the half-tone masks could probably be used for photographic Fourier syntheses.

I wish to thank Dr H. Lipson and Mr C. A. Taylor for their invaluable advice and suggestions. To the Department of Scientific and Industrial Research I am indebted for the financial support given for this work.

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The Structure of Graphitic Carbons

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The structure of the graphitic carbons is intermediate between the three-dimensional crystalline structure of graphite and the 'random layer structure' of the non-graphitic carbons. In the graphitic carbons the graphite-like layers are grouped in parallel packets within which there is a random distribution of orientated and disorientated layers.

The inter-layer spacing in the non-graphitic carbons is constant at 3·44 A. and in graphite it is constant at 3·354 A. In the graphitic carbons the apparent inter-layer spacing decreases with increasing graphitization. But the apparent inter-layer spacing is in reality a mean value. Whatever the degree of graphitization, the small groups of orientated and disorientated layers within the parallel-layer packet retain, in the main, the spacings characteristic of graphite and the non-graphitic carbons respectively. Only among the first disorientation spacings on either side of a group of orientated layers is there a spacing of some intermediate value.

Introduction

The X-ray diagrams of non-crystalline carbons show, with varying degrees of distinctness, diffuse bands corresponding roughly to the positions of the (002), (100) and (110) lines of graphite. It is too often supposed that all such materials contain minute crystallites of graphite. In reality, when the diagram is highly diffuse, the only diffraction effects observed are the (00*l*) reflexions together with two-dimensional (*hk*) bands of the type described by Warren (1941), indicating that the carbon contains small layer-planes of graphite-like structure which are stacked in parallel groups but not otherwise mutually orientated (Biscoe & Warren, 1942). The three-dimensional crystalline structure of graphite is not present. Any tendency towards such a structure would be revealed by a radical change in the shape of the (*hk*) bands, and at least some indication of the positions of the (*hkl*) ($l \neq 0$) reflexions of graphite. Such deformation of the (*hk*) bands occurs only in the less diffuse diagrams.

Thus, carbons showing pure two-dimensional (*hk*) bands contain no true graphitic structure, and will be referred to as *non-graphitic carbons*. A detailed account of the structure of one such carbon has already been given (Franklin, 1950*a*), and a comparative study of other non-graphitic carbons will be described elsewhere.

Certain non-graphitic carbons, when heated to sufficiently high temperatures, show a gradual change from the 'random layer structure' described by Biscoe & Warren (1942) towards the ordered structure of crystalline graphite. At temperatures above 1700° C. deformation of the (*hk*) bands sets in and is followed, with further increase in temperature, by the appearance of the (*hkl*) ($l \neq 0$) reflexions of graphite. By suitably varying the temperature of preparation it has been found possible to prepare a continuous series of such structures intermediate in type between the non-graphitic carbons and graphite. The present paper is concerned with the nature of these intermediate structures, which are here referred to as *graphitic carbons*.

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Experimental

Graphitic carbons were prepared from a pitch coke, a petroleum coke, and from polyvinyl chloride.

The carbons were prepared by pre-heating these substances for 2 hr. at 1000° C. in a laboratory tube furnace in an atmosphere of oxygen-free nitrogen, and then heating to higher temperatures in an induction furnace in an atmosphere of argon. The maximum temperature for each preparation was maintained for 15–20 min. except where otherwise stated.*

The X-ray apparatus and experimental method were the same as those previously described (Franklin, 1950*a*) except that the 76 mm. focusing camera was replaced by one of diameter 125 mm.

Method

The (002) *line*

In X-ray powder photographs of non-graphitic carbons the (002) line of the graphite diagram is replaced by a more or less diffuse band the position of whose maximum is displaced towards smaller angles. Owing to the diffuse character of this band the position of its maximum does not give directly the inter-layer spacing. It has been shown that large errors may be introduced if certain important corrections to the experimental intensity curve are not applied (Franklin, 1950*a*). Neglect of these corrections is responsible for the numerous excessively high values for the inter-layer spacing (up to 4 A.) which are to be found in the literature. In order to obtain from a diffuse experimental intensity curve the true position of the diffraction maximum it is necessary, after correction for polarization, absorption and geometrical factors, first to subtract the background due to incoherent scattering and to coherent scattering by that part of the carbon (if any) which does not participate in the layer structure, and then to divide by the square of the atomic scattering factor, f, and multiply by s^2 ($s=2 \sin \theta/\lambda$).

To correct for the incoherent scattering and the scattering by the non-organized carbon the absolute intensity scale must be established for each experimental curve. For this purpose the layer diameter is determined from the shape of the (11) band by means of the Warren equations (the (11) band is used rather than the (10) band because the atomic scattering factor is anomalous in the latter (Franklin, 1950*b*)). Using this layer diameter together with the intensity of the (11) band and the intensity of the background scattering it is possible to determine by trial and error (fitting calculated intensity curves to the experimental curve) both the absolute scale and the proportion of non-organized carbon. This enables both the incoherent scattering and the contribution of the non-organized carbon to be subtracted. (The proportion of non-organized carbon is found to be negligible in carbons containing layers of diameter greater than about 25 A.) The residual (002) band is then divided by the square of the atomic scattering factor and, in order to obtain the true form of the diffraction maximum, multiplied by s^2.

If the inter-layer spacing, d, is constant throughout the substance, the above procedure leads to a symmetrical diffraction peak. The position of the maximum then gives d according to the Bragg equation. If the inter-layer spacing is not constant, the corrected (002) band may be unsymmetrical. This is further discussed below.

