Carbon 1963, Vol. 1, pp. 3–9. Pergamon Press Ltd. Printed in Great Britain

MEASUREMENT OF INTERLAYER SPACINGS AND CRYSTAL SIZES IN TURBOSTRATIC CARBONS*

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(*Received* 23 *October* 1962)

Abstract—Interlayer spacings and crystal sizes of turbostratic carbons are frequently obtained by the direct and improper application of the Bragg, Scherrer, and Warren equations to the experimental X-ray scattering profile. The components of this scattering profile and their sources are considered, and the applicability of the Scherrer and Warren equations to turbostratic carbons is discussed. An analytical method is outlined for separating the incoherent scattering, the scattering due to crystallographically amorphous atoms and single graphitic-type layers, and the 002, 004, 10, 11 and 20 bands from the experimental data. Proper application of the Bragg, Scherrer, and Warren equations to these bands yields useful and accurate values of the interlayer spacings and crystal sizes. It is shown that these values differ significantly from the results obtained directly from the experimental profile.

1. INTRODUCTION

IN THE study of turbostratic carbons the crystal size and the interlayer spacing are frequently measured parameters. The diameter, L_a, and the height, L_c, of the crystal, considered as a right cylinder, are measured in the crystallographic a and c directions. They may be obtained from measurements of the broadening of the appropriate X-ray diffraction peaks. The interlayer spacing is obtained from the angle at which the corresponding peak is diffracted. The derivation of these parameters by a full analysis of the experimental X-ray data is both complex and time-consuming and, for this reason, they are often evaluated directly from the experimental X-ray profile. It should be emphasized that such results are not very valuable; not only is it apparent that neither crystal size nor interlayer spacing have been measured but it is also clear that no special relation between these data and the re ults obtained by a more careful analysis can be assumed. In view of the importance of knowing crystal sizes and interlayer spacings in turbostratic carbons as accurately as possible, it is proposed to discuss the proper evaluation of the experimental data and to compare the results obtained in this way with those derived directly from the experimental data.

Only fully turbostratic carbons will be considered; any three-dimensional ordering of the graphitic layers introduces complications in the form of modulations in the scattering curve.[1] Such carbons usually contain a certain amount of crystallographically amorphous materials and crystals whose dimensions are under 100 Å.

2. RELATION BETWEEN CRYSTAL SIZE AND LINE-BROADENING

In 1918 SCHERRER[2] gave an expression relating the edge dimension, L, of a cubic crystal to the pure X-ray diffraction line broadening, B, given by a powder comprised of such crystals:

$$L = K\lambda/B \cos \theta$$

where λ is the wavelength of the X-radiation, θ is the Bragg angle, and K is a constant of the order of one (the so-called Scherrer constant). The validity and applicability of this formula has since been investigated by a large number of people; this work has been reviewed by DRENCK [3] and by KLUG and ALEXANDER[4]. In summary it may be said that the Scherrer formula may be used to

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determine crystal sizes of small crystals from three-dimensional reflections of the appropriate indices, such as the L_c dimension of carbons from the broadening of the 002 reflection provided that the following qualifications are borne in mind:

(a) The crystallographic direction of L is perpendicular to the planes whose reflection is being studied. The value of L obtained may be taken as a 'mean' crystal dimension, although its relation to the true mean may be complex[5], depending on the nature of the distribution of crystal sizes present. The mean may be weighted in favor of the larger crystals, because a small quantity of these will disproportionately increase the peak height.

(b) To obtain the true diffraction broadening, B, from the experimental line broadening, due allowance must normally be made for instrumental line broadening. For the very broad peaks at present under consideration, this correction is negligible. It will, of course, be appreciated that by 'experimental line broadening' we mean after making all the necessary corrections to the observed intensity curve; this will be the subject of considerable discussion later. It should be mentioned that line breadths may be measured either as a simple breadth in radians (2θ) at some fraction of the peak height, or as an integral breadth, defined as $[\int I_{2\theta}\delta(2\theta)]/I_{\max}$. Different Scherrer constants must be used depending on which 'breadth' is used. In the present work the simple line breadth will be used.

