

## X-ray Diffraction Studies of Neutron-Irradiated Graphite

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When graphite is bombarded in a nuclear reactor there is a steady deterioration of the structure with production of interstitial atoms, giving an increase of  $c$  dimension and decrease of  $a$ . Over a wide range of irradiation the parameter changes are linear with the dose. The amount of damage decreases with increase of the temperature of irradiation and the original structure can be restored by subsequent annealing. A simplified model of the damaged material is set up, involving two parameters  $\alpha$  and  $\epsilon$ , where  $\alpha$  is the probability that an occasional interlayer spacing is increased by the amount  $\epsilon$ . There is some evidence that the interstitial groups tend to position themselves with a degree of regularity.

### Introduction

The structure of graphite has been studied by X-ray diffraction for more than 30 years. Much of this work has centred on determinations of the extent to which departures may occur from the simple hexagonal structure postulated by Bernal (1924). It has been shown that although the planes of carbon atoms have well defined characteristics there is no such precision in the stacking of plane upon plane. Successive planes may be rotated or laterally displaced from the precise orientation relative to their neighbours which the perfect structure would require. Accurate measurements have established that the interlayer spacing between misoriented layers is slightly larger than between correctly oriented layers (Franklin, 1951; Bacon, 1951). Moreover, when samples of graphite produced from different materials and under different temperature conditions, naturally or artificially, are compared it is found that very wide variations may occur in the crystallite dimensions. Not only may the layer dimensions vary by several orders of magnitude, say from 10 to  $10^4$  Å, but also the number of layers in a stack (parallel, but not necessarily in correct orientation) may be anything up to several hundred. The detailed characteristics of any particular graphite sample are mirrored in its X-ray diffraction pattern, and it is with little exaggeration that G. L. Clark has remarked that no two graphite samples have ever given identical X-ray patterns in every detail.

When graphite is subjected to neutron bombardment in a nuclear reactor, some of the carbon atoms are displaced from their allotted positions in the planes

of carbon hexagons. If they acquire sufficient energy from such a collision, then they in turn may displace other carbon atoms. As a result, the already imperfect graphite structure becomes even more defective as vacancies are produced in the hexagonal planes and, to an equal extent, carbon atoms are trapped between the layer planes. A proportion of initially displaced atoms will find their way back to normal sites in the layer planes and this number will increase as the temperature is raised, but in practice there is sufficient resulting disturbance to alter greatly some of the physical properties of the material, such as the elasticity and the thermal and electrical conductivities. Such changes in physical properties are of considerable importance in the design and operation of graphite-moderated reactors, and investigations of their underlying causes by X-ray examination of irradiated material have proceeded in several laboratories since the earliest days of pile operation. Only recently, at the time of the Geneva Conference on the Peaceful Uses of Atomic Energy, has information on irradiated graphite been released for publication. In the absence of any restriction on the publication of information, the data which are now available would have been appearing at intervals over the years. It has seemed to us, as two who were engaged in this work for some time, that it would be of some advantage to the general crystallographer if we combined our individual contributions on this subject. This, accordingly, we have tried to do. The subject matter is based on two classified reports written at the end of 1952 (Bacon, 1952; Warren & Chipman, 1953), about the time when we were first able to discuss together our independent investigations; in addition we include some comments in the light of further knowledge. We do not pretend that this paper represents a full review of the subject, but rather that it should serve as an introduction for

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any crystallographer wishing to interpret future published work.

### Experimental measurements

It is believed that the first X-ray measurements of irradiated graphite were carried out by Zachariasen (1945), who established, in particular, that there was an increase in the  $c$  dimension of the unit cell, together with a much smaller decrease in the  $a$  dimension.

Such changes in unit-cell dimensions would be expected to produce dimensional changes in macroscopic blocks of graphite. The aim of the initial X-ray measurements was to detect changes in unit-cell dimensions after as small irradiations as possible, with a view to predicting at what stage embarrassingly large changes might occur in the dimensions of graphite blocks constituting a pile moderator. In fact it was to be found that overall dimensional changes are only qualitatively related to the changes of  $c$  and  $a$  in the crystallites, even when due account is taken of the preferential orientation of crystallites which exists in a graphite block prepared by extrusion or pressing processes. The bulk volume expansion under irradiation is only about one-fifth of the crystal volume expansion, no doubt because of the open porous structure of the graphite blocks which have an apparent density of only about  $1.60 \text{ g.cm.}^{-3}$  in comparison with a crystallite density of  $2.25 \text{ g.cm.}^{-3}$ . A similar discrepancy is noted for the thermal expansion coefficients, which are equal to  $29 \times 10^{-6}$  and  $6 \times 10^{-6}/^\circ\text{C}$ . for the crystallite volume and bulk volume respectively of this type of graphite. The 'tightening' of the structure in this way by irradiation results in an increase of Young's modulus.