The above somewhat lengthy procedure is, of course, necessary only when the (002) band is highly diffuse. When the number of layers per parallel-layer group (obtained from the integral breadth of the (002) band) exceeds about eight the background scattering can be subtracted empirically, and when it exceeds about fifteen even the correction factor s^2/f^2 does not appreciably change the position of the maximum, which can therefore be read directly from the experimental curve.

For all measurements of the inter-layer spacing the carbon was mixed with a small quantity of powdered quartz, and the distance of the (002) maximum from the nearby (101) line of the quartz was measured photometrically. In this way, for carbons giving sharp (002) lines, values of the inter-layer spacing accurate to 0·001 A. were obtained. The accuracy of the measurement decreases with increasing diffuseness of the (002) line.

The (*hkl*) *lines*

Corrections for polarization, absorption and geometrical factors, subtraction of the background due to incoherent scattering, and division by the square of the atomic scattering factor, f, were carried out as for the (002) band. Before searching for a quantitative interpretation of the deformed (*hk*) bands or diffuse (*hkl*) lines in the graphitic carbons it is then necessary to apply further geometrical corrections to the experimental intensity curve to obtain the true form of the bands or lines in reciprocal space.

In reciprocal space the 'random layer structure' of the non-graphitic carbons is represented by a series of rods parallel to the c^* axis. Since in the graphite-like layers all the atoms are co-planar, the structure factor along a given (*hk*) rod (other than the (00)) is independent of l, and the intensity along the rod (after dividing by f^2) is uniform. If, on the other hand, the layers show some tendency to be mutually orientated as in crystalline graphite, then the uniform (*hk*) rods of the non-graphitic carbons are replaced by rods having more or less diffuse maxima in positions corresponding to the (*hkl*) graphite reflexions. This will reveal itself in the X-ray diagram as a modulation of the two-dimensional (*hk*) bands.

The transition from the observed modulated (*hk*) band to the (*hkl*) rod in reciprocal space is simple provided

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* I am greatly indebted to M. le Prof. Ribaud for putting at my disposal the facilities of his high-temperature laboratory.

that the layer planes are large enough for the influence of the finite diameter of the rod to be negligible in the region considered. It is shown below that this condition holds for the graphitic carbons, and we need therefore only consider diffraction by a layer structure in which the layers are large.

Consider the intensity of that part of the powder diagram which represents a single (*hkl*) rod—that is, which represents constant and integral values of h and k and continuously varying values of l. For a non-graphitic carbon this takes the form of an (*hk*) band in which the intensity (for large layers) is proportional to $1/[s(s^2-s_0^2)^{\frac{1}{2}}]$ (Warren, 1941), s_0 being the vector giving the position of the point (*hk*0) in reciprocal space, and s that of any other point on the (*hkl*) rod ($s=2\sin\theta/\lambda$). For the graphitic carbons this band is modulated by a function which is the intensity distribution in reciprocal space. To obtain the true intensity distribution we therefore, for each value of s, multiply the observed intensity by $s(s^2-s_0^2)^{\frac{1}{2}}$, and assign to it its value of l which is given by $d(s^2-s_0^2)^{\frac{1}{2}}$, d being the inter-layer spacing. In this way we may obtain from a modulated two-dimensional band the intensity of any given (*hkl*) series as a function of l.

For all measurements and calculations the (112) line has been used. There are two reasons for choosing this rather than the (101), the other prominent (*hkl*) line. First, the absence, in graphite, of (11*l*) reflexions having odd values of l gives a clear separation between the (112) and the neighbouring (110) line. This is particularly important in the weakly graphitic carbons, in which the layer-planes are small enough to produce some broadening of the (*hk*0) lines. Secondly, it is probable that there exists in all graphitic carbons a type of disorder related to the rhombohedral form of graphite described by Lipson & Stokes (1942). This disorder, namely the intervention of the third equivalent position of the graphitic layer-plane, has been discussed in detail by Wilson (1949, pp. 67–74) for the analogous case of cobalt. It is without effect on all (*hkl*) reflexions having (h–k) a multiple of 3, and causes all other (*hkl*) reflexions to be drawn out parallel to the c^* axis. It is doubtless due to this cause that in all graphitic carbons the (101) line is considerably more diffuse (in reciprocal space) than the (112).

In all cases where measurable graphitization occurs the layer diameter exceeds 80 A., and it increases rapidly with increasing graphitization. It has been found that the broadening of the (112) line due to the finite size of the layers is always negligible compared with that due to the limited extent, perpendicular to the layers, of groups of parallel and orientated layers. Thus the simple method described above for obtaining the intensity of an (*hkl*) line as a function of l can safely be applied to the (112) line.

Results

General

Only certain non-graphitic carbons show, on heating to temperatures between 1700° and 3000° C., a continuous and homogeneous evolution from a non-graphitic to a graphitic structure. These will be referred to as *graphitizing carbons*. Other non-graphitic carbons, the *non-graphitizing carbons*, show no trace of homogeneous development of a graphite structure even after heating to 3000° C. The distinction between these two classes of carbons appears to be sharply defined, and will be further discussed elsewhere. We are here concerned only with the graphitizing carbons.