(c) The Scherrer constant assumes various numerical values depending on the shape of the crystals, the indices of the reflecting plane, the precise definition of the crystal dimension, and on whether simple or integral line breadths are used. In most cases K is close to unity, and when the simple line breadth is measured at half the maximum intensity it is in fact frequently taken as one. Using simple diffraction theory, RANDALL *et al.*[6] obtained in this case the value of 0.89. They also considered the width of the peak at other fractions of the peak height, and we will use their value of $K = 0.57$ at $\frac{3}{4}$ of the peak height.

(d) The proper application of the Scherrer formula to very small crystals is doubtful. This is because[7] such small crystals are associated with very diffuse reciprocal lattice points for which the interference function may be non-zero over an appreciable volume about this point. If this is the case, the variation of the structure factor across the reciprocal lattice point may be significant. This is further complicated by an integration which assumes relatively sharp reciprocal lattice points and a mathematical approximation (in VON LAUE's derivation[8]) of the interference function which is particularly inappropriate for very small diffraction gratings. It is precisely because of these objections that DIAMOND[9–12] evolved his method for measuring the crystal size (and crystal size distribution) of very small crystals of turbostratic carbons. To use a relatively simple method for measuring the crystal size of these materials, however, we are forced to assume the applicability of the Scherrer equation; but the above observations—the quantitative effect of which is not known—must be noted.

(e) Variations in the interlayer spacing will give rise to additional broadening of a reflection. As it is not possible to separate this effect, it is normally ignored.

The relation between crystal size and line-broadening of two-dimensional reflections from random layer lattices, as exemplified by the dimension L_a and the 10, 11 and 20 reflections due to the graphitic layers of turbostratic carbons, has been studied by WARREN.[13] He obtained an equation similar to that of Scherrer, but with a much larger value of the constant K:

$$L = 1.84\lambda/B \cos\theta.$$

Reference to Warren's paper shows that:

(a) This equation is an approximation, the more precise form being

$$L = 0.92\lambda/\Delta(\sin\theta)$$

where $\Delta(\sin\theta)$ represents the width of the peak at half the maximum intensity. For the very wide peaks under consideration it may be preferable to use this.

(b) WARREN considers the shape of the two-dimensional peak to be wholly described by his $F(a)$ function.[13] It is simple, therefore, to calculate from his data the relation between crystal size and line broadening at $\frac{3}{4}$ of the peak height. For this we obtain:

$$L = 1.02\lambda/B \cos\theta$$

or more precisely

$$L = 0.51\lambda/(\Delta \sin\theta).$$

In the case of a distribution of crystal sizes, as distinct from a uniform crystal size, the formulae relating crystal size to line broadening at $\frac{3}{4}$ of the peak height may be expected to give a larger value than those relating to the broadening at $\frac{1}{2}$ of the peak height, due to the effect of the larger crystals increasing the peak intensity in the manner already mentioned.

In using Warren's formulae, a number of qualifications must again be noted. Firstly, both the 10 and 11 reflections will give a 'mean diameter' of the graphitic layers, although it is found that the two reflections do not always give the same result. POLLACK and ALEXANDER[14] find that the measured value of L_a from the 10 reflection is usually greater than that from the 11 reflection. As before, the measured value may be weighted in favor of the larger crystals. Secondly, it is to be emphasized that not only must certain corrections be made to the observed intensity curve, but that Warren's formula is properly to be applied only to the pure 10 or 11 intensity curves. Thirdly, Warren's formulae are of equally doubtful applicability to very small crystals for the same reasons as given above.

As a result of detailed studies of the distribution of layer diameters in turbostratic carbons of very small crystal size, DIAMOND developed[9] an empirical Scherrer-type equation relating L_a to the width of the 11 band:

$$L_{11} = 0.71\lambda/\Delta\ (\sin\theta).$$

It is difficult to compare this directly with the Warren equation given above, where $K = 0.51$, due to the differences in applicable correction factors and the different way in which the line breadth is measured. Diamond's empirical formula holds for 8 Å $< L_a <$ 20 Å, and possibly for higher values of L_a.

3. ANALYSIS OF THE INTENSITY PROFILE

Consider the components of the total X-ray scattering that may be expected in the range $\sin\theta/\lambda = 0.06$–$0.50$ from a turbostratic carbon of small crystal size.