Initially the high-purity graphite used as moderator material was investigated, and it is to be remembered that this material is not particularly well-crystallized, having a value of  $p$ , the probability of layer displacement, of about 0.2 compared with a value of 0.02 for highly crystallized material (Bacon, 1951). Two methods of procedure were followed for determining the small changes of  $c$  and  $a$  in irradiated samples, bearing in mind that no high-angle lines are available for precise determination of the  $c$  dimension. In each case Cu  $K\alpha$  radiation was used with a 19 cm. camera modified to run at constant temperature (to  $\pm 0.5^\circ\text{C}$ .) by incorporating a circulating stream of water. First, powdered graphite was mixed with sodium chloride and the extrapolation curve for the unit-cell side of the latter yielded a correction factor for the interplanar spacing of each of the graphite lines (Bacon, 1948). Secondly, small cylindrical specimens of diameter 0.020 in. were turned on a lathe from a block of solid graphite and the differential expansion of the  $c$  and  $a$  axes was determined by measuring the separation of the neighbouring 1120 and 0006 lines. The latter method was quicker and had the advantage that the solid specimens were sufficiently robust to be inserted into containers for irradiation, thus permitting the

identical material to be re-examined subsequently. These methods were sufficiently accurate to detect changes in  $c$  and  $a$  of  $0.0006 \text{ \AA}$  and  $0.00005 \text{ \AA}$  respectively, the lower accuracy in the measurement of  $c$  being due to the broadened contour of the 0006 line which results from the limited extension of the crystallites along the  $c$  axis.

### Results

The first measurements, the results of which are illustrated in Fig. 1 for changes of  $c$  up to 0.5%,

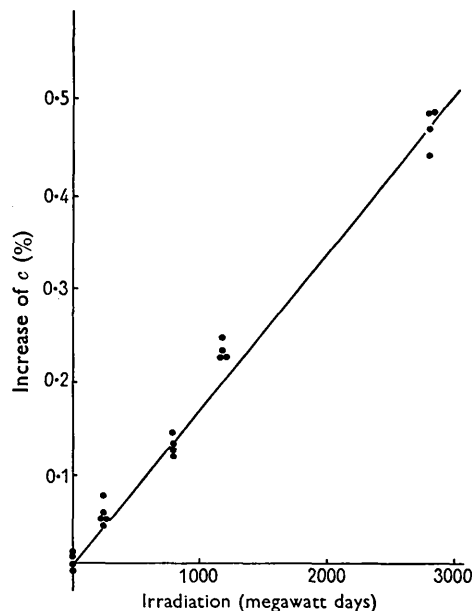


Fig. 1. Variation of the increase of  $c$  dimension with radiation dose, up to  $\Delta c/c = 0.5\%$ .

show that to a first approximation, at least,  $\Delta a$  and  $\Delta c$  are linear functions of the radiation dose. This linearity is certainly maintained up to  $c$  values of  $7.3 \text{ \AA}$ , corresponding to an increase of about 8%, for the most highly irradiated specimens which we ourselves have examined in this way. In the Materials Testing Reactor in the U.S.A. larger irradiations have permitted values of  $c$  as large as  $8.2 \text{ \AA}$  to be attained (Woods, Bupp & Fletcher, 1955) without saturation being reached.