The photographs reproduced in Fig. 1 show successive stages in the transformation of a graphitizing carbon from the non-graphitic 'random layer structure' to the crystalline structure of graphite. Fig. 1 (*a*) shows a typical diagram of a non-graphitic but graphitizing carbon. In Fig. 1 (*b*) and 1 (*c*) the deformation of the (*hk*) bands (especially the (11)) is already visible, while in Fig. 1 (*d*), and subsequent photographs, the (101) and (112) reflexions of graphite can be clearly distinguished.

Table 1. *The graphitic carbons*

Raw material	Temperature of treatment (° C.)	Layer diameter (A.)	Apparent M from (002)	Apparent M from (004)	Apparent inter-layer spacing (A.)	p
Polyvinyl chloride	3000	600	150	95	3·361	0·25
	2700	430	140	80	3·365	0·315
	2500	380	140	77	3·368	0·35
	2140 (5 hr.)	360	100	76	3·371	0·43
	2310	260	110	57	3·380	0·62
	2140 (2 hr.)	300	97	54	3·387	0·625
	2160	260	82	51	3·397	0·73
	2040	90	73	44	3·417	0·85
	1720	70	41	27	3·427	~1·0
Petroleum coke	2310	220	80	50	3·385	0·62
Pitch coke	2140 (5 hr.)	430	—	73	3·374	0·50
	2310	210	80	49	3·383	0·58
	2140 (2 hr.)	230	89	46	3·395	0·72
	2040	—	59	—	3·418	0·88
	1720	65	32	20	3·428	~1·0
Naphthalene black	3000	210	—	34	3·393	0·70
Acheson graphite	—	—	—	—	3·359	0·15

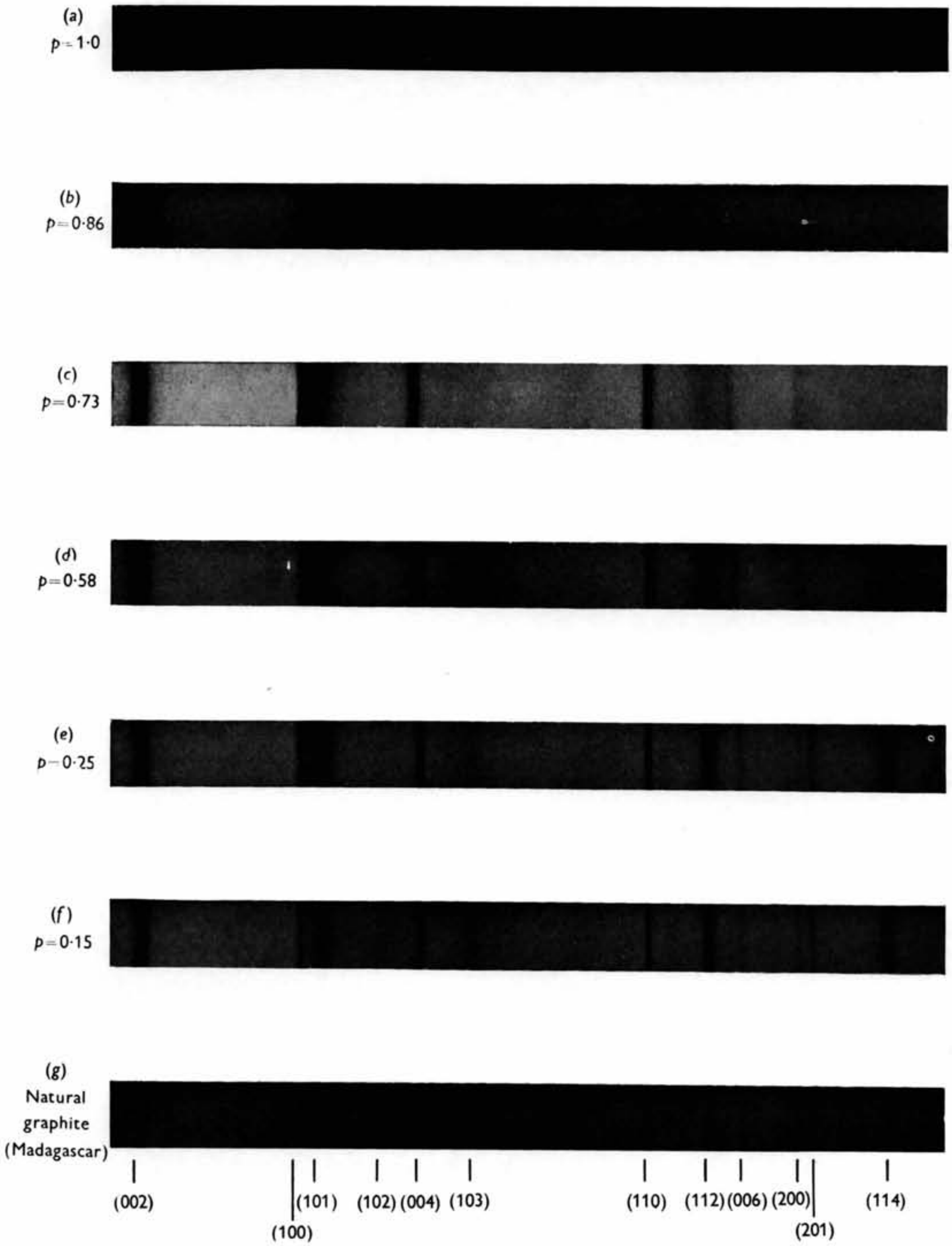

Fig. 1. Diagrams showing the transition from non-graphitic carbon to graphite.