There will be coherent Bragg scattering due to the parallelism of the graphitic layers. This produces the 002 and 004 three-dimensional reflections; the 006 reflection is generally too weak to be seen. There will also be Bragg scattering from the graphitic layers themselves, this gives rise to the 10, 11 and 20 two-dimensional reflections.

There will be a zero order reflection; the precise cause of this reflection in the medium angle region is confused in the literature. It is proposed to adopt the practice of ALEXANDER and SOMMER[15] in assuming that only single unassociated layers are involved.

In addition to these reflections, there will also be a considerable amount of independent scattering. This will be composed of independent coherent scattering arising from the crystallographically amorphous carbon atoms present and of incoherent Compton radiation that will be scattered by all of the atoms present.

Apart from a small amount of air scatter which may be significant at low angles and scattering or radiation from non-carbon atoms, the above will comprise all of the scattering. It may be specifically stated that (apart from cosmic radiation) there is no such thing as 'background', the introduction of which generally indicates an incomplete appreciation of the scattering processes.

To study the intensity profile of any particular reflection, it is necessary to separate it from the total scattering curve. This not only involves the removal of the independent scattering, but also the necessity to resolve the overlapping of some of the very broad reflections produced by an overlapping of the very diffuse reciprocal lattice points.

The X-ray scattering intensities obtained experimentally should be smoothed graphically and tabulated at suitable angular intervals preparatory for calculation. These intensities must first be corrected for nonlinearity of the detector[14], followed by subtraction of the air scatter. The intensities must then be corrected for absorption and for polarization.

The experimental data have now been converted to a form suitable for scaling to absolute electron units, and for subsequent subtraction of the Compton scattering. This procedure has been discussed in detail.[16] The residual intensities, to be denoted by I_c, are thus due to coherent scattering only.

As the reflections are very broad, it will be assumed that a correction for the thermal vibration of the atoms is not required.

We must now consider the intensity and the subtraction of the independent scattering, and the separation of the 002, 10 and 11 bands.

3.1 *Determination of amorphous material and single layers*

It is first necessary to deviate from the main path of the analysis to discuss the overlapping of the 002 and 10 bands. It may be supposed that the intensity of the 10 band will become negligible at some value of θ on the low angle side of its peak. Warren's results* may be used to estimate this angle. In Warren's terminology we wish to find θ for $F(a) \simeq 0$, where $a = 2\pi \frac{1}{2} L_a (\sin\theta - \sin\theta_0)/\lambda$. An estimate of L_a must now be made by using Warren's crystal size-line broadening equation on the data so far corrected. With this value of L_a, θ_0 can be calculated using a further equation given by Warren:

$$\sin\theta_p - \sin\theta_0 = 0.16\lambda/L_a.$$

An extension of Warren's calculations for $F(a)$ shows that for

$$a = -1.5 \qquad F(a) = 0.051$$
$$-2.0 \qquad\quad 0.008.$$

If we assume $F(a)$ to be negligible for $a = -2.0$, then for a given value of L_a, it is possible to calculate a value of θ below which the intensity of the 10 band is negligible.

Below this critical value of θ, the coherent intensity is due to the 00 and 002 bands and to the independent coherent scattering. In electron units, the contribution of each of these to the total scattering will be as follows:

(a) The independent scattering will contribute an amount Af^2 where A is the weight fraction of crystallographically amorphous material present and f is the atomic scattering factor.

(b) The 00 band will contribute[15] an amount $0.01515Sf^2\lambda^2\mathrm{cosec}^2\theta$, where S is the weight fraction of single layers present.

(c) The 002 band will contribute an amount

$$\frac{(1 - A - S)\cdot I_{002}^{\mathrm{sym}}\cdot f^2}{\sin^2\theta\cdot\cos\theta}$$

where I_{002}^{sym} is the symmetrical reflection—with respect to sin θ—that is required for the measurement of the line broadening, and $\sin^2\theta\cdot\cos\theta$ is the combined Lorentz-cone factor.*