As the  $c$  dimension increases the graphite structure becomes more and more imperfect, with a continuous deterioration of the X-ray powder diffraction photograph. Fig. 2 illustrates this for a series of irradiations giving values of  $c$  up to our maximum of about 8%. As the radiation dose progresses the first change to be noted is the movement of the 0006 line to a lower  $\theta$  position, as in curves (ii) and (iii) of Fig. 2. In curve (iii) a significant movement of the lower-angle line 0004 has already taken place. This movement can be followed through curves (iv) and (v) and it will be seen that the 0004 line becomes broader and asym-

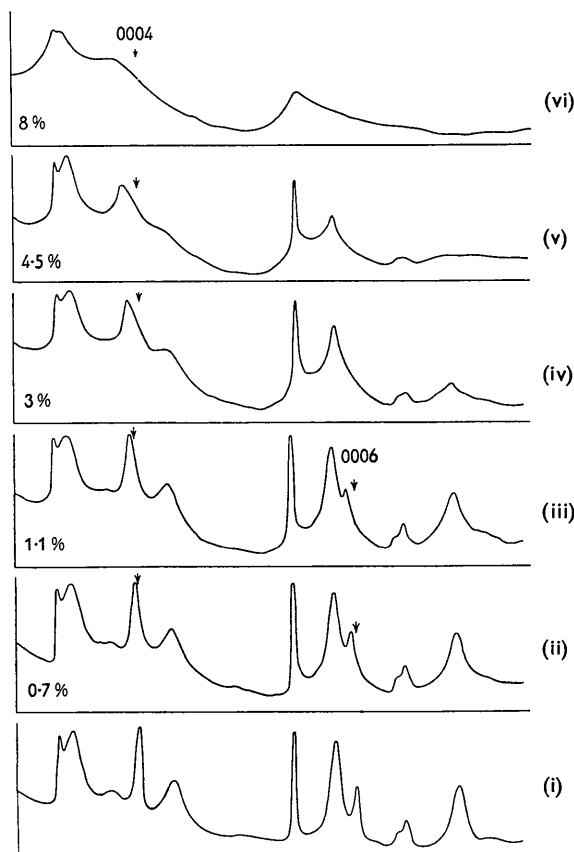


Fig. 2. Photometer traces of X-ray diffraction photographs of irradiated graphite, showing the continuous deterioration of the structural perfection. The arrows on curves (ii)–(vi) indicate the position of the (0004) and (0006) peaks before irradiation (curve (i)). The numbers at the left-hand side of the curves are equal to the percentage increase of  $c$  dimension, this serving as an index of the degree of irradiation. The 0002 line is outside the range (to the left) of these photometer traces.

metrical with a decrease in peak intensity. The corresponding changes in the much weaker 0006 line result in its complete disappearance beyond curve (iii). In curve (vi) even the 0004 has become very poorly defined, but the  $c$  spacing can still be measured fairly accurately from the 0002 line on photographs which have had much smaller exposures than those used for preparing the photometer records of Fig. 2. Measurements of the 0002 line for both the highly irradiated sample and the normal non-irradiated material are shown in Fig. 3, not only for the 'pile graphite' used for Fig. 2 but also for a sample of a very highly crystalline artificial graphite having a  $p$  value of about 0.02.

Like the increase of  $c$  dimension, the reduction of  $a$  dimension is approximately linear with exposure, certainly in the early stages of irradiation for which the 000 $l$  lines still remain symmetrical and  $c$  is accordingly well defined. There is a ratio of about 10 between the coefficients of the  $c$  expansion and the  $a$  contraction,

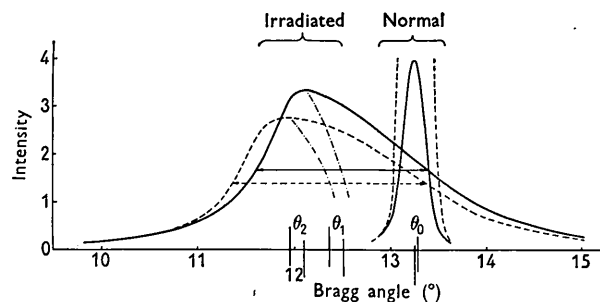


Fig. 3. 0002 line shapes for normal and heavily-irradiated graphites, the experimental intensities being corrected for geometrical and polarization factors. The full-line curves are for an artificial graphite with  $p = 0.20$ ; the broken lines are for a much better-crystallized sample with  $p = 0.02$ . The angles indicated are  $\theta_0$ , for the two normal materials;  $\theta_1$ , the centres of the half-peak-intensity positions after irradiation (corresponding to  $\Delta c/c = 6\%$ ); and  $\theta_2$ , the peak-intensity positions after irradiation (corresponding to  $\Delta c/c = 9.3\%$ ).