When a series of graphitic carbons is arranged in order of increasing degree of graphitization—that is, increasing development of the (*hkl*) ($l \neq 0$) graphite lines—it is found that there are other parameters which vary regularly and continuously throughout the series. The diameter of the graphitic layers and the number of layers per parallel packet increase, and the (00*l*) spacings decrease. The results of these measurements are summarized in Table 1. The values recorded for the layer diameter were obtained from the half-peak width of the (100) and (110) lines, or from the (10) band where this is only slightly deformed. Since they have not been corrected for the geometrical line breadth the larger values are certainly too small, but they serve to illustrate, nevertheless, the increase in layer diameter which occurs with increasing graphitization. The apparent values of M, the number of layers per parallel packet, were obtained from the half-peak widths of the (002) and (004) lines. (The significance of the difference between these two *apparent* values will be discussed later.)

The (hkl) lines

The shape of the (112) line in reciprocal space, calculated as described above, is shown for a series of graphitic carbons by the full-line curves in Fig. 2. The apparent inter-layer spacing, d_{002}, for each carbon is also indicated, showing clearly the decrease in inter-layer spacing which occurs with increasing development of the (*hkl*) lines. (Since we are comparing the shape rather than the absolute intensity of the different (112) lines, all the maxima have been made to coincide at $I = 1{\cdot}00$ in Fig. 2.) The experimental (112) curves shown in the figure have not been corrected for the geometrical line breadth. This is, however, negligible for all but the two most highly graphitized carbons. For these a correction was applied before proceeding to a quantitative interpretation of the curves (see below), it being assumed that the geometrical line breadth is given by the breadth of the (100) line.

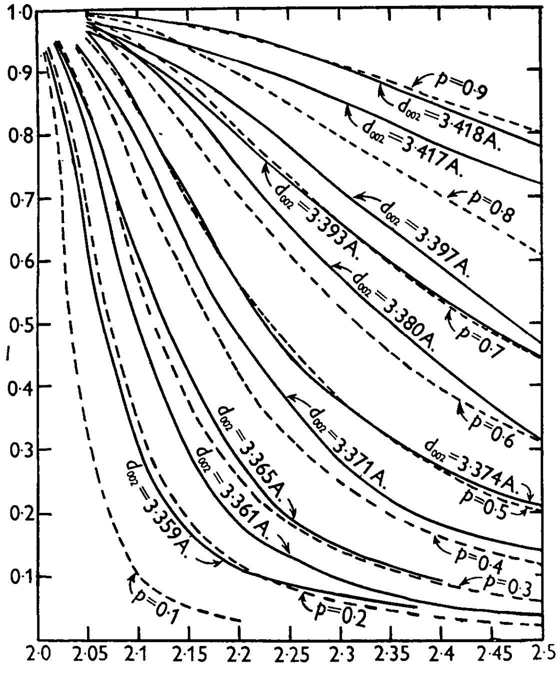

Fig. 2. The shape (in reciprocal space) of the (112) line in graphitic carbons. Experimental results are shown by the full-line curves. Broken curves give the theoretical shape of the (112) line assuming a random distribution of orientated and disorientated layers.

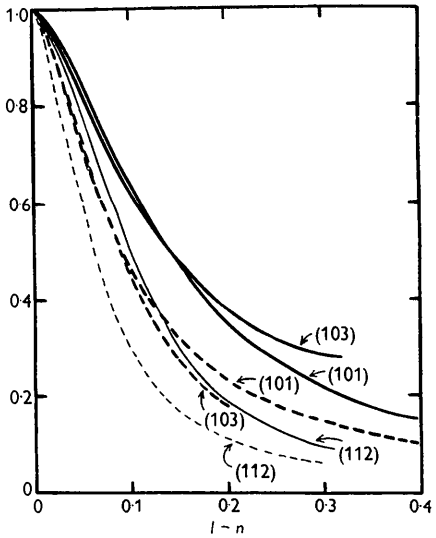

Fig. 3. Comparison of the shapes of the (101), (103), and (112) lines. Full-line curves represent a carbon prepared from polyvinyl chloride at 3000° C., and broken curves an Acheson graphite.

In the more highly graphitized carbons it is possible to measure with reasonable accuracy the (101) and (103) lines in addition to the (112). The (114) line, although strong, cannot be completely separated from neighbouring weaker lines. It is seen in Fig. 3 that the shape (in reciprocal space) of the (101) and (103) lines is identical—although both are considerably broader than the corresponding (112) line, mainly owing to the effect (described above) of the intervention of the third equivalent position of the graphite layer-plane.

The inter-layer spacing

The decrease in the inter-layer spacing which accompanies increasing graphitization has already been noted by Rooksby (1942), and has been accurately measured by Bacon (1950) for a few highly graphitized carbons. It will here be considered in more detail.

