

## The Interlayer Spacing of Graphite

BY G. E. BACON

*Atomic Energy Research Establishment, Harwell, Didcot, England*

(Received 22 March 1951 and in revised form 19 May 1951)

From a study of well-crystallized graphites direct evidence is obtained of the different spacings between oriented and disoriented layers, respectively, in a stack of parallel graphite layers. It is shown that when the proportion of disoriented layers is small there is practically a linear relation with the mean interlayer spacing deduced from 000 $l$  lines.

### Introduction

Many workers, such as Hofmann & Wilm (1936) and Bacon (1950*a*), have published information on the variation with crystallite size of the interlayer spacing of graphite. More recently, Franklin (1950, 1951), in studies of both non-graphitic and graphitic carbons, concludes that the measured interlayer spacings are really only mean values. She suggests that to a first approximation the groups of oriented and disoriented layers in a graphitic carbon retain, respectively, the spacings of 3.354 and 3.44 Å. which are characteristic of the extreme numbers of the series, namely, highly crystalline graphite and non-graphitic carbon. The first purpose of the present paper is to present more direct evidence in support of this conclusion from measurements with more highly crystalline graphites. It is shown that, in contrast to the variation of interlayer spacing given by 000 $l$  lines, there is no variation in the value deduced from  $hkl$  lines. Secondly, a further study is made, in the light of Franklin's conclusions, of the variation of the apparent interlayer spacing with the proportion,  $p$ , of disoriented layers. It is found that for small values of  $p$  there is approximately a linear relation.

### Experimental determination of $c_{0008}$ and $c_{11\bar{2}6}$

Measurements were made to determine the spacings of the neighbouring 0008 and 11 $\bar{2}$ 6 lines sufficiently accurately to determine whether there existed a significant difference between the values of  $c$ , the unit-cell dimension, deduced from the two lines. This was attempted for the four samples of graphite (Ceylon graphite and three artificial samples  $A_1$ ,  $A_2$  and  $A_3$ ) used in the writer's earlier work (Bacon, 1950*a*). Accurate determination of spacings from the line positions was made by using, in principle, the method previously described (Bacon, 1948).

In the case of the most crystalline sample,  $A_3$ , the measurement was straightforward. The X-ray specimen was prepared by extrusion, after mixing the sample with diamond to provide a correction curve, and the  $\alpha_1$ ,  $\alpha_2$  components of 0008 and 11 $\bar{2}$ 6 were measured separately on a standard film-measuring instrument.

For the Ceylon graphite the 11 $\bar{2}$ 6 line had already become too diffuse for complete resolution of the  $\alpha_1$ ,  $\alpha_2$  components and the line was therefore microphotometered and resolved graphically by the method discussed by Pease (1948). On the other hand, the 0008 line was too weak for accurate estimation of position by photometry and was determined with the film-measuring instrument, measurement of the neighbouring diamond lines 400 and 331 being made by both methods in order to correlate the readings from the two instruments. With the third sample,  $A_2$ , increasing diffuseness made it necessary not only to use both methods of measurement but also to use a solid, turned specimen in order to avoid the additional background produced by the diamond and the gum tragacanth binder. In this case a small spacing correction was estimated from the position of the 12 $\bar{3}$ 0 graphite line, and correlation between the two instruments was achieved by measuring the positions of razor-blade scratches drawn on the film. It was finally concluded that this particular sample represented the extreme to which such methods could be applied. With  $A_1$ , the least crystalline of the samples used in the earlier work, the 0008 and 11 $\bar{2}$ 6 lines were too diffuse for accurate measurement.

In Fig. 1 values of  $c_{0008}$  derived from the above measurements are shown together with those previously reported for the same samples. The two sets of results are within the experimental error, except for sample  $A_2$ , where the new results seem to be slightly lower. This may be a genuine difference, showing an increase in the proportion of disoriented layers when a sample is powdered, as has already been noticed (Bacon, 1950*b*). Also shown in Fig. 1 are the values of the  $c$  dimension calculated from the spacing of the 11 $\bar{2}$ 6 planes, using also the value of the  $a$  dimension known from the previous work (1950*a*). The abscissa is the average thickness,  $t$ , for which, according to the Hofmann & Wilm (1936) model of graphite layer stacking, the layers are stacked regularly in proper orientation. The values of  $t$  are those previously determined from line-width measurements.