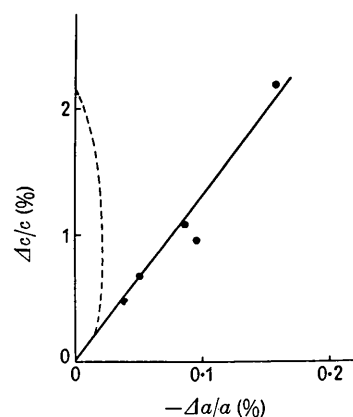


Fig. 4. The relation between the expansion of the  $c$  dimension and the contraction of the  $a$  dimension. The full line shows the approximate linearity found for neutron irradiation, in contrast with the broken line, which shows the results for thermal expansion.

as illustrated in Fig. 4. This figure also contrasts the behaviour under irradiation with the changes of  $c$  and  $a$  when graphite is heated. The broken curve in the figure expresses the thermal expansion data of Nelson & Riley (1945). According to these authors, the thermal expansion in the plane of the layers is indeed negative initially, as the temperature is raised above room temperature, but it soon becomes zero. After a contraction of about 0.02% has taken place the  $a$  dimension then commences to increase again with further rise of temperature. This is quite different from the behaviour under neutron irradiation, where a contraction of 1.1% has occurred for the sample shown in curve (vi) of Fig. 2. This is to be compared with a value of  $\Delta c/c$  of 9.3%, if defined by the position of the 0002 peak in Fig. 3, or 6% as defined by the centre of the region bounded by the two positions of half peak-intensity for the 0002 line.

*Measurements with different types of graphite*

Comparative measurements of  $\Delta c$  have been made with different varieties of artificial graphite. When two samples with  $p$  values of 0.02 and 0.2 were irradiated together the increases in  $c$  dimension were 0.47% and 0.46% respectively. In a further series of experiments graphites with  $p$  values ranging from 0.14 to 0.83 were irradiated to give values of  $\Delta c/c$  of about 3%, but there were no regular variations which could be ascribed to the different  $p$  values. Certainly the two curves given in Fig. 3 for the contours of the 0002 lines for  $p = 0.02$  and  $p = 0.2$ , after our most intense irradiation, are not identical; but in the absence of any detailed model which accounts quantitatively for the broadened asymmetrical lines it would be unwise to deduce that there was evidence for any direct influence of crystallite perfection on the value of  $c$  which is attained. Indeed, it has been shown directly that the increase of  $c$  for pairs of correctly oriented layers is the same as for parallel but disoriented layers. This has been done by deducing values of  $c$  from precise measurements of the 0008 and 11 $\bar{2}$ 6 lines, in a similar way to the direction demonstration by one of us (Bacon, 1951) of the truth of Franklin's (1951) postulate that there are two characteristic spacings, 3.354 Å and 3.44 Å, in any stack of graphite layers. The values of  $\Delta c/c$  deduced from 0008 and 11 $\bar{2}$ 6 were 0.48% and 0.49% respectively, showing that the interstitial atoms were able to push apart oriented layers just as effectively as disoriented parallel layers.

*Effect of annealing after irradiation*

If the irradiated samples are annealed after the neutron exposure, then the original dimensions of the graphite unit cell and the normal appearance of the X-ray diffraction photograph are restored. Both the period of the annealing and, more important, the temperature of annealing are significant, and the recovery produced depends on both these factors. In

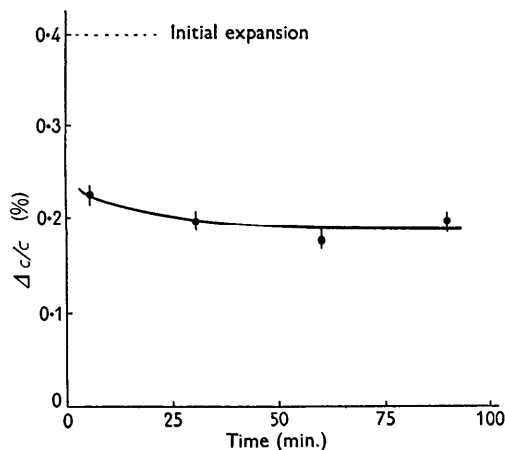


Fig. 5. The recovery from expansion of the  $c$  dimension in terms of the time of annealing at 320° C., for a sample having an initial value of  $\Delta c/c$  equal to 0.4%.

addition the per cent recovery under given conditions of time and temperature depends on the amount of irradiation damage initially produced, since this will determine the nature and extent of such defects in the structure as have to be removed.