Among the non-graphitic graphitizing carbons—i.e. carbons capable of forming graphite at high temperatures but in which the graphitic structure is as yet undeveloped—the inter-layer spacing is practically constant. This is illustrated in Table 2. While the number of layers per parallel group (determined from the *integral* breadth of the *corrected* (002) band) varies from four to fifteen and the layer diameter (determined from the

Table 2. *The non-graphitic graphitizing carbons*

Raw material	Temperature of treatment (° C.)	Mean number of layers per parallel group M	Layer diameter (A.)	Inter-layer spacing (A.)
Polyvinyl chloride	1000 (¼ hr.)	3·5	18	3·450 ± 0·005
	1000 (2 hr.)	4·5	18	3·440 ± 0·005
	1000 (13 hr.)	4·9	27	3·440 ± 0·005
	1220	8·8	30	3·445 ± 0·002
	1480	15·4	40	3·440 ± 0·002
Petroleum coke	1000 (2 hr.)	4·1	22	3·440 ± 0·005
	1220	9·2	35	3·448 ± 0·002
	1480	13·0	—	3·439 ± 0·002
Pitch coke	1220	9·6	35	3·451 ± 0·002
	1480	13·4	40	3·439 ± 0·002

shape of the (11) band) from 18 to 40 A., the inter-layer spacing lies always between 3·44 and 3·45 A. Since, when the number of layers per parallel group is very small, the accuracy of measurement of the inter-layer spacing is only ± 0·005 A. it may be stated that the inter-layer spacing is, within experimental error, constant for carbons containing less than about ten layers per group. When the number of layers per group increases from ten to fifteen there is a slight but definite tendency of the spacing to decrease, but this may be due to incipient graphitization. The important point is that this inter-layer spacing, 3·44 A., which is remarkably constant throughout the whole range of non-graphitic graphitizing carbons, is very different from that in graphite.* The spacing in graphite is 3·354 A., a value which was obtained by Nelson & Riley (1945) for one natural graphite, and has been confirmed for several others during the course of the present work.

Thus there exist in the graphitizing carbons two distinct and well-defined values of the inter-layer spacing, 3·44 A. when the structure is perfectly non-graphitic, and 3·354 A. in true graphite. Intermediate values are observed for all partially graphitic carbons, and the spacing decreases as the degree of graphitization increases.

Discussion

Variation of the inter-layer spacing in graphitic carbons

If we suppose that the partially graphitic carbons are homogeneous on the atomic scale, it is hard to see why the inter-layer spacing should vary. It is inconceivable that it should depend on variations in the layer diameter when this is as much as several hundred Ångström units, or that it should depend on the number of layers per parallel packet when this, too, is very large. If such a dependence existed, it would be strongest among the non-graphitic carbons, in which the layer diameter and the number of layers per packet are small; but in the non-graphitic carbons the inter-layer spacing is constant (Table 2). It seems clear that the inter-layer spacing in the graphitic carbons must be directly related to the degree of mutual orientation of the layers.

Measurements of the widths of the (002) and (004) lines (Table 1, columns 4 and 5), show that there is a mixture of at least two inter-layer spacings in the graphitic carbons. The (004) line is always considerably broader (in reciprocal space) than the (002), whereas if the inter-layer spacing were rigorously constant in a given carbon, all (00l) lines would have the same shape. We are therefore led to suppose that *the graphitic carbons contain a mixture of orientated and disorientated layers, the spacing of the latter being greater than that of the former.*

The distribution of orientated and disorientated layers

It remains to investigate whether the transition from a disorientation with a spacing of 3·44 A. to an orientation with a spacing of 3·354 A. is continuous or discontinuous. If it is discontinuous, the simplest hypothesis is that in the whole series of graphitic carbons there exist only these two spacings; that a certain fraction of the layers are mutually orientated as in crystalline graphite and the rest are non-orientated; where orientation exists the spacing is 3·354 A., and where there is a disorientation (random translation or rotation parallel to the plane of the layer) the spacing is 3·44 A. The measured spacing, d_{002}, would then in reality be a mean value, and the shape of the (hkl) lines would depend on the proportion and distribution of the orientated layers.

In order to test this hypothesis we may use the shape of the (112) lines to deduce the proportion of orientated layers in the various graphitic carbons. But for this purpose it is first necessary to make some assumption concerning the distribution of such layers within the solid.

If there existed a strong tendency for the orientated layers to be gathered in large groups, separated by large non-graphitic regions, the X-ray diagrams would differ from those observed. Not only would the (00l) lines be doublets, corresponding to the two spacings 3·44 and 3·354 A., but the deformed (hk) bands seen in Fig. 1 would be replaced by sharp (hkl) reflexions superimposed on pure two-dimensional (hk) bands. It is clear, therefore, that such a separation does not occur, but rather the orientated and disorientated layers are intimately mixed, forming a single phase. As a first

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* It should be noted that the non-graphitic carbon previously described (Franklin, 1950*a*), in which the inter-layer spacing was found to be 3·7 A., is a *non-graphitizing* carbon.

approximation it will therefore be assumed that there is a *random distribution* of orientated and disorientated layers.

The intensity distribution of X-rays scattered by various systems of parallel layers in random stacking has been calculated for infinite packets of parallel layers by Hendricks & Teller (1942), and, more generally, for packets of finite size, by Méring (1949). Numerical calculations have shown that for all graphitic carbons the values of M, the total number of layers per parallel packet, is sufficiently large in relation to the proportion of orientated layers for the application of the formula for infinite packets of layers to be valid for the (hkl) lines. (For these calculations the apparent value of M obtained from the half-peak width of the (002) line was used. The true value of M is even larger than the apparent value, since there is always some broadening of the (002) line due to the presence, in the graphitic carbons, of more than one inter-layer spacing.) Moreover, the theoretical intensity distribution for the (112) line is further simplified, owing to the equivalence, for this line, of the three possible positions of the orientated layers in the hexagonal or rhombohedric structures of graphite. It is given by

$$I=(1-U^2)/(1+U^2-2U\cos\phi),$$

with $\phi=\pi l$ and $U=1-p$, where p is the probability that a random disorientation occurs between any two given neighbouring layers.