It is concluded from Fig. 1 that, in contrast to the variation shown by  $c_{0008}$ , the value of  $c_{11\bar{2}6}$  is constant,

at least to a first approximation. The former, of course, depends on the mean interlayer spacing of a stack of parallel layers, some oriented and others disoriented, and Méring (1949) has shown that in the case of a random distribution of two closely similar spacings the value of  $\frac{1}{2}c$  deduced from the peak of a 000 $l$  line will, in fact, equal the mean interlayer spacing in the stack. On the other hand,  $c_{11\bar{2}6}$  refers only to the interlayer spacing within an oriented group.

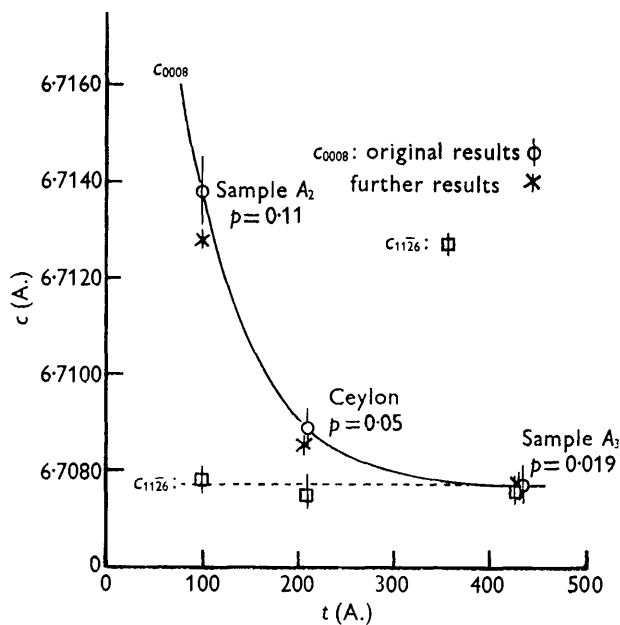


Fig. 1. Comparison of  $c$  spacings derived from 0008 and 11 $\bar{2}$ 6.

### Measurement of proportion of disoriented layers

In her second paper, Franklin (1951) presents in detail the evidence for believing that the distribution of disoriented layers in a parallel stack of graphite layers is random, rather than approximately regular as is assumed in the Hofmann & Wilm model. Over the whole range of graphitic carbons she chooses the relationship  $d = 3.440 - 0.086(1 - p^2)$

to give the mean interlayer spacing in terms of  $p$ , the proportion of disoriented layers. This is a parabolic curve having zero slope when  $p = 0$ , i.e. for very perfect graphite, which is at variance with the writer's conclusion (Bacon, 1950*a*) that, on the Hofmann & Wilm model, there is a linear variation of  $c$  with  $1/t$ , or  $p$ , near the origin. The disagreement is not due to the assumption of regular, rather than random, errors in the layer stacking, for it can be deduced, most conveniently by comparison of the formula given by Wilson (1949, p. 76, equation (29)) with that given by the writer (1950*a*, p. 138), that the form of the curve near the origin of  $1/t$  or  $p$  is the same on whichever model the line widths are interpreted. Moreover, the experimental curve drawn by Franklin (1950) is practically linear at the origin. In order to confirm

this divergence from the parabolic curve, for small values of  $p$ , the writer's earlier results were reinterpreted, for direct comparison, on the assumption of a random distribution of disoriented layers.