When a sample for which  $c$  had increased by 0.4% was annealed at 320° C. for a period of 8 hr. about half of the dimensional change was restored. Annealing for various shorter times showed (Fig. 5) that most of this recovery has taken place after a few minutes annealing. Fig. 6 shows the variation of dimensional recovery

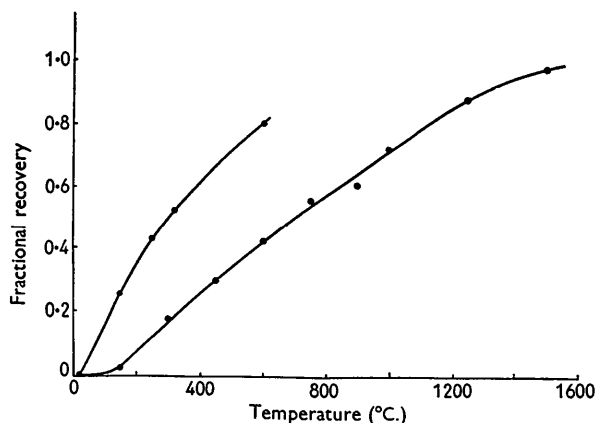


Fig. 6. The effect of the temperature of subsequent annealing, for 8 hr. periods, on the amount of recovery of damaged graphite. The recovery is expressed as the fractional reduction of the initial change of  $c$  dimension. The upper curve refers to a sample for which the irradiation gave a change  $\Delta c/c = 0.45\%$ ; the lower curve is for  $\Delta c/c = 6\%$ .

with annealing temperature, the temperature being maintained for 8 hr. in each case. The two curves show the results obtained with two different samples which showed initial  $c$  increases of 0.45% and 6% respectively. With the more heavily damaged sample a higher temperature is required for restoration of the same proportion of the total dimensional change; this means that the type of defect which is accumulating after long irradiation is more difficult to remove. It is also found that restoration of the original  $a$  dimension is achieved at a lower temperature of annealing than for the  $c$  dimension. The photometer curves in Fig. 7 show how the structural perfection of irradiated graphite is steadily restored by annealing at successively higher temperatures.

It is of some interest to compare the annealing behaviour of the two varieties of graphite with  $p = 0.02$  and  $p = 0.2$ . After intense irradiation, giving a value of  $\Delta c/c$  of about 6%, the X-ray diffraction patterns of the two damaged materials are very similar. On annealing at successively rising temperatures the details of line width and intensity characteristic of the original materials are progressively restored, and at 1500° C. the two original patterns—the one relatively poorly crystalline, the other highly crystalline—have effectively been regained. It follows, therefore, that up to

this amount of damage there is no breaking up of the original crystallites. The layers are forced apart and they may buckle and bend, but their dimensions and the probability of layer displacement within the stacks of layers are maintained. The atomic displacements take place without permanently disrupting the layer framework. Presumably on further irradiation actual break-up of the crystallites would occur. As already

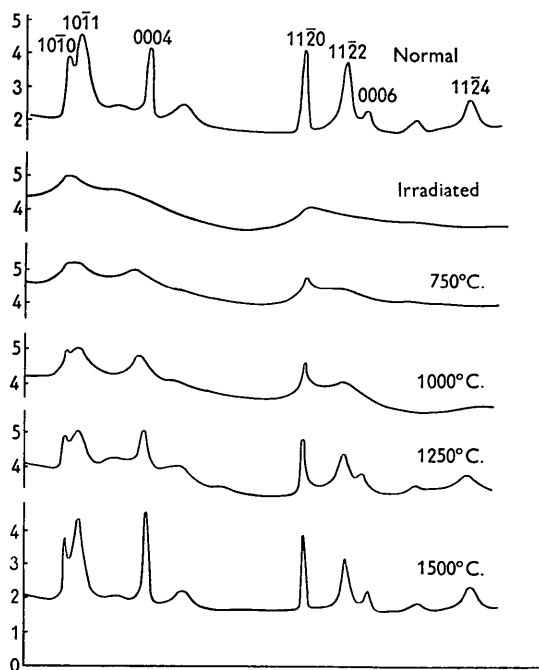


Fig. 7. The restoration of the crystalline perfection of damaged graphite by subsequent annealing at various temperatures, as evidenced by the X-ray diffraction patterns. The top curve shows the sample before irradiation. The second curve shows the appearance after an irradiation giving  $\Delta c/c = 6\%$  and the lower curves indicate the restoration by annealing at temperatures of 750°, 1000°, 1250° and 1500° C. respectively.

mentioned,  $c$  values of up to 8.2 Å have been observed in the U.S.A.; it would be interesting to know whether in such a case the original structure characteristics of the material can be regained by annealing at temperatures as low as 1500° C., but no data on this have yet been published.