The theoretical intensity distribution in the (112) line for different values of p, calculated on the assumption of a random distribution of orientated and disorientated layers grouped in large packets of parallel layers, is shown by the broken curves in Fig. 2. It is clear that the shape of the theoretical and experimental curves is closely similar. Since the shape of the (112) line depends not only on the proportion of orientated layers, but is also highly sensitive to their distribution, the good agreement between the calculated and theoretical curves throughout the whole range of graphitic carbons, for values of p varying from 0·15 to 0·88, is significant. It suggests strongly that the hypothesis of a random distribution of orientated and disorientated layers is very nearly if not exactly correct. We are therefore justified in using the set of curves shown in Fig. 2 to determine, from the shape of the (112) line of any graphitic carbon, the value of p, the proportion of disorientated layers.

The distribution of the inter-layer spacings

If, as was suggested above, the inter-layer spacing were 3·354 A. at each orientation and 3·44 A. at each disorientation, a random distribution of orientated and disorientated layers would imply a random distribution of these two spacings, and, since the difference between them is small, the apparent spacing, d_{002}, would be equal to the mean spacing (Méring, 1949). There would then be a linear relationship between d_{002} and p.

In Fig. 4 d_{002} is plotted against p. There is clearly a single relationship between these two variables for the whole range of graphitic carbons, representing materials prepared at temperatures ranging from 1700 to 3000° C. and from such widely different starting materials as polyvinyl chloride on the one hand and a pitch coke on the other. The relationship, however, is not linear. If the above simple hypothesis were correct, all the points would lie on the straight line joining the two extreme points which represent respectively graphite and the non-graphitic (graphitizing) carbons. We must therefore investigate the possible causes of the deviation of the experimental curve from this straight line.

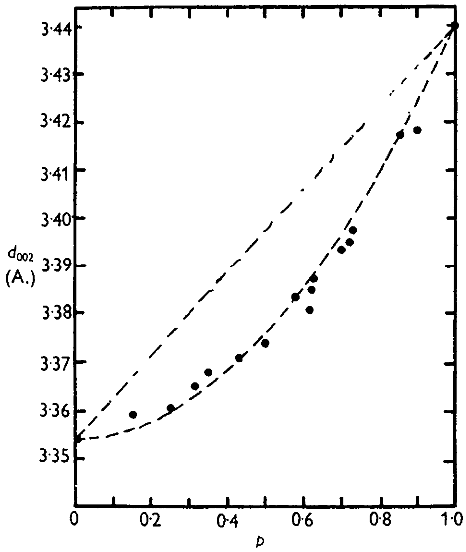

Fig. 4. Relationship between d_{002}, the apparent inter-layer spacing, and p, the proportion of disorientated layers calculated from the (112) line on the assumption of a random distribution of orientations and disorientations. The curve represents the relationship calculated assuming that there exist only three inter-layer spacings, 3·354 A. at an orientation or at a disorientation isolated between two orientations, 3·399 A. at the first disorientation on either side of an orientated group, and 3·440 A. at all other disorientations.

In order to deduce the straight-line relationship, two assumptions were made. The first was that there is in the graphitic carbons a random distribution of orientated and disorientated layers, and the second that there exist only two possible inter-layer spacings, 3·354 and 3·44 A., corresponding respectively to orientation and disorientation. Reasons have been given for believing that the first assumption is justified (see Fig. 2). It seems, therefore, that the second, the existence in the graphitic carbons of only two possible values of the inter-layer spacing, corresponding respectively to orientated and disorientated layers, is an over-simplification. It will be seen, however, that it is probably not entirely false.

The orientated layers

If the transition from disorientation to orientation of a layer were continuous there would, effectively, be a degree of disorder among the orientated layers. Any such disorder would introduce a supplementary broadening of the (*hkl*) lines which would vary continuously with l. The supposed random distribution of orientated and disorientated layers, on the other hand, would give an equal breadth to, for example, all (10l) lines having odd values of l; and the additional effect of 'mistakes' due to the third possible position of the orientated layer plane would also leave all such lines identical in shape (Wilson, 1949).

If the disorder among the orientated layers consisted in a lack of constancy in the inter-layer spacing, the resulting supplementary line broadening would increase with increasing l. If there were a *slight* disorientation, due to a small rotation or displacement in the plane of the layers, the supplementary broadening would decrease as l increased (becoming zero for the (00l) lines). The closely similar shapes of the (101) and (103) lines (Fig. 3) makes it probable that neither of these effects is important. Moreover the existence, in the orientated part, of spacings intermediate between the two extreme values would cause the experimental results to lie above rather than below the straight line in Fig. 4.

It seems, therefore, that the hypothesis of a sharp separation of graphitic carbons into orientation spacings of 3·354 A. and disorientation spacings of 3·44 A. is probably correct as far as the orientation spacings are concerned. That is, there is a more or less abrupt transition from a disorientation to an orientation, and the spacing of orientated layers never differs greatly from 3·354 A. There remains, however, the possibility that the spacing of the disorientated layers may be to some extent dependent on the degree of graphitization.