### Correction for geometrical broadening

The determination of the values of  $p$  was made by comparison of the line shapes of 11 $\bar{2}$ 4 and 11 $\bar{2}$ 6 in reciprocal space with those given by the intensity formula

$$I = \frac{1 - U^2}{1 + U^2 - 2U \cos \phi}, \quad (1)$$

where  $\phi = \pi l$ ,  $l$  being the crystallographic index, and  $U = 1 - p$ . For the 11 $\bar{2}l$  lines this is deduced from the more general formula given by Hendricks & Teller (1942). In the case of the well-crystallized samples which are being considered the effect of geometrical broadening on the calculated line shapes is appreciable, and in order to minimize errors as far as possible this was allowed for empirically. The geometrical broadening was measured using the 331 diamond line, which occurs very close to the 11 $\bar{2}$ 6 graphite line, and it was found that the shape of this line in reciprocal space was very closely approximated by the function

$$1/(1 + 7500\omega^2)^2,$$

where  $\omega$  is the increment of the  $l$  index away from the 11 $\bar{2}$ 6 position. The curves given by (1) for various values of  $p$  were accordingly corrected analytically by the above function (for this analysis the writer is indebted to Dr J. Howlett). The corrected curves for a number of values of  $p$  are shown as the full lines in Fig. 2, on which are also shown the measured experimental curves for the three samples  $A_3$ , Ceylon and  $A_2$ . The figure shows the good agreement of shape between the experimental curves and those calculated. Further, the curve for  $A_2$ , for example, can be contrasted with the chain dotted curve which is of equal half-width but of the form  $\sin^2 k\omega/(k\omega)^2$ , corresponding to a regular, rather than random, distribution of disorientations in a parallel stack of graphite layers. The width of the diamond 331 line used for determining the geometrical broadening is about half of the width of the sharpest curve drawn in Fig. 2.

With the least crystalline sample,  $A_1$ , for which  $p$  is about 0.2, the 11 $\bar{2}$ 6 line was too diffuse for accurate measurement and 11 $\bar{2}$ 4 was employed. In this case sodium fluoride was used as a standard substance, the geometrical broadening being given by its conveniently situated 420 and 422 lines. Similar agreement between the observed and calculated shapes of the 11 $\bar{2}$ 4 line was obtained.

In all cases the line profiles obtained by photometry were initially analysed graphically into their  $\alpha_1$ ,  $\alpha_2$  components.

### Discussion of results

Fig. 3 shows the results of the re-interpretation for the four well-crystallized graphite samples, covering the

range 0.0–0.2 in  $p$ , together with Franklin's results up to a value of 0.6 in  $p$ . It is felt that the two sets of results are in good agreement and are best represented by the full-line curve, practically linear at the origin, rather than by the broken parabola which gives the

less than  $\frac{1}{2}k'$ , i.e. the spacing between a disoriented layer and an oriented group is rather nearer to that of a pure disoriented structure than to that of a pure oriented structure. With increase of  $p$  the gradual change from (2) to (3) may be due to a reduction of the