#### *Effect of the temperature of irradiation*

If the graphite is maintained at an elevated temperature during the irradiation, then the amount of damage which is produced is much reduced. For example, material irradiated at 150° C. showed only about one-third of the increase of  $c$  which was found for an equal room-temperature irradiation. This reduction is much larger than can be achieved by subsequent annealing at this temperature after irradiation. The rapid reduction of damage with increase of the irradiation temperature is to be regarded as a very for-

fortunate occurrence when the design of graphite-moderated piles for high-temperature operation is considered. At the other extreme of temperature, an understanding of the mechanism of irradiation damage is more likely to come from irradiation, and subsequently X-ray measurement, at reduced temperatures where the interstitial atoms will be less mobile. Some measurements at liquid-nitrogen temperature have already been published by Keating (1955), who finds that the increase of  $c$  is then more than twice as great as that found for the same irradiation at room temperature.

#### **The nature of irradiation damage**

From the type of X-ray data which have been described it is not easy to build up any very detailed model of the number and distribution of interstitial atoms and vacancies within the structure, even with the help of knowledge of the changes in other physical properties on irradiation (Woods *et al.*, 1955; Kinchin, 1955). Moreover, the vacancies are not likely to exert much effect on the X-ray pattern.

Warren & Chipman (1953) have attempted to deduce a direct picture of the damaged structure from precise measurements of the shape of 000 $l$  reflexions, applying methods similar to those developed by Warren & Averbach (1950, 1952) for investigating the effect of cold-work distortion and particle-size broadening on the X-ray diffraction patterns of metals. In principle, the line shapes are represented by a Fourier series and from the Fourier coefficients is synthesized a distribution function which gives the variation of the distance  $L = \frac{1}{2}nc$  between any pair of graphite layers. A curve can be derived to show the variation of the distance between neighbouring layers, second nearest layers and so on. The difficulty in applying this direct method is that in order to find the distribution functions for small values of  $n$  it is necessary to measure a large number of orders of 000 $l$  spectra, so as to get a converging series, and it is of course  $n = 1, 2$  which give the most valuable information about radiation damage. It is difficult, because of overlapping of lines, to measure beyond 0006 on powder photographs. Beyond this the 000 $l$  lines tend to be submerged by much more intense neighbouring  $hkl$  lines, even if the former are accentuated by using samples with a high degree of preferential orientation. Moreover, by the time 0,0,0,12 is reached  $(\sin \theta)/\lambda = 0.9 \text{ \AA}^{-1}$ , and 75% of the scattering by carbon is modified Compton scattering. As a result of these limitations the direct method of analysing the radiation damage becomes of limited value. The most useful procedure was found to be a study of the shapes of the 0002 and 0004 reflexions in terms of various likely models of the damaged structure. The restriction to low-angle lines means of course that little distinction could be made between the claims of two or more models which differed only in their near-neighbour characteristics.

Peak shapes for 0002 and 0004 were measured with a Norelco Geiger-counter spectrometer, using filtered  $\text{Cu } K\alpha$  radiation, for samples made from well-crystallized natural graphite flakes. The flakes were built up to give laminated specimens with a high degree of preferential orientation in order to accentuate the 000 $l$  reflexions as much as possible. Samples *A* and *B* were made from two batches of irradiated material, characterised by  $\Delta c/c$  values of 3.1% and 9.1% respectively. The peak shapes are illustrated in Fig. 8. They