The disorientated layers

It has been shown (Table 2) that the spacing of disorientated layers is constant at 3·44 A. in all perfectly non-graphitic graphitizing carbons; that is, the disorientation spacing is constant when there are no orientated layers present. But it seems possible that in the graphitic carbons the presence of groups of the more closely packed orientated layers might cause some reduction in the spacing between the neighbouring disorientated layers. The true mean inter-layer spacing in any graphitic carbon would then be less than that calculated simply from the proportion of orientated layers. It would be reduced by a quantity depending on the number of *groups* of such layers.

In order to investigate the possible influence of this effect on the mean inter-layer spacing the following simplifying assumptions may be made:

(i) A group of orientated layers reduces the spacing only of the first disorientated layer immediately on either side of it.

(ii) The magnitude of the effect is independent of the size of the group of orientated layers.

(iii) A single disorientation spacing isolated between two orientated groups is reduced, in relation to a normal non-graphitic disorientation spacing, by twice as much as is such a spacing having an orientated group on one side only.

With these assumptions, the supplementary reduction of the true mean inter-layer spacing, due to the influence of orientated layers on the spacing between neighbouring disorientated layers, is proportional simply to the total number of *groups* of orientated layers. This distribution of inter-layer spacings is illustrated schematically in Fig. 5.

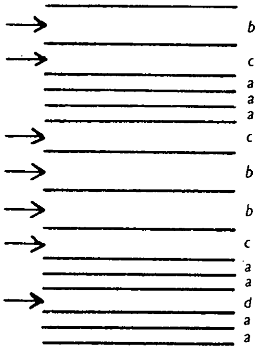

Fig. 5. Schematic representation of inter-layer spacings in graphitic carbons. (*a*) Orientation spacings, 3·354 A. (*b*) Normal disorientation spacings, 3·44 A. (*c*) Reduced disorientation spacing on either side of orientated group. (*d*) Doubly reduced, isolated disorientation spacing. The arrows indicate the positions of disorientations.

For a random distribution of orientations and disorientations it may readily be shown that the ratio of N, the total number of groups of either, to M, the total number of spacings in a packet of parallel layers, is given by

$$N/M = p(1-p),$$

provided that M is large. In graphitic carbons M is large enough for this equation to be valid for all values of p.

Taking the spacing in a pure non-graphitic graphitizing carbon to be 3·440 A., the true mean inter-layer spacing is then given by

$$d = 3{\cdot}440 - k'(1-p) - 2k''p(1-p),$$

where $k' = 0{\cdot}086$ A. is the reduction in spacing corresponding to the change from a pure non-graphitic to a pure graphitic structure and k'' is the reduction in spacing at the first disorientation in contact with an orientated group.

When d is calculated in this way as a function of p for different values of k'' it is found that the best agreement with the experimental values of d_{002}, the apparent inter-layer spacing, is obtained by putting $k'' = \frac{1}{2}k'$.* This is

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* It should be noted that this comparison of d, the true mean spacing, with d_{002}, the apparent spacing, is perhaps not quite strictly justified. It has been shown (Méring, 1949) that the two quantities are identical in the case of a random distribution of closely similar inter-layer spacings. But with the additional hypothesis of a third spacing at the boundary disorientated layers the distribution of spacings is no longer random. An exact evaluation of the effect of this new distribution on the apparent inter-layer spacing has not been attempted. It seems probable, however, that the apparent spacing would not differ greatly from the mean spacing in this case, since, although the distribution of spacings is not completely random, it retains, nevertheless, a high degree of disorder.

equivalent to supposing that the spacing between a disorientated layer and an orientated group lies halfway between the two spacings corresponding to a pure orientated and a pure disorientated structure, while the spacing at a single disorientation isolated between two orientated groups is the same as that within an orientated group.

The true mean spacing, d, is then given by

$$d = 3{\cdot}440 - 0{\cdot}086\ (1 - p^2). \tag{1}$$

This relationship between p and d is shown by the curve in Fig. 4, where it is seen that agreement with the experimental results is good over the whole range of graphitic carbons.

Thus the experimental results can be explained by supposing that, while the spacing within the groups of orientated layers remains constant at 3·354 A., the presence of these more closely packed groups causes a diminution of the first disorientation spacing at each orientation–disorientation boundary, such as to produce an intermediate spacing equal to the mean of the two principle spacings. Qualitatively this result is perhaps not surprising though the magnitude of the effect is rather larger than might have been expected. However, it is shown below that, when a possible error due to the disymmetry of the (002) line is taken into account, the decrease in spacing at each group boundary which it is necessary to assume to explain the experimental results may be slightly less than that suggested here. Moreover, the decrease in spacing may well be distributed among two or three neighbouring disorientation spacings rather than entirely concentrated in the first.

Dissymmetry of the (00*l*) *lines*

In graphitic carbons having p appreciably less than unity the (00*l*) lines, although narrow, are always unsymmetrical, the intensity falling off more slowly on the small-angle side. It seems that the most probable explanation of this dissymmetry is a *slight* inhomogeneity in the degree of graphitization. The (00*l*) lines become sharper as the degree of graphitization increases, owing to a continuous increase in the number of layers per parallel packet (Table 1). If, therefore, a given carbon is in reality a mixture of parts having slightly different degrees of graphitization, the contribution of those parts having a larger value of p and diffusing, therefore, to the small-angle side of the (00*l*) lines, will be the more diffuse. If there were a *large* dispersion of the value of p in a given carbon, the shape of the (112) line would be altered and the agreement between the experimental and theoretical curves shown in Fig. 2 would not exist. But, since the (00*l*) lines in graphitic carbons are always narrow, the degree of dispersion of p necessary to account for the dissymmetry is small.