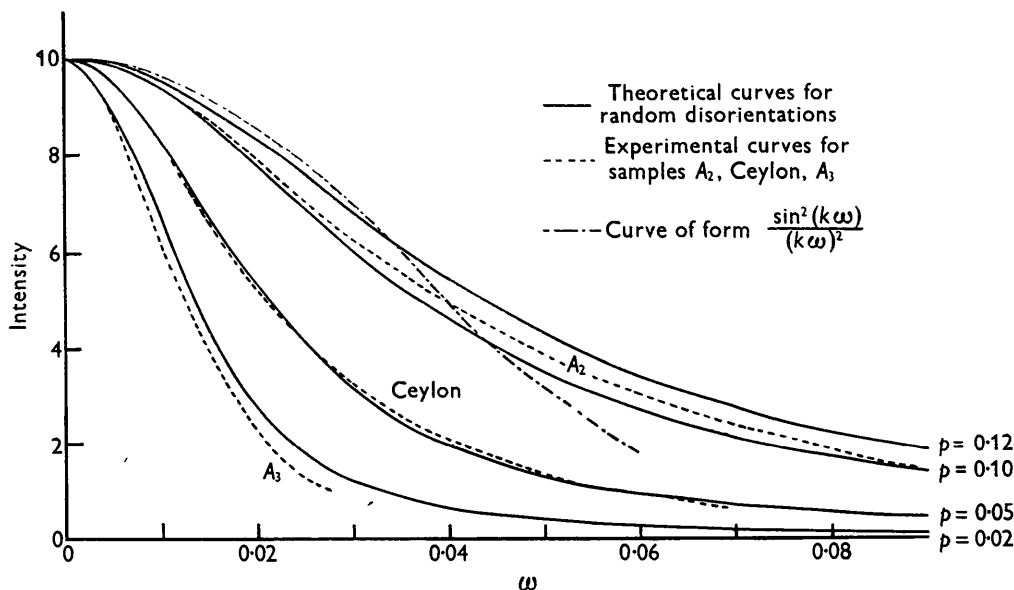


Fig. 2. Line shapes in reciprocal space for  $11\bar{2}6$ . Comparison of experimental results with theoretical curves corrected for geometrical broadening.

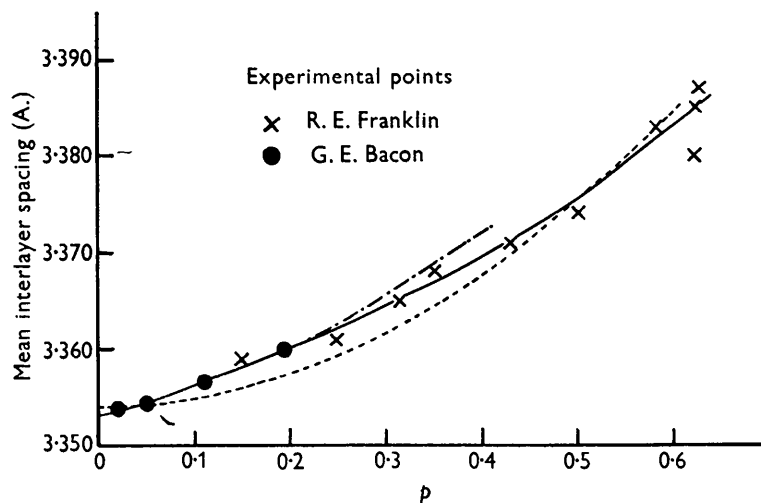


Fig. 3. Variation of mean interlayer spacing with  $p$ . — experimental curve; ----  $d = 3.440 - 0.086(1-p) - 0.086p(1-p)$ ; - · - · -  $d = 3.440 - 0.086(1-p) - 0.064p(1-p)$ .

best fit to Franklin's results as  $p$  increases to unity. The form of the relation near the origin is well approximated by the chain dotted curve whose equation is

$$d = 3.440 - 0.086(1-p) - 0.064p(1-p), \quad (2)$$

in contrast to the parabola, which can be written

$$d = 3.440 - 0.086(1-p) - 0.086p(1-p). \quad (3)$$

This means that Franklin's  $k''$  (1951, p. 259) is rather

spacing for disorientations which are next but one to an oriented group. This has previously been neglected, Franklin having made the simplifying assumption that a group of oriented layers reduces the spacing only of the first disoriented layer immediately on either side of it. When  $p$  is small the frequency of occurrence of two adjacent disorientations is small, so that (2) would apply; with increase of  $p$  more successive disoriented layers will appear and if, as seems likely, there is a

slight shortening of the second disorientation spacing, then a change towards (3) would take place. The probability of occurrence of two adjacent disorientations is equal to  $p^2(1-p)$  and it is, in fact, found that improved agreement over an increased range of  $p$  can be obtained by adding a further term,  $0.03p^2(1-p)$ , to the right-hand side of (2).

This paper is published by permission of the Director of the Atomic Energy Research Establishment. The author is also indebted to Dr R. E. Franklin for a copy of her second paper prior to publication.

## References

- BACON, G. E. (1948). *Acta Cryst.* **1**, 337.  
 BACON, G. E. (1950*a*). *Acta Cryst.* **3**, 137.  
 BACON, G. E. (1950*b*). *Acta Cryst.* **3**, 320.  
 FRANKLIN, R. E. (1950). *J. Chim. phys.* **47**, 573.  
 FRANKLIN, R. E. (1951). *Acta Cryst.* **4**, 253.  
 HENDRICKS, S. B. & TELLER, E. (1942). *J. Chem. Phys.* **10**, 147.  
 HOFMANN, U. & WILM, D. (1936). *Z. Elektrochem.* **42**, 504.  
 MÉRING, J. (1949). *Acta Cryst.* **2**, 371.  
 PEASE, R. S. (1948). *J. Sci. Instrum.* **25**, 253.  
 WILSON, A. J. C. (1949). *X-ray Optics*. London: Methuen.

## Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

*Acta Cryst.* (1951). **4**, 561

**The  $a$  dimension of graphite.** By G. E. BACON, *Atomic Energy Research Establishment, Harwell, Didcot, England*, and R. E. FRANKLIN, *Wheatstone Physics Laboratory, King's College, London W.C. 2, England*

(Received 19 May 1951)

It was previously reported (Bacon, 1950) that accurate measurements of the position of the  $(12\bar{3}0)$  line for different graphites indicated an apparent slight variation of the  $a$  dimension. At the same time, however, measurements of the  $(12\bar{3}1)$  line gave a constant  $a$  value, suggesting that, in accordance with theoretical work (Bradburn, Coulson & Rushbrooke, 1948), the true  $a$  dimension, for this range of graphites, is constant.

The anomalously low values of  $a$  obtained from the  $(hki0)$  lines can be explained in exactly the same way as the displacement shown by Warren (1941) to occur in the maxima of the  $(hk)$  bands in random-layer structures. All the graphites examined in the work referred to above were imperfectly crystalline, the degree of disorder between neighbouring layers being such that the intensity of  $(hki0)$  reflexions in reciprocal space always falls off much less rapidly along the  $c^*$  axis than perpendicular to it. This is illustrated in Fig. 1, which shows schematically the reciprocal space in the neighbourhood of an  $(hki0)$  point.

The case of the least-crystalline sample,  $A_1$ , of those previously measured may be considered semi-quantitatively. The breadth of the  $(11\bar{2}0)$  line leads to an estimated layer diameter,  $b$ , of 1500 Å. (although the line broadening is too small for this to be determined accurately). The shape of the  $(11\bar{2}4)$  line for this sample is in agreement with the hypothesis (Franklin, 1951) of a random distribution of oriented and disoriented layers, and indicates a fraction 0.2 of disorientations (Bacon, 1951). Using these figures it is found that the intensities of the streak at  $Q_0$  and  $Q$  (Fig. 1) have fallen only to 90 and 83% of the intensity at the equator. Consequently, the displacement of the maximum of the  $(11\bar{2}0)$  line will be almost as large as for a random-layer structure having layers of the same diameter.

Warren (1941) shows that the displacement in the latter case is such that the difference between the true and apparent spacings is given by

$$\Delta d = d \frac{0.16\lambda}{b \sin \theta},$$

where  $d$  is the true spacing. Applying this equation to the  $(11\bar{2}0)$  line of the sample  $A_1$ , we find that the

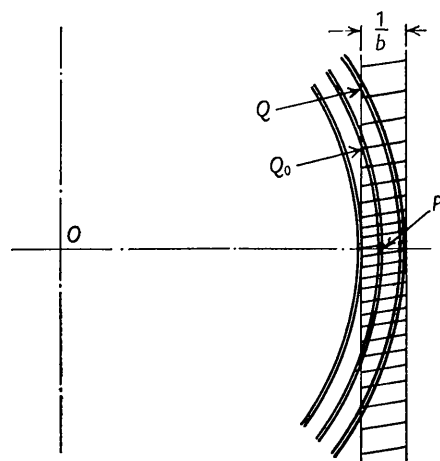


Fig. 1.  $OP_0 = \frac{1}{d} = \frac{2 \sin \theta}{\lambda}$ .

difference between the true and apparent values of the lattice parameter,  $a$ , is 0.0007 Å. This is exactly equal to the experimental difference between the apparent  $a$  values given by the  $(11\bar{2}0)$  lines of  $A_1$  and of a much more highly crystalline graphite,  $A_3$  (Bacon, 1950).

The precise agreement is, of course, fortuitous, but it