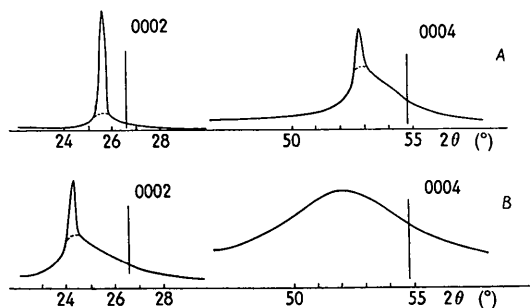


Fig. 8. The shapes and positions of the 0002, 0004 lines for two samples of highly oriented graphite after irradiation. For sample *A*,  $\Delta c/c = 3.1\%$ ; for sample *B*,  $\Delta c/c = 9.1\%$ . The vertical lines show the positions of the 0002, 0004 peaks before irradiation.  $\theta$  is the Bragg angle.

have the same essential features as are present in the powder photographs of Fig. 2 but show rather more markedly the quite sharp pip sitting on a broad asymmetric peak (compare 0004 on curve (iii) of Fig. 2). This can be likened to a sharp crystalline reflexion superimposed on a broad background of temperature diffuse scattering. The pip forms a smaller part of the higher-order peak, corresponding to the greater effect of temperature vibration on higher-order reflexions. Sample *B*, with three times the radiation dose, corresponds to a higher temperature on this interpretation, and here the 0004 pip has vanished. In Fig. 9

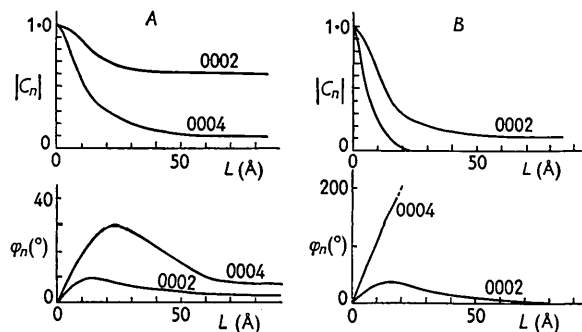


Fig. 9. Fourier coefficients corrected for instrumental broadening for the 0002, 0004 lines of samples *A* and *B*. The coefficients are expressed by a magnitude  $|C_n|$  and a phase angle  $\varphi_n$ . For 0002 *A*, 0004 *A* and 0002 *B* the origin for the damaged curve is taken at the centre of the sharp pip (see Fig. 8); for 0004 *B* it is taken at a  $\sin \theta$  value which is twice that of the 0002 *B* pip. The abscissa is the length  $L = \frac{1}{2}nc$ , where  $n$  is a whole number.

are given the magnitudes  $|C_n|$  and phase angles  $\varphi_n$  of the Fourier coefficients  $C_n$  into which these peak shapes can be analysed; the abscissa for these curves is the harmonic number  $n$  multiplied by the spacing  $\frac{1}{2}c$  to give a distance  $L = \frac{1}{2}nc$ . The values of  $|C_n|$  fall to a limiting value  $|C_n|_{\text{lim.}}$  in contrast to the case of a cold-worked metal, where they fall off continuously with increase of  $L$ . The difference in the graphite case is a consequence of the existence of the sharp pip. Pursuing the temperature vibration analogy, according to which  $|C_n|_{\text{lim.}} = \exp(-2M)$ , where  $M$  is the Debye factor, it is deduced that the root-mean-square displacements perpendicular to the layers for the two irradiated samples are 0.38 Å and 0.78 Å respectively. However, the temperature vibration analogy breaks down on two counts. First, the diffuse scattering should be symmetrical about the peak, whereas experimentally it is quite asymmetric; secondly, values of  $2M$  equal to more than 2 are involved, whereas the temperature theory is built on the approximation that  $2M$  is small compared to unity. Thus this simple model, which was first considered for graphite by Zachariasen in 1945, has to be discarded. We recall also how Fig. 4 indicates the different behaviours under neutron irradiation and thermal expansion.

As a next model we can consider a stack of layers most of which are spaced at the normal value  $\frac{1}{2}c$  but where there is a small probability  $\alpha$  that any particular spacing is increased by a quantity  $\epsilon$  to allow for the effect of interstitial atoms. The resulting value of  $\Delta c$  would then be  $2\alpha\epsilon$ . If the layer spacings occur at random, then it can be shown that a displaced peak is produced which is symmetrically broadened and the Fourier coefficients decrease continually with increasing  $n$ . Both of these conclusions are at variance with the experimental result.