If the above explanation of the dissymmetry of the (002) line is correct, the mean inter-layer spacing is given, not by the position of the maximum, but by the position of the centre of gravity of the line. Thus the true mean spacing would be greater than the apparent spacing. However, detailed examination of the experimental intensity curves for the (002) lines shows that this effect alone can account for at most one-third to one-quarter of the discrepancy between the straight line and the experimental points in Fig. 4. In order to explain the experimental results it is therefore still necessary to invoke the hypothesis, described above, of an intermediate inter-layer spacing among the disorientated layers in contact with orientated groups.

Conclusion

In the passage from the non-graphitic graphitizing carbons, through the series of graphitic carbons, to graphite, the shape (in reciprocal space) of the (*hkl*) ($l \neq 0$) graphite lines gives a measure of the degree of graphitization. It is found that, with increasing graphitization, the size of the graphitic layers and the total number of such layers per parallel packet increases continuously, while the apparent inter-layer spacing decreases. Consideration of all the evidence derived from powder photographs of a series of graphitic carbons having different degrees of graphitization has led to the following interpretation of the variation of the apparent inter-layer spacing and the development of the (*hkl*) lines.

In the graphitic carbons the graphite-like layers, of diameter varying from 80 to more than 600 A., are grouped in parallel packets of from 30 to more than 150 layers. Within these packets a fraction of the layers are orientated with respect to the neighbouring layers as in crystalline graphite, while the remainder are in random disorientation—owing to displacement or rotation in the plane of the layer. The orientated and disorientated layers are sharply differentiated one from the other, and are in approximately random distribution within the parallel packet.

The inter-layer spacing is constant at 3·44 A. in the non-graphitic carbons, and in graphite it is constant at 3·354 A., whereas in the graphitic carbons the apparent inter-layer spacing decreases with increasing graphitization. This apparent inter-layer spacing in the graphitic carbons is in reality a mean value. In all graphitic carbons, whatever the degree of graphitization, the small groups of orientated and disorientated layers within the parallel-layer packet retain certain of the structural characteristics of crystalline graphite and of the non-graphitic carbons respectively. Among the orientated layers the inter-layer spacing is constant and always equal to that in graphite, 3·354 A. Among the disorientated layers the inter-layer spacing is, in the main, equal to that in the non-graphitic carbons, 3·44 A. But the presence of the more closely packed orientated groups causes some perturbation of the disorientation spacing, 3·44 A., with the result that among the first disorientated layers on either side of each orientated group there is a spacing of some intermediate value.

This description of the structure of the graphitic carbons is the simplest which has been found to be consistent with all the experimental results. In any attempt to produce an alternative structure, the variation of the apparent inter-layer spacing with the degree of graphitization in the graphitic carbons and its constancy in both the non-graphitic graphitizing carbons and in graphite, the different breadths of the (002) and (004) lines, the shape (not merely the breadth) of the (112) lines, the similarity of the (101) and (103) lines, and the form of the relationship between the breadth of the (112) line and the apparent inter-layer spacing, must all be taken into account.

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Optical Methods in X-ray Analysis. I. The Study of Imperfect Structures

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The correspondence between the diffraction of X-rays by crystals and of light by gratings can be used to test hypotheses put forward to explain the X-ray diffraction patterns of imperfect structures. Two-dimensional gratings of holes in cardboard are made and their diffraction patterns observed in a specially constructed large spectrometer (the Bragg X-ray microscope). Illustrations are given of the application of the method to (*a*) the transition from the cubic to the hexagonal close-packed structure, and (*b*) the ordering process in the alloy $AuCu_3$. From the latter investigation it would appear that the X-ray diffraction effects observed can be accounted for entirely by changes in the degree of short-range order.

Some rules are given for guidance in the interpretation of the X-ray diffraction patterns of imperfect structures.

Introduction

It is well known that the fundamental difficulty in the study of matter by means of X-rays is the lack of a method both of focusing the radiation and of preserving the full resolving power. Because of this, direct images of crystal structures cannot be formed and processes of mathematical computation have to be used instead. For perfect structures the calculations are relatively simple, although they are limited in application to structures for which it is possible to derive, in one way or another, the relative phases in which the diffracted beams reach the image plane; but for imperfect structures, which give rise to diffuse reflexions and streaks on X-ray photographs, no general method of solution is known.

The usual way of solving such problems is one of trial-and-error: various types of fault are postulated in turn and their diffraction patterns are calculated and compared with those observed until agreement is reached. Certain general principles can be used as guides in making these postulations (James, 1948) and they have been used with success in connexion with, for example, the faults in graphite (Warren, 1941) and cobalt (Edwards & Lipson, 1942). Even so, the complete solutions demand considerable mathematical skill (Wilson, 1942) and can often be carried out only approximately. A rapid method of deciding which approach to a particular problem is likely to be most fruitful would therefore be desirable.

The basis of such a method has been described by Bragg & Lipson (1943) who made use of the correspondence between the diffraction of X-rays by crystals and the diffraction of light by ruled gratings. A large-scale optical system was constructed and used to examine the diffraction patterns of gratings which were coarse enough for various types of defect to be introduced deliberately.

While experiments of this type are adequate to con-

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