We have, then, that

$$I_c = \frac{(1 - A - S) I_{002}^{\mathrm{sym}}\cdot f^2}{\sin^2\theta\cos\theta} + Af^2$$
$$+ 0.01515Sf^2\lambda^2\,\mathrm{cosec}^2\theta$$

and, in addition, that I_{002}^{sym} is symmetrical with respect to sin θ. It is now necessary to assume that the intensity of the 002 reflection has dropped to zero in the region of 10° (2θ), otherwise it is not possible to solve for the two unknowns A and S. (An inspection of the equation shows that, in principle, this is not true; in practice, however, it is a necessary condition due to the relative sizes of the various terms.) TOWNSEND has shown [19] that the intensity of the 002 band may or may not be zero in the region of 10° (2θ), depending on the amount of displacement disorder present. Because of this, the procedure outlined will give a maximum value of S, but no other significant error will be introduced.

To evaluate A and S, two equations are thus obtained: the first equates the intensity at about 10° (2θ) to the 00 band plus the independent coherent scatter,

$$I_c\,(\sin^2\theta\cos\theta)/f^2 = A\sin^2\theta\cos\theta + G\cos\theta$$

where $G = 0.01515S\lambda^2$, and $\theta \simeq 5°$. The second makes the 002 peak symmetrical by subtracting, essentially, a suitable amount of independent coherent scatter,

$$I_c(\sin^2\theta_1\cos\theta_1)/f^2 - A\sin^2\theta_1\cos\theta_1 - G\cos\theta_1$$
$$= I_c(\sin^2\theta_2\cos\theta_2)/f^2 - A\sin^2\theta_2\cos\theta_2 - G\cos\theta_2$$

* Some considerable familiarity is assumed with the publications of WARREN and his co-workers, in particular with references [13] and [17].

* The form of the trigonometrical factor to be used here is not at all clear from the literature. The work of PIKE[18] indicates that if a Lorentz-cone factor is applicable, then $\sin^2\theta\cos\theta$ is of the correct form. A number of authors, however, consider the 002 reflection as a modulation of the 00 band and use a $\sin^2\theta$ term as a demodulating factor. In view of the relatively high intensity of the 002 reflection, this position seems unrealistic and must be further criticized for the omission of both the Lorentz and cone factors. In practice, however, there is little difference between the two trigonometrical factors, since the small values of θ at present under consideration cos θ is close to one.

where $\sin\theta_1 + \sin\theta_2 = 2\sin\theta_{002}$, θ_{002} being the position of the peak of the 002 band. It is advisable to take at least three different values of θ_2, all large, but remembering that it must not exceed the critical value for the onset of the 10 band.

In this way A, the weight fraction of crystallographically amorphous carbon, and S, the maximum weight fraction of single layers present, are determined. The amorphous and single layer contributions, respectively Af^2 and $Gf^2\mathrm{cosec}^2\theta$, are now subtracted from the set of coherent scattering intensities, I_c, leaving an intensity distribution in electron units due only to the 002, 004, 10, 11 and 20 bands. (It should be noted that while the intensity of the 00 band may be very small in units of $0.01515S\lambda^3\cos\theta$, it may be quite large in electron units, i.e. units of $0.01515Sf^2\lambda^2\mathrm{cosec}^2\theta$.)

3.2 *Determination of d_{002} and L_c*

The intensities of the 002 band only are now multiplied by $(\sin^2\theta\cos\theta)/f^2$ to convert them to a symmetrical I^{sym}_{002} reflection. We are now in a position to (a) measure the true angle of the peak of the reflection; from this—using Bragg's law—the interlayer spacing can be obtained, (b) measure the width of the reflection in radians 2θ at desired fractions of the maximum intensity above zero, and hence determine L_c, the mean size of the crystals in the 'c' direction, using the Scherrer formula.

Knowing that the $I_c\ (\sin^2\theta\cos\theta)/f^2$ curve is symmetrical, it can be extrapolated as necessary on the high angle side of the peak, reconverted to electron units, and subtracted from the 10 band. This latter band may now be considered.

3.3 *Determination of L_a (10 band)*

Reference to the work of WARREN[13] and of HOUSKA and WARREN[17] shows that the intensity profile of two-dimensional reflections, when broad and in electron units, should be multiplied by the factor

$$\sin\theta(\sin\theta + \sin\theta_o)^{\frac{1}{2}}/F^2,$$

where θ_o is the true position of the peak and F is the structure factor, before application of the Warren crystal size-line broadening formula. For the present purpose this may be approximated by the expression

$$\sin\theta(\sin\theta + \sin\theta_o)^{\frac{1}{2}}/f^2.$$

No correction is made for the Lorentz or cone factors as these have already been incorporated by Warren.