As a further modification we assume that the increased spacings of our previous model are not spaced out at random. We say that the increased spacings cannot occur close to one another but are spaced out in approximate regularity once every  $N$  layers, where  $N = 1/\alpha$ . Exact regularity would of course produce superstructure reflexions, which are not observed. Analysing the line shapes of 0002 and 0004 in this way we arrive at the following results for the irradiated samples: *A*, *B*:

Sample	$\Delta c/c$	$\epsilon$	$\alpha$
<i>A</i>	3.1%	0.94 Å	0.097
<i>B</i>	9.1%	1.64 Å	0.124

To interpret these results in terms of the model, imagine a large number of lines to be drawn perpendicular to the graphite layers, and ask what kinds of spacings will be crossed as we follow these lines through the crystal. For sample *A*, about 90% of the inter-layer spacings are 3.35 Å and about 10% have the larger value  $3.35 + 0.94 = 4.29$  Å. For sample *B*, about 88% of the spacings are 3.35 Å and about 12% have the larger value  $3.35 + 1.64 = 4.94$  Å. The values of  $\epsilon$

given above can of course only be considered as effective averages of the increase in spacing. The way in which this model produces the asymmetric shape of the background peak can be seen by considering the variation of the distance  $L = \frac{1}{2}nc$  between particular pairs of layers. For large values of  $n$  there is an average interplanar spacing equal to  $\frac{1}{2}c + \alpha\epsilon$  and a symmetrical variation of  $L$  above and below the value  $L = n(\frac{1}{2}c + \alpha\epsilon)$ . For low values of  $n$  there is a small probability of a large fractional increase in  $L$  (corresponding to the inclusion of an expanded spacing) and a large probability of a small decrease in  $L$  below the average value  $n(\frac{1}{2}c + \alpha\epsilon)$ , since it is more likely that no expanded spacing will be included. Thus the lower harmonics in the series of terms are asymmetrical.

Fig. 10 gives a schematic representation of this

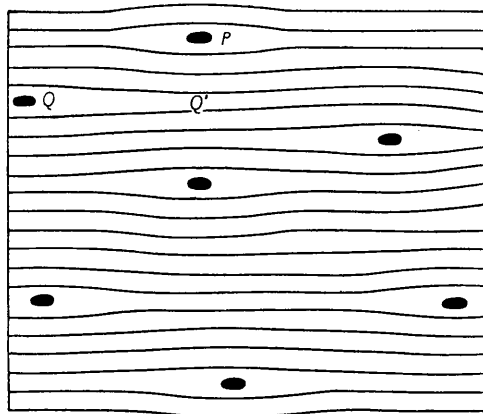


Fig. 10. Schematic representation of radiation-damaged graphite, showing the approximate regularity in the positioning of the interstitial groups, and the local increase in layer spacing at each interstitial.

model of damaged graphite. In the vicinity of an interstitial atom the increase in spacing is probably greater than the computed  $\epsilon$ , and on either side of the interstitial the increase drops continuously to zero. It seems fairly certain that the lateral extent of the region of increased spacing about an interstitial group is small, as suggested by Fig. 10. If, instead, the increased spacing extended laterally over a large distance, it would become probable that such increased spacings would exist in neighbouring layers at random, thus leading to the earlier model which we discarded.

Let us suppose in Fig. 10 that during the irradiation one interstitial group has already lodged at posi-

tion  $P$  and another than arrives at  $Q'$ . The latter position is highly compressed by the interstitial already at  $P$  and, since lateral movement of an interstitial between the layers should be very easy, the interstitial at  $Q'$  moves away from near  $P$  to some new position  $Q$ . This minimizing of the distortion energy tends to position the interstitials in a fairly regular way, as we assumed in our model, and prevents any pair from becoming very close neighbours of one another. It might have been expected that the value of  $\epsilon$  would be the same for both samples, with an  $\alpha$  value for  $B$  which was three times that for  $A$ , in line with the threefold irradiation and increase of  $\Delta c$ . However, the values given above are not in agreement with this prediction. There may be a minimum distance of separation of two interstitials in the same layer (be they initially single atoms or groups of atoms) such that on longer irradiation the interstitials tend to coalesce into larger units.

In principle it should be possible to obtain a good deal of further information from measurements of small-angle X-ray scattering. These could indicate any regularity in the positioning of interstitials and, if such exists, an average nearest-neighbour distance and the number of interstitials. Measurements of this kind have been made but with no significant conclusions. The small-angle scattering already present in the non-irradiated samples is so large that the effect of irradiation is a small difference and can therefore be estimated only very inaccurately.

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