On replotting the intensity data after making this multiplication, the 004 reflection shows up as a modulation on the high angle side of the 10 band. This can be removed freehand or by analysis. The analytical method is as follows: Warren showed that for values of $a\ [= 2\pi^{\frac{1}{2}} L_a(\sin\theta - \sin\theta_o)/\lambda]$ greater than 3, the intensity profile in electron units of the high angle tail of a two-dimensional reflection is given by

$$k\cdot\frac{f^2}{\sin\theta(\sin^2\theta - \sin^2\theta_o)^{\frac{1}{2}}}$$

where k may be considered as a constant. In terms of the units obtained after the above multiplication by $\sin\theta(\sin\theta + \sin\theta_o)^{\frac{1}{2}}/f^2$, the profile of the tail is proportional to $(\sin\theta - \sin\theta_o)^{-\frac{1}{2}}$. From the approximate values of L_a and θ_o already found, the value of θ above which the quoted proportionality holds may be obtained. After extrapolating analytically the low angle side of the 11 band, by the method given previously for the 10 band, to zero intensity, the proportionality constant, k, may be found by considering the intensity profile of the 10 band between the 004 and 11 bands. The shape of the 10 band may now be calculated in the region of the 004 reflection.

An intensity curve due to the 10 band only is thus obtained, and Warren's equation at $\frac{1}{2}$ and $\frac{3}{4}$ of the peak height, above zero intensity, can be applied to calculate L_a.

If it is desired, the greater part of the calculation so far can be repeated using this better value of L_a to calculate the overlap between the 002 and 10 bands.

3.4 *Determination of L_a (11 band)*

Using the $(\sin\theta - \sin\theta_o)^{-\frac{1}{2}}$ proportionality, the intensity profile of the 10 band in the region of the 11 band is now calculated. These intensities are then converted back into electron units and subtracted from the residual absolute intensities, leaving intensities due only to the 11 and 20 bands. The 004 does not extend this far.

The 11 band intensities are multiplied by the factor

$$\sin\theta(\sin\theta + \sin\theta_o)^{\frac{1}{2}}/f^2$$

using the value of θ_0 for the 11 band. It is found that the 20 reflection appears as a modulation of the 11 band, and this may be removed freehand or by calculation as in the case of the 004 band above. This gives the intensity profile due to the 11 band only, and Warren's formula can be applied to calculate a further value of L_a, the peak height again being measured above the zero intensity level.

The preceding analysis of the X-ray scattering pattern has given the following information:

(1) The weight fraction of crystallographically amorphous carbon.

(2) The maximum weight fraction of single layers present.

(3) The interlayer spacing.

(4) The mean crystal size in the c direction (two values).

(5) The mean crystal size in the a direction (four values).

Reference to the literature shows that a more detailed analysis may yield information concerning crystal size distributions. The above analysis must, however, be considered a minimum for the measurement of interlayer spacings and mean crystal sizes of carbons of very small crystal size.

4. RESULTS

The method described above was used to analyze Excelsior carbon black (92%C, 7%O, 1%H), a channel black manufactured by the Columbian Carbon Company. The X-ray diffraction intensity data were obtained using a G.E. XRD-3 counter diffractometer with balanced filter monochromation; a self-supporting specimen $\frac{1}{8}$ in. thick was used.

The results obtained were as follows:

weight per cent of amorphous carbon	28 to 30 (about $\frac{1}{4}$ of this is actually oxygen)
maximum weight per cent of single layers	6
L_c at half peak height	13.6 ±0.2 Å
at $\frac{3}{4}$ peak height	14.2 ±0.2 Å
L_a - 10 band at half peak height	14.6 ±0.2 Å
at $\frac{3}{4}$ peak height	20.6 ±0.2 Å
11 band at half peak height	11.2 ±0.2 Å
at $\frac{3}{4}$ peak height	16.7 ±0.2 Å
interlayer spacing	3.56 ±0.01 Å

5. DISCUSSION

It is of interest to compare the results obtained by this rather time-consuming analysis with those obtainable directly from the experimental data, the only correction in this case being to subtract the so-called background. (In view of the large number of corrections that should be applied, it was not practical to consider the effect of using only some of these.) As we have no *a priori* knowledge of the profile of this background, it was drawn in as a straight line connecting the minima on both sides of the peak. To get the required values of $\Delta(2\theta)$ a line was then drawn in at half the peak height and parallel to this base line. The Scherrer or Warren formula was then immediately applied; the results are given in Table 1.

TABLE 1. CRYSTAL SIZES AND INTERLAYER SPACINGS FOR EXCELSIOR BLACK

	Scherrer-Warren formulae		Diamond formula (Å)
	Analytical method (Å)	Crude method (Å)	
d_{002}	3.56	3.67	
L_c	14	14.5	
L_a (10)	18	28	
L_a (11)	14	24	16.5

The result obtained using Diamond's empirical formula[10] for the 11 reflection is also given in Table 1.

From the data given, it can be seen that the "crude" method gives satisfactory results for L_c only. It is clear from an inspection of Fig. 1, which shows the intensities in electron units of the various components of the total X-ray scattering from the Excelsior black, that this is due to the relatively high intensity of the 002 reflection in comparison to the intensity of the independent scattering over the relevant angular range. The precise angle at which its peak occurs is, of course, sensitive to the presence of the independent scattering.

In contrast, there is a larger error in L_a when measured directly from the experimental data; this may be associated with the relatively high intensity of the independent scattering in the region of the 10 and 11 reflections. It may be concluded that, apart from L_c, useful (and reliable) information

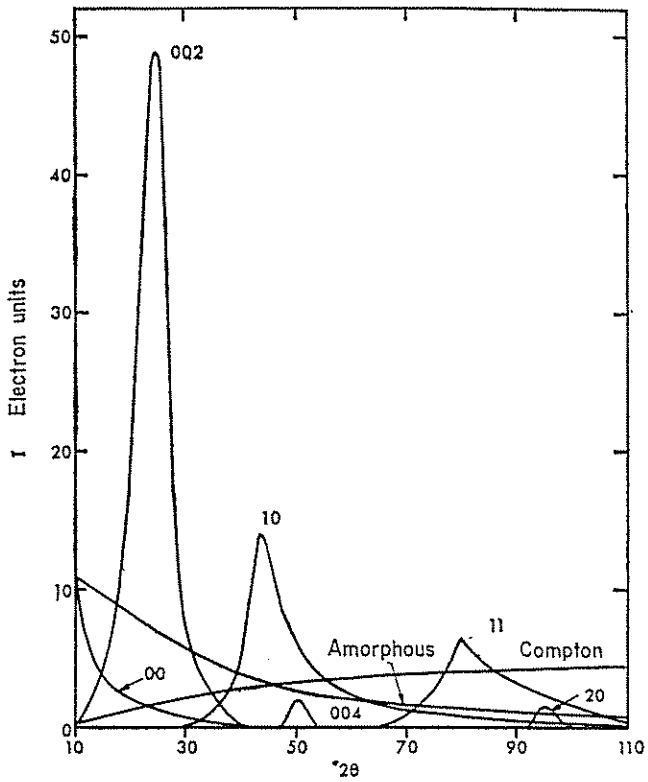

FIG. 1. Components of the total X-ray scattering from Excelsior carbon black.

cannot be obtained directly from the experimental data.

It may also be seen that Diamond's empirical formula gave results in good agreement with the analytical method set out above.

What conclusions can be drawn concerning the 'rapid' measurement of crystallographic parameters of turbostratic carbons? Firstly, L_c may be obtained directly from the experimental data. Secondly, for very small crystals, Diamond's empirical formula may be used to get L_a—the presence of incoherent scattering would not be expected to affect this formula to any great degree and need not therefore be removed. Thirdly, to obtain useful values of L_a for 'larger' small crystals, and of d_{002}, a proper analysis of the experimental data must be made.

Acknowledgement—We wish to acknowledge the financial support of the Coal Research Board of the Commonwealth of Pennsylvania for making this research possible.

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